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Sun, C.

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Controlling the rheology of polymer/silica nanocomposites

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ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op dinsdag 21 september 2010 om 16.00 uur

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Chunxia Sun

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Dit proefschrift is goedgekeurd door de promotoren:

prof.dr. P.J. Lemstra
en
prof.dr.ir. C.M.E. Bailly

Copromotor:
dr.ir. J.G.P. Goossens

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Controlling the rheology of polymer/silica nanocomposites

Summary

The properties of polymers are not solely determined by their chemical structure but also by the processing step, which determines the orientation of the molecules in the final products. Nowadays, the majority of polymers are processed via the melt. Generally, the mechanical properties of polymers increase with molar mass. However, the melt viscosity also significantly increases with molar mass. The (zero-shear) viscosity $\eta_0$ of polymer melts scales with the weight-average molar mass $M_w$ to the power 3.4, when $M_w$ is above a certain threshold value. Consequently, processing polymers is often a compromise between properties and processability with an optimum molar mass.

In addition to chemistry and processing, the final product properties can be modified by additives and/or (nano)fillers. It has been reported that the melt viscosity of polymers can be reduced considerably, with the addition of small amounts of nanoparticles. The technological consequences of the viscosity reduction can be enormous. However, this viscosity reduction cannot be predicted at this moment, and the underlying mechanisms are not yet well understood. The objective of this thesis is to understand the mechanisms that lead to the improvement in processability of semi-crystalline and amorphous polymers, and thus be able to control the processability and property balance. In the present study, isotactic poly(propylene) (iPP)/silica and poly(carbonate) (PC)/silica nanocomposites were investigated.

In the part on iPP/silica nanocomposites, different preparation methods were investigated, i.e., in-situ silica particle synthesis, melt compounding and solution processing. The rheology and crystallization behavior of such prepared iPP/silica nanocomposites were studied.

Considering that melt compounding is one of the most used methods to prepare the polymeric products, melt compounding was applied to prepare iPP/silica nanocomposites. The addition of silica nanoparticles with diameter $\sim 20$ nm induced a viscosity reduction. The viscosity reduction depended on the particle size and distribution. With decreasing silica particle size from $\sim 20$ nm to $\sim 10$ nm, a lower viscosity reduction was observed. After the viscosity reached its minimum value, an increase in viscosity was observed with the further addition of silica nanoparticles. Compared to in-situ silica particle synthesis method and melt compounding, better silica dispersions were obtained via solution methods, in which three different drying procedures were used. These three different drying procedures, i.e., gradually slow evaporation, precipitation and vapor rotation, produced comparable states of dispersion and demonstrated a similar viscosity reduction. The viscosity reduction was explained by the selective adsorption of the high molar mass chains to the silica nanoparticles’ surfaces, while the low molar mass chains were in the polymer matrix.

In addition to the viscoelastic behavior, the addition of silica nanoparticles influences the crystallization behavior of the iPP/silica nanocomposites. The isothermal crystallization kinetics of the iPP/silica nanocomposites were studied using the Avrami
analysis. A two-stage crystallization process was observed: the primary stage characterized by nucleation and spherulitic growth and the secondary stage characterized by crystal perfectioning. The addition of silica increased the crystallization rate first, followed by a decrease of the crystallization rate with the highest crystallization rate for the sample with the lowest viscosity. The addition of silica nanoparticles also increased the crystallization temperature and slightly increased the crystallinity, while the melting temperature remained constant. The nucleating efficiency increased after addition of ~ 0.4 vol% silica nanoparticles compared with pure iPP, after which the nucleation efficiency was saturated or slightly decreased.

The flow-induced crystallization behavior was studied by using in-situ small-angle X-ray scattering (SAXS). It is well known that flow-induced crystallization is governed by the high molar mass fraction of the molar mass distribution. The low molar mass matrix, which experiences lower shear stress due to its low viscosity, results in less orientation under flow. Therefore, uniform and isotropic structures are obtained. The SAXS study showed that the orientation was minimal for the nanocomposites with the lowest viscosity.

In the part of PC/silica nanocomposites, the addition of ~ 0.8 vol% silica (13 nm) induced a ~ 26% viscosity reduction, after considering the effects of molar mass and glass transition temperature $T_g$. The effect of particle size and geometry on the viscoelastic behavior of PC/silica nanocomposites was also studied.

Three different mechanisms were used in literature to explain the decrease in viscosity of nanocomposites, i.e., ball-bearing effect, free volume and selective adsorption; none of them can explain the phenomena observed in the PC/silica nanocomposites. We proposed that the viscosity reduction of the PC/silica nanocomposites can be attributed to the variations in the entanglement density. This explanation was confirmed from calculation and modeling results. The addition of silica nanoparticles increased the molar mass between entanglements.

In addition, the effect of the interaction between PC and silica surface was also studied via adding brominated PC (PC_Br) to PC/silica nanocomposites. The viscosity reduction of the system was related to the weight ratio of PC and PC_Br. The largest viscosity reduction percentage ~ 49% was observed in the (PC/PC_Br)(50/50)/silica system.

The mechanical properties of the PC/silica nanocomposites and the effect of annealing were explored as a function of the silica concentration. The results from uniaxial compression tests demonstrated that the addition of silica nanoparticles slightly increased the modulus and the yield stress of the PC/silica nanocomposites. The increases in the modulus and the yield stress are due to both the reinforcement of the silica nanoparticles and the interaction between PC and silica nanoparticles. With increasing annealing time and silica content, an increase in the yield stress was observed. Negligible changes in the softening and the strain hardening modulus were observed with increasing silica content as displayed by the true stress-strain curves.

In summary, the viscosity of the both studied semi-crystalline polymer (iPP) and amorphous polymer (PC) can be reduced by the addition of silica nanoparticles. The viscosity reduction depends on the size (distribution) and the geometry of the nanoparticles. This viscosity variation does not influence the mechanical properties of the
studied polymers. Different preparation methods can be applied to obtain the rheology and property balance with choosing suitable nanoparticle size and concentration.
1.1. Polymers

Polymers play an important role in our daily live due to their unique characteristics, such as ease of production, light weight, and often ductile nature. They can be broadly divided into thermosetting resins and thermoplastics, which account for 70 % of all produced polymers. Depending on their intrinsic properties, applications, and volume, thermoplastics can be classified into commodity plastics, engineering plastics, and high performance plastics. This classification is, however, subject to change. For example, the strong growth of poly(ethylene terephthalate) (PET) in the past decades, notably in bottle and fiber applications, changed its status from an engineering plastic to a commodity plastic. Generally, plastics show a trend towards commoditization, both in terms of increasing production volume and decreasing market prices. Therefore, it is increasingly challenging to introduce new polymers for engineering applications into the market. As a consequence, the current focus is on exploring and improving the performance of existing polymers.

The properties of polymers are not only determined by their chemical structure, but also by the processing step. Further, the use of additives or fillers may have a large impact on the performance. Maximizing the potential of existing polymers by the use of additives, viz. nanoparticles, has become a major topic in the development of polymers.

1.2. Nanocomposites

Polymer nanocomposites can be defined as two-phase systems consisting of polymers and fillers of which at least one dimension is in the nano-range (1 - 100 nm). The nanofillers can be one-dimensional nanotubes or nanofibers, two-dimensional clay platelets, or three-dimensional spherical particles. The advantage of nanoparticles is that, because of its high specific surface area, already at low concentrations major effects on the macroscopic properties can be obtained. Over the past years, polymer nanocomposites have attracted considerable interest in both academia and industry, but one of the outstanding problems is to control the state of dispersion of the nanoparticles, which is highly determined by the preparation method. Therefore, different preparation methods for polymer nanocomposites will be discussed, followed by how this influences the state of dispersion.

1.2.1. Preparation of polymer nanocomposites

Several processing techniques to disperse nanoparticles into a polymer matrix have been explored, including in-situ preparation, solution processing and melt compounding. The in-situ preparation can be divided into two routes: in-situ polymerization in the presence of nanoparticles and in-situ synthesis of the nanoparticles in the polymer matrix. In the in-situ polymerization method the particles are first dispersed in the monomer(s) followed by the polymerization. This method was used by e.g. Yang et al. for the preparation of poly(amide-6)/silica nanocomposites. First, the silica particles were
mixed with ε-caproamide followed by addition of the appropriate polymerization initiator. The mixture was then polymerized at elevated temperature under a nitrogen atmosphere. Well-dispersed particles were obtained with a particle size of ~ 50 nm, but aggregation occurred on using particle sizes of ~ 12 nm. The aggregation was explained by the increased surface energy of the smaller particles. Ash et al. and Siegel et al. added alumina nanoparticles to methylmethacrylate (MMA) and dispersed them through sonication. Subsequently, the initiator and the chain transfer agent were added. Well-dispersed alumina particles in the PMMA matrix were obtained. An example of the in-situ synthesis of the nanoparticles in the polymer matrix was shown by Jain et al., who developed a strategy for preparing isotactic poly(propylene) (iPP)/silica nanocomposites by combining a solid-state modification of iPP and an in-situ sol-gel reaction. Well-dispersed particles of 20 - 50 nm in the iPP matrix were obtained.

Dispersion of nanoparticles via solution processing is another technique that is frequently used. Vollenberg et al. were able to produce sufficiently well-dispersed poly(imide)-organophilic clay nanocomposites by dissolving poly(imide) and the clay particles in a polar solvent for several hours. Then, the mixture was solvent casted to allow the solvent to evaporate. Tuteja et al. demonstrated that rapid precipitation after solution mixing facilitated a better dispersion of functionalized magnetic nanoparticles compared to the more conventional solvent evaporation. Excellent silica dispersions were achieved by Bansal et al. via a toluene solution mixing of poly(styrene) (PS) with untreated or low molar mass PS-grafted silica nanoparticles. They showed that the choice of the solvent strongly affected the nanoparticle dispersion.

The majority of synthetic polymers are processed via melt compounding. Chan et al. produced nanocomposites using iPP as matrix and calcium carbonate (CaCO$_3$) as filler through melt mixing and obtained reasonably well-dispersed nanocomposites at filler fractions of 4.8 and 9.2 vol%, but extensive aggregation was found at 13.2 vol%. Rong et al. melt-compounded iPP with pre-treated silica nanoparticles to study the influence of interfacial interactions in iPP/silica nanocomposites, whereas Zhou et al. combined in-situ nanoparticle surface modification with melting mixing. They concluded that in-situ grafting and cross-linking of nano-silica during melt mixing with iPP was an effective way to improve the interfacial interaction.

Using a universal technique to make polymer nanocomposites is difficult due to the large variety of physical and chemical characteristics of the used components. Each system requires a special set of processing conditions based on the desired processing efficiency and product properties. Different processing techniques, in general, do not yield equivalent results. As seen from above, one of the key issues in choosing processing techniques is how well the nanoparticles can be dispersed in the polymer matrix. The state of dispersion plays a crucial role in the resulting properties of nanocomposites.

**1.2.2. State of dispersion**

The advantages of nanocomposites can only be exploited if the state of dispersion of the particles can be controlled. For some properties a perfectly homogeneous dispersion is
required, while in other cases, such as carbon nanotubes (CNTs)-filled systems for
electroconductive properties, a percolating network is required, which can be achieved by
trolled aggregation of the particles. A number of factors relating to the mediocre
performance of nanocomposites have been ascribed to the aggregation of particles
including poor dispersion, poor interfacial load transfer, process-related deficiencies, poor
alignment, poor load transfer to the interior of filler bundles, and the fractal nature of filler
clusters.

The filler geometry is a key factor that influences the state of dispersion of
nanoparticles. Fig. 1.1 shows idealized one-, two- and three-dimensional nanoparticles.
Examples include one-dimensional carbon nanotubes (CNTs), two-dimensional layered
silicates and three-dimensional Stöber silica spheres. In general, low-dimensional fillers
are more difficult to disperse than three-dimensional fillers. The difference arises from the
fact that three-dimensional quasi-spherical particles exhibit only point-to-point contacts,
whereas one-dimensional rods or tubes can have contact along the full length of the
cylinder, which increases the particle-particle interaction. Two-dimensional sheets have
even a larger contact area. The increased particle contact area and interaction make a
homogeneous dispersion even more difficult. Therefore, spherical particles were chosen
for this research as it is more straightforward to disperse them than either rods or sheets.

In addition to the filler geometry, the relative size of the nanoparticles and the polymer
also affects the final state of dispersion of the nanoparticles. Mackay et al. showed that if
the radius of gyration \( R_g \) of the linear polymer is greater than the radius of the
nanoparticles, the thermodynamic stability of the nanocomposite was enhanced. If \( R_g \) of
the polymer is smaller than the radius of the nanoparticles, the surface energy mismatch
between the polymer chains and the nanoparticles is larger, which leads to aggregation of
the nanoparticles. Other groups observed a more complex behavior, i.e., the state of
dispersion can be good or poor with increasing \( R_g \). Nonetheless, it is evident that \( R_g \) is
a very important parameter for the state of dispersion.

The polymer-nanoparticle interaction is another parameter that affects the final
nanoparticles’ state of dispersion within the polymer matrix. One of the most efficient
ways to suppress aggregation is modification of the particle surface. Although this
approach is successful in some cases, the particles can self-assemble into highly
anisotropic structures.

Although it is possible to decrease the probability of aggregation to a certain extent, it
is extremely difficult to attain complete homogeneity. Various methods have been used for
the determination of the heterogeneity of nanocomposites. The most frequently used and

![Fig. 1.1. Scheme of (a) one-dimensional, (b) two-dimensional and (c) three-dimensional nanoparticl](image)
Successful technique is optical microscopy. Other approaches include the analysis of particle characteristics, the determination of sedimentation behavior, X-ray diffraction, and the measurement of composite properties.

1.3. Polymer-filler interactions

In a nanocomposite, a considerable portion of the polymer matrix is affected by the filler due to polymer-filler interactions, even at low concentrations. The nature of the interaction between the polymer segments and the filler surface can be divided into two categories: 1) interfaces in which the segment-to-surface interactions are weak and dispersive, and the polymers are physisorbed at the interface; 2) interfaces with strong and specific segment-to-surface interaction, and the polymers are chemisorbed at the interfaces. Isotactic poly(propylene) (iPP) on graphite is an example of the first category, while polymer-metal interfaces, such as poly(methyl methacrylate) (PMMA) on aluminum, are examples of the second category.

In polymer nanocomposites, even very weak interaction between a single monomeric unit and surface can be magnified into powerful attraction or repulsion forces. That is because high molar mass polymers have many segments, which can interact with the nanoparticle surface. In spite of a certain intramolecular order, a linear chain in the melt can be considered as a random coil. If such a chain approaches an impermeable surface, it changes to a train-loop-tail structure (Fig. 1.2). The number of adsorbed units along the linear chain anchored to the particle surface depends on both the surface-to-polymer interaction energy and the molar mass of the linear chain. Generally, the number of adsorbed units to the particle surface increases if the number of repeating units or the molar mass of a polymer chain increases. In addition to the two-dimensional trains, which are anchored to the surface, the rest of the chain is in the vicinity of the surface in the form of tails and loops with their segments extending into the liquid phase. The relative sizes of loops, trains, and tails depend on the length and the flexibility of the chain. Individual polymer chains can physically attach to multiple particles even at low particle concentrations, resulting in bridging networks. An assumption for the adsorption process is that the polymer chains initially attach very rapidly to the bare nanoparticle surface and subsequently slow down proportionally with increasing coverage. For uncharged homopolymers, the attachment is so fast that the adsorption rate is constant up to about 80% coverage. The molar mass distribution and the adsorption energy of the polymer chains have an effect on the adsorption process. For polymers with a broad molar mass distribution, the surface is assumed to be first saturated with a macromolecular monolayer, which is a crude replicate of the original molar mass distribution, and subsequently is composed of low molar mass species. Later, the lower molar mass chains are substituted by the high molar mass chains due to preferential adsorbability, referred to as ‘selective adsorption’. This adsorption process is irreversible, since there are many points along the chain that are attached to the nanoparticle surface. If the polymer chains are strongly adsorbed on the nanoparticles, the polymer matrix becomes a non-continuum medium. It was argued that the interfacial chains are not in equilibrium but rather...
constrained in a non-equilibrium state. The nanoparticles surrounded by the polymer chains or the interfacial chains form new filler particles with an increased effective filler volume.

These filler particles can be regarded as core-shell particles consisting of a hard core surrounded by an immobilized soft polymer shell (Fig. 1.2). The thickness of the polymer shell is related to the molar mass. Scaling theories of adsorbed polymer layers from solution predicted the relationship between the thickness of the adsorbed polymer layer $\delta$ and the polymer molar mass in either a good solvent ($\delta \sim M^{3/5}$) or a $\Theta$ solvent ($\delta \sim M^{1/2}$). Based on the approximation that chain conformations are ideal in polymer melts, both the adsorbed amount and layer thickness are expected to scale with $M^{1/2}$.

Generally, the adsorption process of the polymer chains to the filler surface is too complicated to have a quantitative analysis. Different adsorption processes will affect the properties of the polymer matrix.

1.4. Properties of polymer matrix nanocomposites

Mechanical properties of thermoplastic polymers have been greatly improved in recent years using rigid nanoparticles as fillers. Materials scientists used the incorporation of nanoparticles to overcome creep in materials. In contrast to pure elastomers, filled rubbers display a nonlinear elastic response known as the Payne effect. Some researchers have also showed that the glass transition temperature $T_g$ of polymers can be increased by incorporating nanoparticles. If the nanoparticles have a strong interaction with the polymer, the mobility of the polymer chains is restricted and $T_g$ increases. The strength, stiffness, and toughness of nanocomposites can simultaneously be affected by the state of dispersion of the nanoparticles as well as interfacial interaction between nanoparticles and matrix. With the addition of a low concentration of nanoparticles, the polymer viscoelastic and thermomechanical properties and the crystallization behavior of semi-crystalline polymers can be modified dramatically.

A small volume fraction of spherical nanoparticles can have a large effect on the viscoelastic behavior of the polymer matrix, i.e., the viscosity increases up to an order of magnitude.
magnitude compared to that of neat polymers, the low strain amplitude shear storage modulus is enhanced by a factor of 10, and the low-frequency storage and loss modulus improve several orders of magnitude. These changes were observed when the size of filler is comparable to the size of the polymer chains and to the average interparticle distance between the nanoparticles. Then, a secondary network of polymer chains may be formed which connects the nanoparticles. The formation of this transient network might explain the observations of the viscoelastic properties and rubber-like behavior, and depends on the polymer-particle interaction and, hence, on the lifetime of bridges between the nanoparticles.

The thermomechanical properties of polymer nanocomposites are affected by polymer-particle wetting behavior. One of the thermomechanical properties, which can be profoundly affected by the wetting ability of polymers, is the glass transition temperature \( T_g \). The influences of polymer-substrate interactions on \( T_g \) have been studied by various authors and it was demonstrated that the \( T_g \) of a polymer can either decrease, increase or stay constant depending on the thickness of the film or interparticle distance for bulk materials and interaction with the substrate. This shift can be interpreted as a gradient of \( T_g \) induced by the polymer-interface interaction. By analogy, there is a similar (adsorbed) polymer and (solid substrate) nanoparticle interface in nanocomposites. The \( T_g \) of the bulk was thus also studied via varying polymer-particle interface thickness and interaction. When silica nanoparticles grafted with dense PS brushes were mixed with PS by melt compounding, the low molar mass PS was observed to wet the silica particles and the \( T_g \) of the nanocomposites was unaltered. At higher molar masses, the matrix did not wet the particles and the \( T_g \) decreased. The change is particularly relevant, because the elastic modulus, hardness, conductivity, and various other physical properties can be changed by several orders of magnitude if the temperature is in the vicinity of \( T_g \).

For semi-crystalline polymers, nanoparticles can also affect the crystallization behavior, since they may act as nucleating agents. The addition of nucleating agents (e.g. nanoparticles) provides more nucleation sites, which may result in an increased overall crystallization rate. For example, it was reported that the addition of calcium carbonate (CaCO\(_3\)) to iPP improved the mechanical properties, enhanced the crystallization rate, and reduced the cost of the product. Supaphol et al. studied the non-isothermal crystallization behavior of CaCO\(_3\)-filled syndiotactic PP (sPP). This study revealed that the incorporation of CaCO\(_3\) particles shifted the crystallization temperature to a higher temperature, indicating that CaCO\(_3\) acted as a nucleating agent for sPP. The nucleating efficiency of CaCO\(_3\) in sPP was found to depend strongly on its purity, type of surface treatment, and average particle size.

All previous reports indicate that the polymer properties are strongly modified by the presence of solid nanoparticles. During the past few years, there have been intensive discussions on the origin of the properties improvement in polymer nanocomposites. As discussed, the effect of nanoparticles on polymers depends considerably on the state of dispersion, surface treatment, matrix-filler interaction, and processing conditions.
1.5. Rheology of nanocomposites

According to Einstein, the addition of particles to a liquid leads to an increase in viscosity. This has also been experimentally confirmed for polymer melts and solutions. The increase in viscosity may limit the processability. However, a number of researchers recently found that the melt viscosity of polymers can be reduced by using nanoparticles. Roberts et al. observed a decrease in viscosity by blending small silicate clusters with a radius of approx. 0.35 nm in poly(dimethylsiloxane). Since the particle size approaches the length scale of the monomer, the decrease of the viscosity may be attributed to plasticization. Later, Xie et al. discovered that at high shear rates (> 100 s⁻¹), the viscosity of poly(vinyl chloride) (PVC)/calcium carbonate (CaCO₃) nanocomposites was lower than that of pure PVC and the viscosity continued to decrease with increasing CaCO₃ nanoparticle concentration. The authors explained the decrease in viscosity by a ‘ball-bearing’ effect of spherical nanoparticles. When spherical particle-filled polymers are introduced to a shear flow, a high local shear is developed in the narrow gaps between two nearby rotating spherical particles, which may cause the chains to disentangle. At sufficiently high shear rates, the viscosity decreases as the induced local shear in the gaps increases and chains become more disentangled. A shift in the \( T_g \) of the PVC/CaCO₃ nanocomposites towards higher temperatures and an improvement in mechanical properties were also observed by Xie et al. Similarly, Chen et al. and Lai et al. observed a decrease in viscosity when they added micron-sized particles (glass-beads and barium sulfate) to pure poly(carbonate) (PC). This decrease was also interpreted by the authors with the help of the ‘ball-bearing’ effect.

Mackay et al. reported a decrease in viscosity by blending linear PS with organic particles, synthesized by intramolecular cross-linking of PS chains. The authors attributed the decrease in viscosity to the excluded free volume introduced by the nanoparticles. This decrease in viscosity was accompanied by a significant decrease in the \( T_g \), which may also have an impact on the final properties. The viscosity decrease was only observed for entangled and confined systems defined as \( h < R_g \), where \( h \) is half of the interparticle distance. Wang et al. also explained the decrease in viscosity of PC/CaCO₃ nanocomposites based on the excluded free volume induced by the CaCO₃ nanoparticles, which was confirmed by a \( T_g \) depression.

Jain et al. found that by using less than 1 wt% silica nanoparticles produced via in-situ sol-gel reactions, the melt viscosity of iPP decreased by as much as one decade, while no decrease in \( T_g \) was observed. The viscosity decreased with increasing silica content up to 0.5 wt%; subsequently, the viscosity increased on further increasing the silica content. Moreover, the decrease in viscosity was achieved without sacrificing the mechanical properties. Jain et al. attributed this effect to selective adsorption of the high molar mass chains on the nanoparticle surface, where the nanoparticles were surrounded by high molar mass chains, and the matrix consisted of low molar mass chains.

In summary, four different mechanisms have been reported in literature to explain the decrease in viscosity when nanoparticles are added to the polymer matrix: the ‘plasticizing’ effect, the ‘excluded free volume’, and the ‘ball-bearing’ effect.
the ‘selective adsorption’ mechanism. To date, there are continuing disputes on the exact mechanism to explain the decrease in viscosity and it remains a challenge for theoreticians.

1.6. Choice of systems and experimental approaches

Because of the inherent difference between semi-crystalline and amorphous polymers, the addition of nanoparticles will affect the polymer properties differently. Therefore, it is necessary to study the effect of nanoparticles separately for semi-crystalline and amorphous polymers. In this study, isotactic poly(propylene) (iPP) will be used as the semi-crystalline polymer, while poly(carbonate) (PC) will be used as the amorphous polymer. Both polymers have a similar entanglement density.

iPP was chosen as matrix for the following reasons:
- It is a commercially very important and well-studied semi-crystalline polymer.
- Various studies related to hard particle-filled iPP mechanical properties improvements have been published.
- In our lab, we have observed that by using only a minute amount of specific nano-sized silica additives, the melt viscosity of iPP could be lowered dramatically.\(^{49}\)

PC was chosen as matrix because:
- It is one of the amorphous engineering thermoplastics with a wide variety of applications. However, one of the limitations of PC is its high melt viscosity.
- A few studies were published on the viscosity reduction of PC/silica (nano)composites.

As filler nanosized silica was chosen, which has the following advantages:
- The size and shape of silica particles can be easily controlled by varying the (in-situ) synthesis conditions.
- The surface characteristics can be systematically varied.
- Silica nanoparticles are commercially available and can be purchased either in the form of powder or suspensions.

1.7. Scope and outline of the thesis

Although many reports have been published on the structure-property relations of polymer nanocomposites, the underlying mechanisms are yet not well understood. The objective of this thesis is to understand the mechanisms that lead to the improvement in processability of semi-crystalline and amorphous nanocomposites. The first part is focused on the viscosity reduction of iPP/silica nanocomposites via different methods and to understand the effect of nanoparticles on the rheology and crystallization behavior. The second part is focused on the mechanism of the viscosity decrease in PC/silica nanocomposites.

In Chapter 2 the effect of the preparation method, viz. in-situ silica particle synthesis, melt compounding, and solution processing, the particle size and geometry on the silica dispersion and the viscosity reduction of iPP/silica nanocomposites is discussed.
In Chapter 3 the effect of the silica nanoparticles on the crystallization kinetics of iPP was studied by examining both the isothermal and non-isothermal crystallization behavior. The results obtained from different characterization techniques, i.e., differential scanning calorimetry (DSC), small-angle light scattering (SALS), and polarized optical microscopy (POM), are discussed in this chapter. Further, small-angle X-ray scattering (SAXS) is used to discuss the shear-induced crystallization behavior of the prepared iPP/silica nanocomposites.

Chapter 4 describes the viscosity reduction of PC/silica nanocomposites in relation to the preparation method, particle size and geometry. Different mechanisms for the viscosity reduction are discussed.

The viscoelastic behavior of the PC/silica nanocomposites is examined using dynamic and steady-state experiments in Chapter 5, which will be used in Chapter 6 for the modeling part.

In Chapter 6 the experimental results on the linear viscoelastic properties of the PC/silica nanocomposites are confronted with a model that takes into account all relaxation modes of polymer melts to clarify the most dominant mechanism for the viscosity reduction.

To study the effect of the polymer-filler interaction, blends of PC with brominated PC were used and the results are discussed in Chapter 7.

Chapter 8 presents a discussion on the mechanical properties of PC/silica nanocomposites, including a study on the effect of nanoparticles on the aging kinetics.

1.8. References

16. Li, J.X.; Wu, J.; Chan, C.M. Polymer 2000, 41: 6953-6937.
Chapter 1 Introduction

Abstract

Different methods were used to prepare the isotactic poly(propylene) (iPP)/silica nanocomposites, i.e., in-situ silica particle synthesis in iPP powder, melt compounding and solution method. Relatively well-dispersed silica was observed in iPP matrix prepared via melt compounding and solution method. Similar viscoelastic behavior was observed for the studied iPP/silica nanocomposites. A decrease in viscosity was obtained in the investigated iPP/silica nanocomposites, which depended on the particle size and distribution. An increased $T_2$ relaxation time, characterized by nuclear magnetic resonance (NMR), was illustrated for the samples with low viscosity than for pure iPP. This indicates higher chain mobility for the nanocomposites than pure iPP. The increased chain mobility is related to the selective adsorption of iPP chains to silica surfaces.

Nanoscale effects on the decrease in viscosity of isotactic poly(propylene) (iPP)/silica nanocomposites
2.1. Introduction

Nanocomposites have attracted enormous interest because they theoretically promise a substantial improvement of mechanical properties at very low filler loadings. In general, the addition of (nano)particles to polymer melts leads to an increase of the melt viscosity. However, in some nanocomposites systems a decrease in viscosity was observed. Jain et al. found for isotactic poly(propylene) (iPP)/silica nanocomposites a decrease in viscosity on adding less than 1 wt% silica, while no change in glass transition temperature Tg nor sacrifice of mechanical properties was observed. The results were explained based on a selective adsorption mechanism. A combination of solid-state modification and an in-situ sol-gel reaction to prepare the silica nanoparticles was used on porous reactor powders to prepare the iPP/silica nanocomposites.

The nature of the silica surface via sol-gel reactions is difficult to control, and the surface coverage largely determines the adsorption behavior of the particles. Therefore, in addition to the in-situ silica particle synthesis, commercialized pre-made silica nanoparticles were also applied in this thesis to have a better control of silica surface properties. Furthermore, the dispersion of nanoparticles in polymer melts is difficult to control and both thermodynamic and kinetic processes play an important role. Tuteja et al. presented strategies to disperse isotropic organic nanoparticles in polymers which influenced the viscoelastic behavior and performances of the composites. The results demonstrated that nanocomposites exhibited a viscosity reduction and multifunctional performance enhancements may be fabricated using simple processing procedures. The viscosity reduction was observed in poly(styrene) (PS) nanoparticles-filled PS nanocomposites as well as in fullerene nanoparticles filled-PS and magnetic nanoparticles filled-PS blends, provided the blends were prepared using rapid precipitation. On the other hand, slow evaporation lead to nanoparticles agglomerations and an absence of viscosity reduction. The viscosity reduction may be inaccessible unless a correct processing method is employed.

This chapter discusses three different methods to prepare iPP/silica nanocomposites, i.e., in-situ silica particle synthesis in iPP reactor powders, melt compounding with pre-made silica particles and a solution method, also with pre-made silica particles. The part on the in-situ silica particle synthesis focuses on the main parameters related to the in-situ sol-gel reaction and how these affect the state of dispersion and the amount of silica formed. The relation between the state of dispersion, particle size and the rheological behavior will be discussed in the melt compounding section. For the solution method, three different drying procedures, i.e., gradual solvent evaporation, rapid precipitation and vapor rotation, will be evaluated.

2.2. Experimental
2.2.1. Materials

To prepare iPP/silica nanocomposites via the in-situ silica particle synthesis method, porous iPP powder obtained from Euro-SABIC (The Netherlands) was used without antioxidants and stabilizers. The number-average molar mass, \( M_n \), and the weight-average molar mass, \( M_w \), of the iPP were 60 and 380 kg/mol respectively. The iPP used for melt compounding and solution method was obtained in pellet form from Euro-SABIC (The Netherlands) and had a melt flow index (MFI) of 5.7 g/10 min at 230 °C and under a weight of 2.16 kg.

Pre-made silica nanoparticles with a diameter of 13 nm, dispersed in toluene with approx. 40 wt% silica, were purchased from Nissan Chemical and will be referred to as TOL-ST in this thesis. Silica nanoparticles with diameters of 10, 12 and 20 nm were obtained from Sigma-Aldrich. These particles were suspended in water up to a solid content of ~ 30 wt%, 25 wt% and 40 wt% respectively. Silica nanoparticles with a diameter of 7 nm, dispersed in water with ~ 29 wt% solid content, were purchased from EKA Bindzil®.

Tetraethoxy orthosilicate (TEOS) was obtained from Aldrich Chemicals. Ammonium hydroxide \( \text{NH}_4\text{OH} \) (28% \( \text{NH}_3 \) in water), purchased from Aldrich Chemicals, was used as catalyst for the sol-gel reactions. Toluene was obtained from Biosolve®.

2.2.2. Preparation of iPP/silica nanocomposites

2.2.2.1. In-situ silica particle synthesis in iPP powder

The in-situ silica particle synthesis in the porous iPP powder was carried out in a double-skinned reactor as used by Jain et al. The silica nanoparticles from in-situ sol-gel reactions can be formed inside pores or channels of the iPP powder. The reactor was equipped with a water condenser to minimize evaporation and a mechanical spiral-shaped stirrer. A \( \text{N}_2 \) flow was applied to prevent oxidation. \( \text{N}_2 \) was first purged into the reactor for 15 min to remove oxygen from the reactor. The IPP powder was then added and stirred at 60 °C under \( \text{N}_2 \) for 30 min. Subsequently, TEOS was added slowly to the iPP powder. After stirring for 30 min at 60 °C, a mixture of water and \( \text{NH}_4\text{OH} \) was added slowly under continuous stirring. The amount of \( \text{NH}_4\text{OH} \) was 1 wt% based on TEOS. The molar ratio of TEOS/H\(_2\)O was 1:5. The whole system was heated for 3 hrs at 60 °C and for 5 hrs at 80 °C. The reactor was cooled down while stirring was continued. The final material was stored in a refrigerator. Before further operations, samples were physically mixed with stabilizer (Irganox® 1010) by extrusion.

2.2.2.2. Melt compounding

iPP powder, which was grinded from iPP pellets and mixed with stabilizer (Irganox® 1010), and silica water suspensions were compounded at 190 °C in a twin-screw mini-extruder (DSM Xplore 15 ml microcompounder) under \( \text{N}_2 \) atmosphere for 20 min with a speed of 50 rpm.

To study the effect of particle size, silica nanoparticles with different diameters (Table 2.1) were used. In addition, a mixture of 7 and 20 nm with weight ratio of 50:50 was used to study the effect of the polydispersity of the nanoparticles. Table 2.1 lists also the critical volume fraction of silica nanoparticles \( \phi_c \), which refers to the silica volume fraction when the inter-particle distance \( \Lambda \).
is equal to $2R_g$, while $R_g$ is the radius of gyration of the used iPP chain. The $\phi$ can be calculated based on equation (2.1)$^{11}$ and (2.2):

$$D = A\left[\phi_m / \phi \right]^{1/3} - 1$$

(2.1)

where $D$ is the particle diameter, $\phi$ is the particle volume fraction and $\phi_m$ is the maximum packing fraction of monodispersed spherical particles. For random packing, $\phi_m \approx 0.638$.

$$R_g = \frac{2\pi}{3}b$$

(2.2)

in which $b$ is the segmental length and $n$ is the degree of polymerization of the iPP.

Table 2.1. The information of used silica nanoparticles.

<table>
<thead>
<tr>
<th>Particle diameter $D$ (nm)</th>
<th>$\phi$ (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>0.8</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
</tr>
<tr>
<td>7 + 20</td>
<td>1.8</td>
</tr>
</tbody>
</table>

$\phi$ for the system with $(7 + 20)$ nm was calculated based on equation (2.3) which considers the effect of the particle size distribution:

$$\bar{D}_n = D_n \left[\phi_m / \phi \right]^{1/3} - 1$$

(2.3)

in which the number-average diameter ($\bar{D}_n$) can be calculated based on:

$$\bar{D}_n = \frac{\sum n_i D_i}{\sum n_i}$$

(2.4)

and the particle size distribution parameter ($\sigma$) can be calculated from:

$$\ln \sigma = \sqrt{\frac{\sum n_i (\ln D_i - \ln \bar{D}_n)^2}{\sum n_i}}$$

(2.5)

In equation (2.5), $n$ is the amount of the nanoparticles with diameter of $D$, and $N$ is number of different types of nanoparticles. In the case of a monodispersed particle size distribution, $\sigma$ is equal to 1. When there is polydispersity, $\sigma$ is greater than 1.

2.2.2.3. Solution method

The required amount of silica nanoparticle suspension (TOL-ST) was added to 150 g toluene, followed by the addition of 15 g iPP powder and required amount of Irganox® 1010. The mixture was stirred at 123 °C for 5 hrs using a magnetic stirrer until a transparent and well-dispersed
iPP/silica/toluene solution was obtained. Subsequently, three different drying procedures were applied to remove most of the toluene: slow evaporation, precipitation (into cold methanol) and vapor rotation. Slow evaporation allows most of the toluene to evaporate slowly at room temperature. Precipitation is a method to remove the toluene via pouring the iPP/silica/toluene solution into cold methanol. Vapor rotation method evaporates the toluene at a temperature of 100 °C with a pressure slightly lower than atmospheric pressure using a vapor rotator. To remove the residual traces of toluene, the materials were further dried in an oven under N\textsubscript{2} flow at 110 °C for 3 days, at 140 °C for 2 days, and at 150 °C overnight. The materials were then extruded at 210 °C for 10 min under a N\textsubscript{2} flow on a home-built twin-screw mini-extruder with a screw speed of 75 rpm.

Depending on the drying procedure, the following abbreviations were used: S\textsubscript{X} vol% silica for slow evaporation, P\textsubscript{X} vol% silica for precipitation and V\textsubscript{X} vol% silica for vapor rotation, where X represented the silica content obtained from TGA measurements.

2.2.3. Characterization techniques

**Rheology.** Rheological measurements were performed on a stress-controlled AR-G2 rheometer (TA Instruments) under N\textsubscript{2} atmosphere using a 25 mm parallel plate-plate geometry. Frequency sweeps were performed at 180 °C in a range of 100 - 0.01 rad/s with a constant strain of 10\%, which was within the linear viscoelastic regime.

**Transmission Electron Microscopy (TEM).** Morphological investigations were performed by using a Tecnai 20 transmission electron microscopy (TEM), operated at 200 kV. Ultrathin sections (50 - 70 nm) were obtained at room temperature by using a Leica Ultracut E microtome. Chemical staining of the sections was not required, since the electron density of silica is much higher than that of iPP.

**Thermogravimetric Analysis (TGA).** A Q500 TGA (TA Instruments) was used for the quantitative determination of the silica content in the nanocomposites. Samples were heated under a pressed air atmosphere at 10 °C/min to 900 ºC and held for 15 min. The residue was assumed to be only composed of silica. All measurements were repeated at least twice and an average of the results was used.

**High-temperature Size Exclusion Chromatography (HT-SEC).** High-temperature size exclusion chromatography (SEC) was performed on a Polymer Laboratories PLXT-20 Rapid GPC Polymer Analysis System at 160 °C. The analysis system includes a pump, refractive index detector and viscometer detector, and three PLgel Oxelis (300 × 7.5 mm) columns in series. 1,2,4-Trichlorobenzene (TCB) was used as the eluent with a flow rate of 1.0 mL/min. The molar mass was calculated with respect to poly(styrene) standards (Polymer Laboratories, M\textsubscript{p} = 580 - 7.1x10\textsuperscript{6} g/mol). A Polymer Laboratories PL XT-220 robotic sample handling system was used as autosampler. To prevent the thermal degradation of iPP during measurements, a certain amount of Irganox\textsuperscript{®} 1010 was added to the iPP/silica/TCB solution.

**\textsuperscript{1}H NMR T\textsubscript{2} Relaxation Experiment.** The proton transverse magnetization decays, T\textsubscript{2} relaxation decays, were measured on a Bruker Minispec mq20 nuclear magnetic resonance spectroscopy (NMR) analyzer at a proton resonance of 20 MHz. The Minispec was equipped with a BVT-3000
variable temperature unit. The temperature gradient and stability were about 1 K and 0.1 K respectively.

The decay of the transverse magnetization was measured by using a two pulse sequence $90^\circ-\tau-180^\circ-\tau$ acquisition with spacing time of 0.4 microseconds (ms). The amplitude of the transverse magnetization $I(t)$ is measured as a function of time $t$. The $T_2$ relaxation experiments were performed at 170 and 190 °C.

2.3. Results and discussion

2.3.1. In-situ silica particle synthesis

2.3.1.1. Dispersion of silica nanoparticles in iPP matrix

![Fig. 2.1. TEM images of in-situ formed ~ 0.4 vol% silica filled iPP nanocomposite.](image)

Compared with the in-situ silica particle synthesis procedure used by Jain et al., some modifications were performed in the present work. A N$_2$ flow was first purged into the reactor for 15 min to remove oxygen from the reactor. No direct drying under vacuum at 120 °C for 24 hours was carried out after gelation at 80 °C for 5 hours. This drying procedure used by Jain et al. might cause further sol-gel reactions in the vacuum oven, which lead to the differences in the surface properties of the silica particles. Different states of dispersion of silica nanoparticles in iPP were also expected. The TEM images of ~ 0.4 vol% silica filled iPP nanocomposite prepared in this work are shown in Fig. 2.1. The images show a broad distribution of the particle size: from ~ 20 nm silica particles to ~ 150 nm silica nano-clusters. The size and shape of such prepared silica nanoparticles are comparable to that made by Jain et al. The silica nano-clusters prepared by Jain et al. were in the range of 30 - 100 nm. The morphology of silica nanoparticles prepared from the procedures used both in the present work and by Jain et al. was stable after mixing in a mini-twin screw extruder.

2.3.1.2. Rheology of iPP/silica nanocomposites prepared via in-situ particle synthesis

Fig. 2.2a shows the dynamic viscosity curves of iPP/silica nanocomposites prepared from in-situ particle synthesis. The curves illustrate the effect of the addition of the silica
nanoparticles on the absolute value of complex viscosity $|\eta^*|$ of the iPP at 180 °C. To avoid the crystallization or the formation of nuclei of iPP, if any at lower temperatures, no time-temperature superposition was applied. With increasing silica content, $|\eta^*|$ decreases to a minimum value at a silica volume fraction of ~0.4 vol%, and $|\eta^*|$ increases again for the (iPP + 0.6 vol% silica) nanocomposite. The viscosity curve for the (iPP + 0.4 vol% silica) nanocomposite at low frequencies slightly goes up, which indicates the formation of (early-stage) solid-like structures in the composite. Due to the interaction between polymer and particles, the network of the nanoparticles via polymer matrix, i.e., (early-stage) solid-like structures may form. This was confirmed by the divergence of the slope of log $G''$ versus log $\omega$ for the (iPP + 0.4 vol% silica) nanocomposite, which decreased slightly compared with pure iPP (Fig. 2.3).

Fig. 2.2. The absolute value of complex viscosity $|\eta^*|$ versus frequency $\omega$ for iPP/silica nanocomposites at 180 °C prepared by in-situ silica particle synthesis (a) present work and (b) previous work from Jain et al.

Fig. 2.3. Storage modulus $G'$ and loss modulus $G''$ versus frequency $\omega$ for iPP/silica nanocomposites prepared via in-situ silica nanoparticle synthesis in the iPP powder.

Compared with the viscoelastic behavior of the iPP/silica nanocomposites from the work of Jain et al. (Fig. 2.2b), different viscoelastic behavior was observed. First, the lowest $|\eta^*|$ occurred for the (iPP + 0.4 vol% silica) nanocomposite, i.e., (iPP + 0.8 wt% silica) nanocomposite, while in Jain’s systems, the lowest viscosity was for the (iPP + 0.5
wt% silica) nanocomposite. Second, the (iPP + 0.4 vol% silica) nanocomposite complex viscosity at 0.1 rad/s and 180 °C is ~ 64% lower than the iPP. The decrease in viscosity is smaller than that observed by Jain et al., which was ~ 90%.

The reasons for the difference in viscosity reduction from the present study and the work of Jain et al. are complicated. The state of dispersion of the silica nanoparticles, particle size and structure are key factors to influence the rheological behavior of the iPP/silica nanocomposites. The porosity, the pore size, and the pore size distribution of the iPP powder are relevant to the diffusion coefficient of the precursor TEOS into the iPP pores. The diffusion coefficient of TEOS corresponds directly to the silica dispersion state.

Table 2.2. Silica contents comparison prepared via in-situ silica particle synthesis.

<table>
<thead>
<tr>
<th>Target (vol%)</th>
<th>TGA (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.4</td>
<td>0.1</td>
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<td>0.6</td>
<td>0.2</td>
</tr>
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<td>0.3</td>
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<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>4.6</td>
<td>0.6</td>
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</tbody>
</table>

The conditions used for the sol-gel reaction are also crucial. First, the pH value of the catalyst, which triggers the hydrolysis and condensation reactions, controls the reaction rate and the size of silica nanoparticles. Solubility of small particles is higher at high pH than at low pH, resulting in larger particles (5 - 10 nm). Under basic conditions, particles are negatively charged and hence repel each other. Under acidic conditions, the charge of repulsion is reduced and aggregations occur, resulting in branched network of silica particles (2 - 4 nm). Considering the size and the aggregation, basic catalyst conditions are suitable for in-situ preparation of silica in the iPP pores. Second, the ratio between TEOS/water/NH₄OH is a key parameter for the morphologies of silica nanoparticles or the structures of silica surfaces. There are four different silica surface structures, i.e., Q¹, Q², Q³ and Q⁴. The Q¹ structure is fully condensed silica (SiO₂), and Q⁴ is assigned to the structure with a -SiO- connected to three Si and one H or C atom in the second coordination sphere. The same definition is used for Q² and Q³. The surface energies are different with different silica surface structures, leading to the differences in the interactions between iPP and silica surfaces. Third, the type of the precursor also influences the state of dispersion, size and structure of the nanoparticles due to their diffusion coefficient differences. In addition, time and temperature are two important factors. To sum up, the parameters which are related to the in-situ sol-gel reactions and are relevant to the studied iPP/silica nanocomposites are complicated. Therefore, both in the present work and in the work of Jain et al. difficulties to control silica contents were encountered. Table 2.2 presents the silica content differences between the target values and the values characterized via TGA. Other approaches need to be investigated.
2.3.2. Melt compounding

The iPP/silica nanocomposites prepared from melt compounding are used to study the effect of the particle size on their viscoelastic behavior. Silica particles which were suspended in water and with particle diameter $D = 7$ nm, 10 nm, 12 nm and 20 nm were extruded together with iPP and stabilizer powder. To study the effect of the particle size distribution, two different particles with $D = 7$ nm and 20 nm were mixed together with a weight ratio of 50:50.

2.3.2.1. Dispersion of silica nanoparticles in iPP matrix

Fig. 2.4 demonstrates the dispersion of $\sim 1.5$ vol% silica nanoparticles with $D = 20$ nm in the iPP matrix. Silica nanoparticles form 60 - 500 nm aggregates. Compared with the dispersion of the silica nanoparticles in the iPP matrix prepared via the in-situ method, silica particles are more homogeneously dispersed, but with aggregates.

2.3.2.2. Effect of the particle size and distribution on the viscoelastic behavior of iPP/silica nanocomposites

The absolute value of complex viscosity $|\eta^*|$ versus frequency for the iPP/silica nanocomposites prepared from melt compounding is depicted in Fig. 2.5. At low frequencies, iPP and most of the iPP/silica nanocomposites exhibit a Newtonian behavior, followed by a decrease of $|\eta^*|$ at high frequencies. The curve for the (iPP + 3.5 vol% silica) nanocomposite at low frequencies (Fig. 2.5a) indicates the formation of solid-like network structures of silica particles via the polymer matrix. This was confirmed by a divergence from the slope of log $G'$ versus log $\omega$ which was demonstrated in Fig. 2.5f.

With the addition of 20 nm silica nanoparticles in iPP matrix, $|\eta^*|$ decreases first and then increases while the lowest $|\eta^*|$ value is for the (iPP + 1.8 vol% silica) nanocomposite (Fig. 2.5a). This trend confirms that there are two different viscosity regimes, which was reported by Jain et al. Similar variations were also seen in the iPP/silica nanocomposites with particle size of 12 nm and 10 nm, but the minimum viscosity value occurred at different silica contents (Fig. 2.5). For 12 nm silica nanoparticles, the lowest $|\eta^*|$ is for the (iPP + 0.8 vol% silica) nanocomposite while for 10 nm silica nanocomposites, the lowest
\[ \eta^* \] is for the (iPP + 0.2 vol% silica) nanocomposite. The percentage of the decrease in viscosity \( \Delta \) was defined as:

\[
\Delta = \left( \frac{|\eta_i^*| - |\eta_0^*|}{|\eta_0^*|} \right) \times 100
\]

(2.6)

where \( |\eta_i^*| \) is the complex viscosity of the iPP/silica nanocomposites at a silica content of \( i \), and \( |\eta_0^*| \) is the complex viscosity of pure iPP. \( \Delta \) is decreasing with decreasing silica nanoparticles sizes (Table 2.3). When 7 nm silica nanoparticles were added to the iPP matrix, no significant decrease of \( |\eta^*| \) was found. Fig. 2.5 and Table 2.3 demonstrate that the silica nanoparticle size affects the viscosity reduction of the iPP/silica nanocomposites.

Generally, the physisorption coupled with \( \Lambda \) governs the rheological behavior of the iPP/silica nanocomposites.\(^{7}\) Comparing with the polymer size \( 2R_g \), three different regimes can be defined: \( \Lambda > 2R_g \), \( \Lambda \approx 2R_g \) and \( \Lambda < 2R_g \). At very low silica content, the system is in the \( \Lambda > 2R_g \) regime. In this regime, iPP chains in the matrix do not experience any bridging. As the silica volume increases to a certain critical volume fraction \( \phi_c \), \( \Lambda \approx 2R_g \), a further increase in the silica content results in a smaller interparticle distance, i.e., \( \Lambda < 2R_g \). This leads to the occurrence of bridging. As the volume fraction of silica particles increases beyond certain content, extensive bridging and confinement occurs, which lead to an increase in viscosity. As discussed above, the critical volume fraction \( \phi_c \) is the volume fraction \( \phi \) when \( \Lambda \approx 2R_g \), which was listed in Table 2.1 and Table 2.3. We assume that in our system, silica nanoparticles have a random packing, i.e., \( \phi_0 \approx 0.638 \) and nanoparticles are individually dispersed. Inserting these relationships into equation (2.1), different \( \phi_c \) for different particle sizes can be obtained. In order to compare the volume fraction where the lowest viscosity occurs from experimental data, i.e., \( I_e \) was also listed in Table 2.3.

Table 2.3 demonstrates that \( I_e \leq I_c \). This may be due to the fact that \( I_c \) was calculated based on \( \Lambda \approx 2R_g \), when the iPP chain touches two silica nanoparticles and the viscosity starts to increases. In practice, \( I_e \) occurs when \( \Lambda < 2R_g \), thus \( I_e \leq I_c \).

When the silica nanoparticles diameter is < 10 nm, small viscosity reduction or no viscosity reduction was observed. This might be due to larger aggregates formed in the systems with silica nanoparticles’ diameter \( D = 10 \) nm and 7 nm compared to that for 20 nm due to their dramatically increased silica surface area. In addition, theoretically more than one polymer molecule is required to bridge large particles which may lead the polymer chain to lay flat on their surface in case of strong interaction; whereas for small particles, which have diameter \( D < R_g \), only a small segment of a polymer chain is required to form bridges. One molecule can thus extend through many bridges when smaller nanoparticles are used,\(^{13}\) which lead to a small or no viscosity reduction (Table 2.3) or even an increase in viscosity.

To investigate the effect of the nanoparticles’ distribution, nanoparticles with diameter of 7 nm and 20 nm were mixed together with weight ratio of 50:50. \( D_s \) is 13.6 nm based on equation (2.4). Combining equations (2.3) and (2.5), and \( \Lambda \approx 2R_g \approx 40 \) nm, a critical volume fraction \( \phi_c \approx 1.8 \) vol% was obtained for the system of (7 nm + 20 nm) (Table 2.3).
Chapter 2 Nanoscale effects on the decrease in viscosity of iPP/silica nanocomposites

The experimental data shows $\phi_e \sim 0.9$ vol% silica, at which the viscosity of the iPP nanocomposite was reduced by $\sim 65\%$.

Fig. 2.5. Absolute value of complex viscosity $|\eta^*|$ versus frequency $\omega$ for iPP/silica nanocomposites at 10% strain and 180 °C; (f) $G'$ and $G''$ for iPP/silica (20 nm) nanocomposites at 180 °C.

The difference between $\phi_c$ and $\phi_e$ is large for the iPP/(7 nm + 20 nm) silica nanocomposites. In the iPP/(7 nm + 20 nm) silica nanocomposites, different chain morphologies are expected considering the curvature and the size of used silica nanoparticles. Theoretically, to bridge two 7 nm particles, a shorter segment of a polymer chain is required than to bridge two 20 nm particles. Therefore, the system is more apt to...
form bridging than iPP/20 nm silica system. The ~ 0.9 vol% (7 nm + 20 nm) induced a similar Δ as that for iPP/20 nm silica system with ~ 1.8 vol% silica, implying that there was more effective surface area to adsorb iPP chains. This means that the large silica surface area from 7 nm particles plays an important role.

Table 2.3. Viscosity reduction for iPP/silica nanocomposites with different particle size.

<table>
<thead>
<tr>
<th>Particle size $D$ (nm)</th>
<th>$\phi_i$ (vol%)</th>
<th>$\phi_e$ (vol%)</th>
<th>$\Delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2</td>
<td>1.8</td>
<td>50 -66</td>
</tr>
<tr>
<td>12</td>
<td>0.8</td>
<td>0.8</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>0.2</td>
<td>9</td>
</tr>
<tr>
<td>7</td>
<td>0.2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>7 + 20</td>
<td>1.8</td>
<td>0.9</td>
<td>65</td>
</tr>
</tbody>
</table>

At high frequencies, $\Delta$ is less than at low frequencies. The slope of viscosity against frequency (Fig. 2.5) is slightly smaller for iPP/silica nanocomposites than for pure iPP, indicating a shorter relaxation time in the iPP/silica nanocomposites. Additionally, the smaller slope implies that the viscosity of the iPP/silica nanocomposites is not from the ‘ball-bearing’ effect, which is used to explain the flow promotion in spherical particle-filled polymer systems. If spherical particle-filled polymers are forced to shear, an extremely high local shear is developed in the narrow gaps between the nearby rotating spheres, which induce the polymer chains to disentangle.

In summary, the addition of silica nanoparticles to the iPP matrix may decrease the viscosity of the iPP matrix, which is dependent on the size of the silica nanoparticles and their size distribution (Table 2.3). In addition, the interparticle distance $\Lambda$ and the radius of gyration of polymer $R_g$ are the key factors that determine the critical silica content $\phi_c$.

2.3.3. Solution method

2.3.3.1. Dispersion of silica nanoparticles in iPP matrix prepared from different drying procedures

A good dispersion of the nanoparticles is crucial to expose the entire surface and, thus, to improve the properties. Different preparation procedures may result in different states of dispersion. Therefore, three different drying procedures, i.e., gradually solvent evaporation, precipitation and vapor rotation, were used to prepare the iPP/silica nanocomposites and to check the effect of the drying procedure on the state of nanoparticles’ dispersion in iPP matrix. The state of dispersion of silica nanoparticles in the iPP matrix from these three different procedures is demonstrated in Fig. 2.6. The size of the aggregates is in the range of 25 - 200 nm from both precipitation and vapor rotation methods, while the size of silica aggregates via slow evaporation is relatively large, i.e., in the range of 20 - 500 nm.

The obtained states of dispersion are comparable with that when they were in toluene (Fig. 2.7b). Diluted original silica toluene suspension TOL-ST was dipped onto TEM
Chapter 2 Nanoscale effects on the decrease in viscosity of iPP/silica nanocomposites

Sample support mesh grids. TEM images (Fig. 2.7b) were taken after toluene evaporation. The formation of large aggregates in TOL-ST was probably induced by toluene evaporation during sample preparations.

Fig. 2.6. State of silica dispersion in iPP matrix via (a) slow evaporation S_1.3 vol% silica, (b) precipitation P_1.5 vol% silica and (c) vapor rotation V_1.3 vol% silica.

Fig. 2.7. TEM images comparison of (a) (iPP + 1.3 vol% silica) nanocomposites from slow evaporation and (b) silica TOL-ST suspension.

2.3.3.2. Effect of drying procedures on the viscoelastic behavior of iPP/silica nanocomposites

The dynamic rheological properties of the iPP/silica nanocomposites prepared via solution method were measured for a range of silica contents. Fig. 2.8 shows their dynamic viscosity curves. With addition of silica, the dynamic viscoelastic properties of iPP/silica nanocomposites vary. A large decrease (~70%) in the absolute value of complex viscosity $|\eta^*|$ occurs for the iPP/silica nanocomposites when the silica content is in the range of 0.8 ~ 1.1 vol%, after which $|\eta^*|$ increases again. The iPP/silica nanocomposites made via three different drying procedures have similar dynamic rheological properties (Fig. 2.8). The viscosity ($\omega = 1$ rad/s) variations with silica content are depicted in Fig. 2.8d. The differences in the silica content at which the lowest viscosity from different drying procedures was observed are related to the state of dispersion in the iPP matrix. Via vapor rotation, the addition of ~0.8 vol% silica nanoparticles lead to larger viscosity reduction compared with that of S_0.9 vol% silica. This indicates the better state of silica dispersion in V_0.8 vol% silica than in S_0.9 vol% silica.
Furthermore, the effect of drying procedures on the state of dispersion can be observed by comparing Figs. 2.8a-c. With addition of silica nanoparticles, a Newtonian behavior was displayed in most of the iPP/silica nanocomposites within low frequency range. However, the Newtonian behavior can be varied by changing drying procedures, especially for the iPP/silica nanocomposites with silica content > 0.6 vol%. For example, with addition of ~ 0.9 vol% silica, the iPP/silica nanocomposite prepared from slow evaporation (S_0.9 vol% silica) has a Newtonian behavior, and V_0.8 vol% silica has continuous shear-thinning behavior, while P_0.9 vol% silica has more shear-thinning behavior when \( \omega < 0.1 \text{ rad/s} \) than \( \omega > 0.1 \text{ rad/s} \). The difference in rheological behavior indicates the structure differences, i.e., the differences in the state of dispersion, in the iPP/silica nanocomposite. In both P_0.9 vol% silica and V_0.8 vol% silica, early-stage solid-like structures form, in which one of the silica nanoparticles can feel the existence of another nanoparticle through the iPP matrix, but not from direct bridging effect. Using precipitation, the addition of ~ 0.9 vol% silica nanoparticles into the iPP matrix induced larger viscosity reduction than using vapor rotation to add ~ 0.8 vol% silica nanoparticles (Fig. 2.8d). The rheological behavior differences between P_0.9 vol% silica and V_0.8 vol% silica indicate that the state of silica dispersion in P_0.9 vol% silica reveals more effective silica surface area to the iPP matrix than in V_0.8 vol% silica.

Fig. 2.8. The absolute value of complex viscosity \(|\eta^*|\) versus frequency \(\omega\) for iPP/silica nanocomposites via (a) precipitation, (b) vapor rotation and (c) slow evaporation with a strain of 10% at 180 °C; d) \(|\eta^*|\) (\(\omega = 1 \text{ rad/s}\)) as a function of silica content. The line is to guide the eye.
For the precipitation and vapor rotation systems, the viscosity curves in the low frequencies range go up when the silica content > 2.0 vol%. This is due to the formation of solid-like structures in the nanocomposites. The formation of solid-like structures induced higher shear-thinning, especially in P.2.3 vol% silica and V.2.8 vol% silica, than the samples with the silica content < 2.0 vol%. Therefore, at \( \omega = 1 \) rad/s, the complex viscosity for P.2.3 vol% silica and V.2.8 vol% silica is lower than that for P.1.3 vol% silica and V.1.5 vol% silica. The formation of the solid-like structure can also be seen in the slope divergence of log \( G' - \log \omega \) and log \( G'' - \log \omega \) (Fig. 2.9a). For pure iPP, the slope of log \( G' - \log \omega \) is approx. 2 while the slope of log \( G'' - \log \omega \) is around 1. With addition of silica nanoparticles, the slopes decrease, especially for P.2.3 vol% silica sample (Fig. 2.9a), indicating that extra elastic effects occur, most probably as a consequence of particle-particle interactions. Furthermore, the addition of silica nanoparticles shifted the cross-over point to a higher frequency than for pure iPP. For entangled homopolymers, the reciprocal of the first crossover frequency obtained from \( G'(\omega) \) and \( G''(\omega) \) (on a log-log plot, listed in Fig. 2.9a) corresponds to their longest relaxation time, \( \tau_d \), which is the reptation time for the entangled iPP chains. Therefore, the addition of silica nanoparticles to iPP matrix induced a shorter relaxation time than that for pure iPP.

![Fig. 2.9. (a) Storage modulus \( G' \) and loss modulus \( G'' \) versus frequency \( \omega \), and (b) shifted storage modulus \( G' \) and loss modulus \( G'' \) versus frequency \( \alpha \omega \) for iPP/silica nanocomposites prepared via precipitation at \( T = 180 ^\circ C \).](image)

In general, at low frequency, \( G' < G'' \), whereas at high frequency \( G' > G'' \) (Fig. 2.9a). The intersection of the moduli versus the frequency gives the crossover frequency and the crossover modulus \( G_c \). \( G_c \) is a measure of the polydispersity of the polymer.\(^{15}\) Therefore, \( G_c \) for the iPP/silica nanocomposites, e.g. prepared via precipitation, was compared. Fig. 2.9b presents \( G' \) and \( G'' \) of the iPP/silica nanocomposites which was shifted to the crossover frequency of P.0 vol% silica. The addition of silica nanoparticles shifted \( G_c \) to a higher value, especially for P.1.1 vol% silica. This is partially due to the presence of the silica nanoparticles, which increase the modulus based on the Einstein equation.\(^{16}\) Additionally, when 20 rad/s > \( \omega > 0.01 \) rad/s, the moduli versus frequency curve for P.1.1 vol% silica locates at higher frequency side than P.0 vol% silica (Fig. 2.9b), i.e., the average relaxation of the melt gets faster, which is in agreement with the lower viscosity.
2.3.4. Mechanisms for the viscoelastic behavior of iPP/silica nanocomposites

2.3.4.1. Investigation on molar mass variation of iPP/silica nanocomposites

It is well known that viscosity is very sensitive to molar mass changes. The (zero-shear) viscosity $\eta_0$ increases dramatically with molar mass $M_w$ when the molar mass is above a critical value, following a power law $\eta_0 = k M_w^{3.4}$. Therefore, estimating the molar mass variation of the studied nanocomposites is crucial. However, it is not always convenient to measure the molar mass of iPP via SEC, since it is difficult to dissolve iPP at room temperature. In this study, different methods were thus carried out to characterize the molar mass variations.

Considering that the crossover modulus $G_c$ is a measure of the polydispersity of the polymer, $G_c$ for the studied iPP/silica nanocomposites was indicated by the dashed line in Fig. 2.3, Fig. 2.5f and Fig. 2.9. Generally, the increase in $G_c$ indicates a decrease in the polydispersity and vice versa. The figures demonstrate that with addition of silica nanoparticles, $G_c$ keeps constant or slightly increases, which partially comes from the reinforcement of the silica nanoparticles. Thus, the polydispersity was hardly influenced by the addition of the silica nanoparticles, indicating that there was no degradation, which can broaden or narrow the molar mass distribution of a polymer, depending on the chain statistics. If degradation mainly happens at the high molar mass tail, the polydispersity tends to become narrower and vice versa.

Molar mass stability via extrusion was also investigated. The commercial iPP pellets were extruded using a laboratory twin-screw extruder with different temperatures (e.g. 200 °C, 210 °C and 220 °C) and screw speeds (e.g. 80 rpm, 90 rpm, 100 rpm). The viscosity of extruded samples was characterized afterwards at $T = 180$ °C. One sample after running through the extruder twice at $T = 200$ °C was also compared. For reference, the viscosity of the iPP without extrusion was included. The nicely overlapped viscosity curves indicate that the molar mass of iPP is stable during extrusion. Furthermore, a tiny amount of water in silica suspensions was used. The existence of water molecules may lead to a dramatic degradation of iPP. Therefore, comparable amount of water as used for the (iPP + 3.5 vol% silica) (20 nm) nanocomposites (Fig. 2.5a) was added into pure iPP during extrusion. The rheology for this sample was compared with pure iPP. No viscosity difference was observed compared with the rest. However, the addition of silica nanoparticles may increase the shear stresses during extrusion, and, thus lead to the degradation of iPP matrix. Therefore, the viscosity iPP/silica nanocomposites after extrusion were compared with that before extrusion. For example, the viscosity of P_0.9 vol% silica before extrusion and after extrusion were measured and compared. The results show that the viscosity of the samples before and after extrusion is comparable. Therefore, the viscosity reduction of iPP/silica nanocomposites is not attributed to the molar mass variation.

The molar mass for the iPP/silica nanocomposites was also characterized via high temperature size exclusion chromatography (HT-SEC). As an example, Fig. 2.10a presents...
thus only the molar mass distribution plots of the iPP/silica nanocomposites prepared via precipitation. Most of the plots are overlapping with the pure iPP curve, while there are divergences for the (iPP + 0.4 vol% silica) and the (iPP + 1.3 vol% silica) nanocomposites. The slightly molar mass decreases for the (iPP + 0.4 vol% silica) may be due to degradation. The increase in molar mass for the (iPP + 1.3 vol% silica) nanocomposite is probably from the non-filtered silica particles. In addition, the variations between the molar mass distribution plots for the iPP matrix and the iPP/silica nanocomposites might come from the accuracy of HT-SEC under hot conditions. Therefore, the molar mass distribution plots of one nanocomposite, e.g. P_0.9 vol% silica, were characterized before and after rheological measurements. The nicely overlapped plots (Fig. 2.10b) imply that no degradation occurs during rheological measurements. Considering the rheological measurements were performed under oscillation at 180 °C, which was higher than the temperature used for HT-SEC (160 °C), the differences in the molar mass distribution plots due to degradation, if there is any, should be observed via after HT-SEC. The nicely overlapped plots (Fig. 2.10b) indicate that the measurement errors due to the accuracy of HT-SEC under hot condition can be neglected.

In summary, hardly any degradation was observed in iPP/silica nanocomposites. Therefore, the viscosity reduction of iPP/silica nanocomposites is not because of the molar mass decrease, i.e., degradation. It is proposed that the viscosity reduction observed in iPP/silica nanocomposites is related to the adsorption of iPP chains to silica surfaces. The adsorption results in the relaxation time variation of iPP/silica nanocomposites.

Fig. 2.10. (a) Molar mass distribution plots of iPP/silica nanocomposites prepared via precipitation, and (b) molar mass distribution plots of P_0.9 vol% silica before and after rheological measurements. The plots are based on PS standard at 160 °C.

2.3.4.2. T_2 relaxation time for iPP/silica nanocomposites characterized by NMR

Generally, the polymer-filler interaction plays a crucial role in the properties of nanocomposites. However, it is difficult to determine the role of this interaction because it is often limited to a molecular (interfacial) distance scale (on the order of 10-100 Å), but it has been reported that nuclear magnetic resonance spectroscopy (NMR) can provide information about molecular motion of polymer at interfaces. In this work, proton T_2
measurements were carried out. Proton $T_2$ relaxation is the decay of the transverse magnetization components after an excitation pulse.\textsuperscript{20} In polymers, this decay is basically a dephasing, mainly via dipolar proton-proton interaction. Different mobilities of polymer chains result in different effective dipoles. Thus, phases with different mobility will relax at different rates.

![Fig. 2.11]  
**Fig. 2.11.** $T_2$ relaxation spectra for the iPP/silica nanocomposites from NMR measurements at (a) 170 °C and (b) 190 °C.

![Fig. 2.12]  
**Fig. 2.12.** (a) Comparison between the absolute value of complex viscosity $|\eta'|$ ($\omega = 1$ rad/s at 180 °C) and $1/T_2$ (at 170 °C and intensity ~ 0.3 a.u.) versus silica content and (b) $1/T_2$ (at 170 °C and intensity ~ 0.3 a.u.) versus $|\eta'|$ for iPP/silica nanocomposites.

$T_2$ relaxation of the iPP/silica nanocomposites at 170 °C and 190 °C, e.g. the samples prepared via the precipitation method, is presented in Fig. 2.11. The $T_2$ relaxation time of the (iPP + 0.9 vol% silica) nanocomposite is much longer than the pure iPP. The increase in $T_2$ relaxation time implies an increase of the chain mobilities in the bulk. It is also important to notice that with increasing temperature (Fig. 2.11a & b) the mobility of the iPP/silica nanocomposites increases. This temperature induced increase in the $T_2$ relaxation time may minimize the influences of the silica addition. Therefore, at 190 °C, the $T_2$ relaxation time of the iPP/silica nanocomposites becomes slightly closer to each other. The $T_2$ relaxation time of the (iPP + 0.9 vol% silica) nanocomposite is longer than the (iPP + 1.1 vol% silica) nanocomposite at 170 °C, while at 190 °C, the reverse occurs. This may be due to the dispersion state variations of the silica nanoparticles with temperature.
The results from the NMR $T_2$ relaxation confirm the rheological observations. In Fig. 2.12a, open squares showed $|\eta^*| (\omega = 1 \text{ rad/s at } 180 \degree \text{C})$ of iPP/silica nanocomposites versus silica content while filled circles indicated the variation of the $T_2$ relaxation at 170 °C with the addition of silica nanoparticles. As discussed above, a large decrease (~70%) in $|\eta^*|$ occurs to iPP/silica nanocomposites when the silica content is in the range of 0.8 ~ 1.1 vol%, after which $|\eta^*|$ increases again. A similar trend is observed by the curve of $1/T_2$ relaxation versus silica content, implying that the $1/T_2$ of iPP/silica nanocomposite decreases first compared with the pure iPP and increases again. The minimum value of $1/T_2$ occurs to the (iPP + 0.9 vol% silica) nanocomposite. Therefore, a good correlation between the viscosity reduction and the relaxation time variation $1/T_2$ (Fig. 2.12b) was observed. Fig. 2.12b shows a linear correlation between $|\eta^*|$ and $1/T_2$. The decrease in $|\eta^*|$ indicates the decrease in reptation time, which can be characterized via $1/T_2$ from NMR measurements.

### 2.3.4.3. Selective adsorption mechanism

The selective adsorption used by Jain et al.\footnote{Jain et al.} can be partly applied in the present work to explain the observed viscosity reduction. The selective adsorption is related to the molar mass distribution and polymer-particle interactions. Polymer chains first adsorb very rapidly on the surface of the nanoparticles with a crude duplicate of the original polymer matrix. This is followed by a movement of the low molar mass chains to the surface because of their high mobility. Concurrently, the high mobility of the short chains leads them to move away from the surface. Subsequently, the high molar mass chains transfer themselves to the surface. Since the high molar mass chains have more attached points to the nanoparticles surface, the chains are difficult to move away from the surface. This is thermo-irreversible adsorption. Therefore, most of the high molar mass chains stay next to the nanoparticle surface, form a shell, and most of the low molar chains comprise the polymer matrix. According to the power law $\eta_0 = k M_w^{3.4}$, the (zero-shear) viscosity $\eta_0$ increases with molar mass $M_w$ with a power of 3.4 when molar mass is above a certain value. Therefore, a decrease in viscosity $\eta_0$ is expected in the nanocomposites where the selective adsorption occurs. The lowest viscosity $\eta_0$ thus takes places when all of the nanoparticles' surface areas are effective to the polymer chains with high molar mass and before bridging occurs. This may be obtained when all nanoparticles are individually dispersed.

The selective adsorption procedure thus changes the polydispersity of the iPP/silica nanocomposites. In general, the value of the complex modulus $G'$ where the phase angle $\delta$ is 45° correlates approximately with the value of polydispersity.\footnote{The higher the $G'$, the lower is the polydispersity.} The higher the $G'$, the lower is the polydispersity. Fig. 2.13a illustrates the relation of $G'$ at $\delta = 45°$ and silica content for the iPP/silica nanocomposites prepared from precipitation. Fig. 2.13a shows that $G'$ at $\delta = 45°$ first increases with the addition of silica nanoparticles and then decreases slightly. The highest value for $G'$ at $\delta = 45°$ occurs to the P_0.9 vol% silica, indicating that the P_0.9 vol% silica has the lowest polydispersity, while the molar mass distribution of P_1.1 vol% silica is also narrower than P_0 vol% silica. However, the
increases in $G^*$ at $\delta = 45^\circ$ might be attributed to reinforcement of the silica nanoparticles based on Einstein’s theory. Therefore, the effect of the silica nanoparticles on the increase of the $G^*$ at $\delta = 45^\circ$ was calculated (Fig. 2.13a open circle). The comparison of $G^*$ at $\delta = 45^\circ$ between experimental data (Fig. 2.13a filled square) and the calculated data (Fig. 2.13a open circle) shows clearly that the addition of silica nanoparticles induces a higher $G^*$ at $\delta = 45^\circ$, namely lower polydispersity. Combining that almost no breaking down of large molar mass in the molar mass distribution plot (Fig. 2.10) was observed, the decrease in the polydispersity of the iPP/silica nanocomposites is thus due to the selective adsorption of the iPP chains to the surface of silica nanoparticles.

Han plots, which depict the storage modulus $G'(\omega)$ versus the loss modulus $G''(\omega)$ with frequency as a parameter, were used to elucidate structure differences between the polymer matrix and the filled systems at a fixed temperature. The iPP/silica nanocomposites prepared from precipitation are presented in Fig. 2.13b. The storage moduli $G'(\omega)$, for a given loss moduli $G''(\omega)$, increases with addition of silica in the low frequency region, especially for the P 2.3 vol% silica. This indicates the formation of solid-like structures in the iPP/silica nanocomposites.

Analogous to the Han plots, Cole-Cole plots graph the imaginary viscosity $\eta''$ as a function of real viscosity $\eta'$ (Fig. 2.14). A standard semi-arc is obtained if the deformation behavior of the material can be described by a single relaxation time or with a narrow relaxation time distribution. In complex polymeric systems, more than one relaxation time can occur, leading to the distortion of the arc or to the appearance of a second arc. Therefore, Cole-Cole plots were used to investigate the microstructures or molecular architectures of homopolymers or materials with a wide relaxation time distribution such as heterogeneous polymeric systems, polymer composites, block copolymers and polymer blends. Fig. 2.14 gives the Cole-Cole plots for iPP/silica nanocomposites prepared from precipitation at 180 °C.

From the Cole-Cole plots, we first observe standard semi-arc trends for iPP/silica nanocomposites with volume fraction < 0.9 vol% (Fig 2.14). This indicates that these silica nanoparticles filled polymeric systems exhibit a single relaxation time or a narrow
relaxation time distribution. With increasing silica concentration till 0.9 vol%, a distortion of the arc and the appearance of a second arc are observed, implying a different relaxation time. For P.2.3 vol% silica, the arc was completely distorted, implying the formation of elastic structures, due to nano-silica particle-particle interactions. In addition, the diameter of the semi-arc becomes smaller. At low frequency (or zero frequency) and $\eta'' = 0$ the corresponding real viscosity $\eta'$ is equal to the zero-shear viscosity. In Fig. 2.14, it is evident that this zero-viscosity value changes with silica content, which is similar to the viscosity variation phenomena (Fig. 2.8a). Furthermore, the frequency where $\eta''$ is maximum varies with silica concentration. These changes allow us to calculate the systems’ relaxation times. For example, the maximum value of $\eta''$ for the P.0.9 vol% silica nanocomposite corresponds to the highest frequency value in the studied nanocomposites, suggesting that the P.0.9 vol% silica relaxes the fastest, which is in the agreement with the results from NMR.

![Fig. 2.14. Cole-Cole plot at 180 °C for iPP/silica nanocomposites prepared from precipitation.](image)

### 2.4. Conclusions

Different preparation methods were used to prepare the iPP/silica nanocomposites. Silica dispersions and the rheological behavior of the prepared iPP/silica nanocomposites were characterized.

The samples prepared from in-situ silica particles synthesis in the iPP powder do not have homogeneous state of silica dispersion and silica particles morphologies. Such prepared silica nanoparticles in the iPP matrix reduced the iPP matrix’s viscosity when a suitable iPP porosity and sol-gel reaction procedure were used.

The iPP/silica nanocomposites made from melt compounding were used to study the effect of nanoparticle size and their polydispersity on the viscoelastic behavior. A viscosity reduction percentage ~ 55% was attained for the sample with $D = 20$ nm particles. The viscosity reduction percentage decreases with particle size. There was no decrease in viscosity for the $D = 7$ nm particles filled-iPP nanocomposites. The results from 7 nm and 20 nm nanoparticles blends confirmed ~ 65% viscosity reduction, which implies the importance of the nanoparticles’ distribution.
Solution methods can give good and homogeneous silica dispersions in the iPP matrix. The used dying procedures, i.e., slow evaporation, precipitation and vapor rotation, influence the state of dispersion of the nanoparticles and the rheological behavior of iPP/silica nanocomposites. A comparable viscosity reduction ~ 70% is obtained for the iPP/silica nanocomposites prepared via precipitation and vapor rotation, while the viscosity reduction $\Delta$ for the nanocomposites prepared from slow evaporation is lower (Fig. 2.8d).

After the investigations of the molar mass of the iPP/silica nanocomposites, the results from the plots of $G^*$ at $\delta = 45^\circ$ occurs versus silica content, Han plots, Cole-Cole plots and $T_2$ relaxation time confirm that the high molar mass of iPP chains are adsorbed to the silica surfaces while the low mass chains consist of the matrix, which induces the viscosity reduction observed in iPP/silica nanocomposites.

2.5. References

Abstract

The crystallization behavior of isotactic poly(propylene) (iPP)/silica nanocomposites was studied under both isothermal and non-isothermal crystallization conditions. Under both conditions, the crystallization rate increases first and then decreases with addition of silica nanoparticles, while the addition of ~0.9 vol% silica induces the highest crystallization rate. The nucleating efficiency increases after addition of ~0.4 vol% silica nanoparticles compared with pure iPP, after which the nucleation efficiency is saturated or slightly decreased. After applying shear to the nanocomposites, small-angle X-ray scattering (SAXS) images show significant decreases in the intensity of meridional lobes, while no meridional lobes are observed for the samples which have the lowest viscosity, indicating that there is less chain orientation or small crystals formed in these nanocomposites.
3.1. Introduction

The previous chapter described the influences of silica nanoparticles on the rheological behavior of isotactic poly(propylene) (iPP)/silica nanocomposites, prepared via different methods. A similar viscoelastic behavior was observed for the studied iPP/silica nanocomposites. A decrease in viscosity was obtained with addition of silica nanoparticles to iPP matrix, which depended on the particle size (distribution). The intrinsic properties of semi-crystalline polymers strongly depend on their crystalline morphology. Therefore, it is essential to understand the crystallization kinetics in polymeric systems. The aim of this chapter is to study the crystallization behavior of iPP/silica nanocomposites.

The crystallization process is governed by many factors including the content of fillers, the thermal history, the processing conditions and the states of dispersion. Generally, the incorporation of fillers into iPP can change its crystallization behavior. It was reported that the addition of nanofillers improved the nucleation efficiency and the crystallization temperature of iPP due to the heterogeneous nucleation effect of the filler. Khare et al. studied the effect of calcium carbonate (CaCO$_3$) on the crystallization behavior and the crystal modification of iPP by using X-ray diffraction and optical microscopy and found that the incorporation of CaCO$_3$ increased the crystallization rate of iPP and decreased the spherulite size with increasing CaCO$_3$ content. The crystallization temperature, crystallization rate and Avrami-Ozawa exponent of iPP were dependent on CaCO$_3$ content. Fu et al. reported that the addition of polyhedral oligomeric silsesquioxane (POSS) increased the crystallization rate of iPP under both isothermal and non-isothermal conditions, while the crystallization rate was significantly reduced at a POSS concentration of ~ 30 wt%. This was attributed to an increasing number of POSS molecules dispersed in the iPP matrix at the molecular level, which significantly decreased the diffusion of iPP during crystal growth.

During polymer processing operations such as extrusion, injection molding and fiber spinning, the molten polymer is exposed to varying levels of flow fields (elongation, shear, etc.). It is well established that polymers under the influence of a shear field exhibit an increased crystallization rate and different morphologies in comparison to crystallization from a quiescent melt. Several researchers investigated the effects of shear (and elongation) on the crystalline morphology of iPP. The crystallization behavior and resultant morphology are not only determined by the flow conditions, such as temperature, deformation strain and deformation rate, but also by the molar mass (distribution) of polymers. It was reported that small amounts of high molar mass chains promote the formation of shish-kebab structures during flow-induced crystallization. Stretched chains have a high segmental orientation that allows them to crystallize faster than coiled chains and form fibrillar crystals. The addition of nanoparticles affects the molecular configurations and its ability to organize, align, and form nuclei. On one side, the addition of nanoparticles can strengthen the flow due to the increased viscosity, which result in more nucleation sites because of the anisotropy of the
polymer chains, and thus increases the crystallization rate. On the other side, the addition of nanofillers can hamper the formation of shish structures because the orientation of polymer chains is hindered due to polymer-particle interaction.\textsuperscript{5} Thus, the effect of nanoparticles on (flow-induced) crystallization and subsequent morphologies or microstructures, i.e., the nature and the distribution of the oriented and unoriented fractions in the crystalline phase, are still not clear.

To study the iPP/silica nanocomposites' crystallization behavior under non-isothermal, isothermal and shear conditions, differential scanning calorimetry (DSC), small-angle light scattering (SALS) and small-angle X-ray scattering (SAXS) were used. The crystallization behavior of iPP/silica nanocomposites under non-isothermal and isothermal is characterized using DSC, while SALS is used to investigate crystal structure development of iPP/silica nanocomposites under isothermal condition based on the pioneering work of Stein and co-workers.\textsuperscript{34-36} They developed a theory to interpret the observed light scattering patterns. When the polymer crystal undergoes phase transformations, the shape, the size and the intensity of its scattering pattern will change. The variations in the scattering pattern are a result of density fluctuations in polymer melts.\textsuperscript{34,35} In literature it was reported that time-resolved, polarization-dependent SALS is very sensitive to micrometer-scale density and orientation fluctuations arising from polymer crystallization. For semi-crystalline polymers, the fluctuations arise from spatial variations in the crystalline volume fraction and the arrangement of crystalline aggregates within the sample. However, the theory can only be applied to samples with isotropic scattering since it is based on isotropic correlation functions. Although this is rarely the case, in most studies\textsuperscript{37-39} the method is still widely used because to our knowledge, no other available alternatives have been reported. In this study, SALS is used to follow the changes in size and internal order of superstructures formed during the crystallization of iPP/silica nanocomposites. Additionally, in-situ small-angle X-ray scattering (SAXS) is carried out to monitor real-time morphological changes during shear-induced crystallization.\textsuperscript{40}

3.2. Experimental

3.2.1. Materials

Commercial iPP pellets, with a melt flow index (MFI) of 5.7 g/10 min at 230 °C and under a weight of 2.16 kg, were supplied by Euro-SABIC. Silica nanoparticles with an average diameter of 13 nm were purchased from Nissan Chemical. These particles were suspended in toluene with a solid content of approx. 40 wt%. All materials were used as received.

3.2.2. Preparation of iPP/silica nanocomposites

The iPP/silica nanocomposites were prepared using different methods as described in Chapter 2. Since the crystallization behavior of the nanocomposites prepared by different preparation methods was similar only results from solution methods with different drying procedures, i.e., slow evaporation (S), precipitation (P) and vapor rotation (V), are presented in this chapter.
3.2.3. Characterization techniques

Differential Scanning Calorimetry (DSC). The thermal behavior of neat iPP and iPP/silica nanocomposites was studied using a TA Instruments Q1000 calorimeter. Hermetically sealed aluminum pans were used with a typical sample weight of 5-7 mg. The samples were first heated to 220 °C and equilibrated for 5 min in order to remove the thermal history. Subsequently, the samples were cooled at a rate of 10 °C/min to 30 °C, where they were kept for 1 min, and reheated to 220 °C at a rate of 10 °C/min. For isothermal crystallization experiments, the samples were cooled to 135 °C at a rate 30 °C/min and were kept at 135 °C for 150 min. The isothermal crystallization temperature of 135 °C was selected because of the suitable time span of the experiments. The maximum of the melting endotherm from the second heating run was used to determine the melting temperature ($T_m$), whereas the maximum of the crystallization exotherm was used as the crystallization temperature ($T_c$). The crystallinity ($X_c$) after normalizing for the iPP fraction, was calculated by using 209 J/g as the heat of fusion for 100 % crystallinity of iPP.

Polarized Optical Microscopy (POM). The isothermal crystallization behavior was characterized by polarized optical microscopy (a Zeiss Axioplan 2 microscopy equipped with a Zeiss Axiocam camera). The resulting images were analyzed with the accompanying AxioVision v3.0.6 software. During the measurement, samples were sandwiched between two glass slides and fixed on a Linkam THMS-600 hot-stage for temperature control.

Small-Angle Light Scattering (SALS). The development of crystalline structures during isothermal crystallization was investigated using small-angle light scattering (SALS). The sample, fixed between two glass slides, was placed on a Linkam THMS-600 hot-stage for temperature control. A 632.8 nm HeNe laser, which was placed underneath the sample, was guided through a pinhole and then through the sample. The scattered light from the sample was projected onto a semi-transparent PP screen, and the scattering patterns on the screen were captured using a 16-bit 512x512-CCD camera (Versarray: 512B Princeton CCD with a ST-133 controller). The scattering angles were calibrated with a 100 lines/mm grid. The data acquisition time was typically 12 s per image and was controlled by a program written in VPascal, which runs under an image analysis software V++ for Windows (version 4.0, Digital Optics Ltd). Two polarizers were mounted on both top and bottom sides of the sample. A program was designed to control the rotation of the bottom polarizer, thus allowing measurements to be performed under linear polarized or cross-polarized conditions.

Small-Angle X-ray Scattering (SAXS). In-situ flow-induced crystallization studies were carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. Time-resolved small-angle X-ray scattering (SAXS) measurements were performed at beamline BM26/DUBBLE. Scattering patterns were recorded on a two-dimensional gas-filled detector (512 x 512 pixels) placed at approximately 7 meters from the sample. Scattering and absorption of air were minimized by a vacuum chamber placed between sample and detector. The wavelength used was $\lambda = 1.03 \, \text{Å}$. To calibrate the SAXS detector, the scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used. The experimental data were corrected for background scattering, i.e., subtraction of instrumental factors.
Chapter 3 Crystallization behavior of iPP/silica nanocomposites

Fig. 3.1. Anisotropic two-dimensional SAXS images with the definition of azimuthal intensity regions. The arrow shows the applied flow direction.

A Linkam CSS-450 high-temperature shearing stage was used for in-situ SAXS studies to control the shear conditions. To limit unwanted extraneous scattering, diamond windows were used. The nanocomposite discs with a thickness of ~300 μm were mounted between two diamond windows. The gap distance between two windows was adjusted to the desired sample thickness. After maintaining the sample at 200 °C for 4 min to erase the thermal history, the samples were compressed to 240 μm to ensure a good contact between the windows and the sample. A crystallization temperature of 135 °C was used for a sufficiently long time of nucleation and crystal growth under quiescent conditions. The following experimental temperature profile was applied to the in-situ SAXS studies: 1) the sample was heated from room temperature to 200 °C at 30 °C/min; 2) the samples were held at 200 °C for 5 min. After 4 min, the sample was compressed, then cooled to 135 °C with a cooling rate of 30 °C/min; and 3) the sample was retained at 135 °C (± 1 °C) for 30 min to follow the structure development. The shear was applied when the temperature of the sample reached 135 °C. Two-dimensional SAXS patterns were collected immediately after the required temperature was reached, and before, during and after cessation of the applied shear. Only one shear condition was applied at a nominal shear rate of 60 s⁻¹ for 3 s.

Two-dimensional (2D) SAXS images were used for the characterization of the anisotropic morphologies. For this purpose, it is necessary to define three azimuthal regions. The azimuthal region definitions adopted in the present work are given in Fig.3.1.

3.3. Results and discussion

The results on the effects of silica nanoparticles on the crystallization behavior are presented in this part. First, the melt behavior of iPP/silica nanocomposites is discussed based on the DSC results. Second, the nucleation efficiency of silica nanoparticles is presented, after which the crystallization kinetics of iPP/silica nanocomposites under isothermal conditions is characterized via DSC and SALS. The results on the shear-induced crystallization behavior of iPP/silica nanocomposites are discussed based on SAXS images in the last.
3.3.1. Melting behavior of iPP/silica nanocomposites

The melting behavior of the iPP/silica nanocomposites obtained from the second heating run of DSC measurements is depicted in Fig. 3.2. The narrow melting peaks exhibited by the iPP/silica nanocomposites suggest the formation of a lamellar morphology with a narrow size distribution. All samples show a constant melting temperature $T_m$ of ~ 163 °C, which is the characteristic melting point of iPP α-phase. A small melting peak at ~ 149 °C is observed for samples made via slow evaporations with silica contents of > 0.4 vol%. This peak becomes more prominent when 0.6 vol% silica is added and it can be assigned to iPP crystals with a β-modification, which is known to have a melting temperature of ~ 148 °C.

Fig. 3.2d shows the melting curves of S_0.6 vol% acquired from DSC first and second heating runs. In the first DSC heating run, only a melting peak at ~ 164 °C for the α-phase is present. In the second heating run, the peaks for β-phase and α-phase appear at ~ 149 °C and ~ 163 °C respectively. This indicates that the formation of β-phase is not related to the thermal history of the sample during the preparation procedures. It is worth noting that not all iPP/silica nanocomposites show the β-phase peak in the second DSC heating runs (Fig. 3.2). The β-phase peak appears in the precipitation samples when silica content is above 0.9 vol%, while no β-phase is seen in samples made by the vapor rotation. The appearance
of the β-phase may be related to the differences in the state of dispersion, which was
discussed in Chapter 2.

3.3.2. Nucleation efficiency

In general, inorganic fillers which are added to a polymer matrix act as nucleating
agent, since the fillers introduce a heterogeneous surface in the melt. At high temperature,
polymer chains can already folded around the fillers, forming nuclei. This effect is referred
to as nucleating effect. The focus of this part is given to the nucleating effect of the
nanoparticles on the iPP matrix.

The nucleating efficiency is calculated based on the calorimetric efficiency scale
proposed by Fillon et al. and is calibrated according to their procedure based on the
‘ideally’ nucleated polymer attainable via self-nucleation. Two limits need to be defined:
the lower limit refers to the virgin (non-nucleated) iPP and the upper limit refers to an
optimally self-nucleated PP. The nucleation efficiency (NE) is a percentage of the range
identified by two limits and is expressed as:

$$NE = \frac{T_c - T_{c1}}{T_{c2\text{max}} - T_{c1}} \times 100\%$$

where $T_{c1}$ and $T_{c2\text{max}}$ are the crystallization temperatures of the virgin and the best self-
nucleated iPP respectively. $T_c$ is the crystallization temperature obtained in the presence of
nucleating agents (in this case silica nanoparticles). NE is thus equal to 0 for non-
nucleating cases and 100 for the optimum efficiency.

In our experiments, the evolution of the crystallization temperature for iPP after self-
nucleation carried out at different temperatures (170 °C, 169 °C, 168 °C, 167 °C and
165 °C) and a fixed cooling rate (10 °C/min). From these curves, $T_{c2\text{max}}$ for the best self-
nucleated was chosen as the upper limit and $T_{c1}$ of the virgin iPP was taken as the lower
limit. The higher temperature $T_{c2\text{max}}$ is 142.6 °C, whereas the lower temperature $T_{c1}$ is
115.7 °C, i.e., a difference of 26.9 °C defines the efficiency scale.

The nucleating efficiency of silica nanoparticles is listed in Table 3.1 as a function of
silica concentration. It shows a nucleating efficiency ~ 20%, which is comparable to most
commercially available nucleating agents. The nucleating efficiency increases after
addition of 0.4 vol% silica nanoparticles into iPP matrix compared with pure iPP,
followed by saturation or a slight decrease when the silica concentration is > 1.1 vol%.

The degree of supercooling ($\Delta T$) of iPP/silica nanocomposites prepared from
precipitation is also given in Table 3.1, where:

$$\Delta T = T_n - T_c$$

in which $T_n$ is the melting peak temperature and $T_c$ is the crystallization peak temperature.
$T_c$ is found to be shifted to higher temperatures with the addition of nanofillers, whereas
$T_n$ is hardly affected by the addition of silica nanoparticles. Therefore, $\Delta T$ is reduced with
addition of silica nanoparticles (Table 3.1). When a polymer crystallizes with less
supercooling (smaller $\Delta T$), it crystallizes more uniformly.
Table 3.1 illustrates that the degree of crystallinity $X_c$ slightly increases with the addition of nanofillers, while the addition of ~ 2.3 vol% silica nanoparticles slightly decreases $X_c$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta T$ (°C)</th>
<th>NE (%)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_0 vol%</td>
<td>162.6</td>
<td>116.0</td>
<td>46.6</td>
<td>0</td>
<td>48.6</td>
</tr>
<tr>
<td>P_0.4 vol%</td>
<td>162.7</td>
<td>120.7</td>
<td>42.0</td>
<td>18.9</td>
<td>50.8</td>
</tr>
<tr>
<td>P_0.9 vol%</td>
<td>162.4</td>
<td>121.8</td>
<td>40.6</td>
<td>22.7</td>
<td>49.7</td>
</tr>
<tr>
<td>P_1.1 vol%</td>
<td>162.5</td>
<td>121.5</td>
<td>41.0</td>
<td>21.6</td>
<td>49.5</td>
</tr>
<tr>
<td>P_2.3 vol%</td>
<td>162.8</td>
<td>120.3</td>
<td>42.5</td>
<td>17.1</td>
<td>47.5</td>
</tr>
</tbody>
</table>

3.3.3. Crystallization kinetics of iPP/silica nanocomposites

The crystallization kinetics of polymers under isothermal conditions for various modes of nucleation and growth can be described by the Avrami equation, which was developed for isothermal crystallization, although it has also been used to study non-isothermal processes. The Avrami equation provides further insight into the kinetics of non-isothermal crystallization, the physical meaning of $K(T)$ and $n$ cannot be related to the non-isothermal case in a simple way. Therefore, the crystallization kinetics of iPP/silica nanocomposites under isothermal conditions is investigated in this part using Avrami equation (3.3).

$$X(t) = 1 - \exp[-K(T)t^n]$$

(3.3)

where $X(t)$ is the relative crystallinity at crystallization time $t$, $n$ is the Avrami exponent which depends on the mechanism of nucleation and the geometry of crystal growth, and $K(T)$ is the Avrami rate constant related to nucleation and growth parameters. Although the use of Avrami equation provides further insight into the kinetics of non-isothermal crystallization, the physical meaning of $K(T)$ and $n$ cannot be related to the non-isothermal case in a simple way. Therefore, the crystallization kinetics of iPP/silica nanocomposites under isothermal conditions is investigated in this part using Avrami equation (3.3).

$X(t)$ can be calculated according to the following equation:

$$X(t) = \frac{Q_t}{Q_\infty} = \frac{\int (dH / dt) dt}{\int_0^\infty (dH / dt) dt}$$

(3.4)

where $Q_t$ and $Q_\infty$ are the integrated heat flows generated at time $t$ and infinite time respectively, and $dH/dt$ is the heat flow rate. The half-time of crystallization ($t_{1/2}$) is defined as the time when $X(t)$ reaches 50% and is often used to characterize the rate of crystallization. $t_{1/2}$ is calculated from the Avrami parameters:

$$t_{1/2} = \left(\frac{\ln 2}{nK(T)}\right)^{1/n}$$

(3.5)
$X(t)$ as a function of time for iPP/silica nanocomposites is plotted in Fig. 3.3a. Compared with pure iPP within the initial stages, $X(t)$ of the iPP/silica nanocomposites increases faster (Fig. 3.3a), which signifies the nucleating effect of silica nanoparticles. In addition, the increased crystallization rate of iPP/silica nanocomposites is also indicated via the increased slope of $X(t)$ versus time (Fig. 3.3a). The crystallization rate increases until the silica content reaches ~0.9 vol\% and decreases again.

All plots in Fig. 3.3a have similar sigmoidal trends. The curvature of the plots, when the crystallization is close to complete, is due to spherulitic impingement in the later growth stages of crystallization. The difference can be understood by analyzing the isothermal crystallization kinetics from the Avrami equation (3.3).

According to equation (3.3), the values of the Avrami exponent $n$ and the Avrami rate constant $K(T)$ can be determined from the slope and intercept of the plot $\log[-\ln(1-X(t))]$ versus $\log t$. Fig. 3.3b shows the Avrami plots of iPP/silica nanocomposites with various silica content over a range of $X(t)$ from 1 to 100\%. The linear region of the graphs (where $X(t)$ typically ranges from 3 to 90\%) represents the primary crystallization stage, i.e., the formation of nuclei with a critical size and their subsequent growth.\(^{59}\) The occurrence of secondary crystallization (i.e., impingement of the spherulites and/or insertion of new crystals in between the already existing ones) is characterized by a deviation from linearity in the Avrami plots. Based on the Avrami plots, it is difficult to determine the exact $X(t)$ at which secondary crystallization begins.\(^{51}\)

**Fig. 3.3.** (a) Development of relative crystallinity $X(t)$ with time and (b) Avrami plots for iPP/silica nanocomposites from isothermal crystallization at 135 °C.

The slope of Avrami plots $n$, the Avrami rate constant $K(T)$ and the half-time of crystallization ($t_{1/2}$) for iPP/silica nanocomposites are listed in Table 3.2. When $n \approx 3$, it signifies three-dimensional growth; when $n \approx 2.5$, it indicates 2- and 3-dimensional crystal growth. The $n$ value given in Table 3.2 indicates that the crystals in iPP/silica nanocomposites grow in 3-dimensional. The values for $K(T)$ and $t_{1/2}$ illustrate the effect of nanofillers on crystallization growth rates. The increase in $K(T)$ and decrease in $t_{1/2}$ indicate increases in crystallization rate. Table 3.2 shows that with increasing silica content, $K(T)$ increases first and then decreases, with a maximum value for P 0.9 vol\%. Meanwhile, $t_{1/2}$ decreases first and then increases, with a minimum value for P 0.9 vol\%.
These results imply that the crystallization rate of iPP/silica nanocomposites increases first and then decreases with the addition of silica nanoparticles. The highest crystallization rate occurs for P_{0.9} vol%. Therefore, depending on their concentration, nanoparticles can either enhance crystallization rate by providing nucleating surfaces or retard crystallization by suppressing the crystal growth. At higher silica concentration, e.g. 2.3 vol%, the interparticle distance $\Lambda$ is smaller than the size of a polymer coil, $2R_g$. This leads to the occurrences of bridging.

Table 3.2. Crystallization kinetic parameters of iPP/silica nanocomposites under isothermal conditions (135 °C).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$n$</th>
<th>$K(T)$</th>
<th>$\tau_{1/2}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P_{0} vol%</td>
<td>3.3</td>
<td>$7.1 \times 10^{-6}$</td>
<td>23.1</td>
</tr>
<tr>
<td>P_{0.35} vol%</td>
<td>2.6 (3.3; 2.4)</td>
<td>$6.8 \times 10^{-5}$</td>
<td>24.8</td>
</tr>
<tr>
<td>P_{0.4} vol%</td>
<td>3.0</td>
<td>$3.7 \times 10^{-5}$</td>
<td>19.4</td>
</tr>
<tr>
<td>P_{0.6} vol%</td>
<td>2.9</td>
<td>$7.4 \times 10^{-5}$</td>
<td>16.8</td>
</tr>
<tr>
<td>P_{0.9} vol%</td>
<td>3.0</td>
<td>$2.0 \times 10^{-4}$</td>
<td>10.5</td>
</tr>
<tr>
<td>P_{1.1} vol%</td>
<td>3.1</td>
<td>$1.3 \times 10^{-4}$</td>
<td>11.5</td>
</tr>
<tr>
<td>P_{1.3} vol%</td>
<td>3.1</td>
<td>$4.4 \times 10^{-5}$</td>
<td>15.1</td>
</tr>
<tr>
<td>P_{2.3} vol%</td>
<td>3.0</td>
<td>$5.8 \times 10^{-5}$</td>
<td>15.4</td>
</tr>
</tbody>
</table>

The crystallization behavior studied from DSC shows that with increasing nanofiller concentration, the crystal growth rate increases to a maximum, and then decreases. The samples with the highest crystal growth rates have the lowest viscosities, which might be a result of the selective adsorption of iPP chains. Selective adsorption compels the nanocomposite matrix to be composed of mostly low, rather than high, molar mass chains with high mobilities. The chains with a higher mobility can move faster to the crystal growth front, and therefore, a higher crystallization rate is observed. When silica contents are above a certain threshold value, the selective adsorption is hampered due to bridging effects, which hinder the diffusion of iPP chains to form crystals. Therefore, a decreased in crystallization rate is observed at high silica concentrations. In addition, the increase in crystal growth can also attribute to a lower entanglement density. Lippits et al. demonstrated that disentangled chains crystallize faster than entangled chains. The increase in the crystallization rate for P_{0.9} vol% silica might be attributed to the fact that the addition of silica nanoparticles induces a lower entanglement density. In summary, the increased crystallization rate observed in iPP/silica nanocomposites can be explained by both selective adsorption and decreases in entanglement density. Till now, distinguish between the selective adsorption and the loss of entanglements is not yet clear.

### 3.3.4. Small-angle light scattering (SALS)

A beam of polarized light incident on the sample interacts with the microstructure of the crystallizing sample and is scattered. The pattern of the scattered light depends on the relative positions of two polarizers. If two polarizers are parallel to each other, the
scattered pattern is labeled as polarized $V_v$; whereas when two polarizers are crossed, the scattered pattern from the sample is called depolarized $H_v$. The polarized $V_v$ scattering is caused by two factors: 1) refractive index changes due to concentration or density fluctuations, which are equal to changes in the isotropic part of polarizability, and 2) fluctuations in the anisotropy part of the polarizability and orientation of the optical axis. In other words, $V_v$ measures mean-square fluctuations in anisotropy as well as in polarizability $\langle \eta^2 \rangle$. The depolarized scattering $H_v$ depends only on the fluctuations of optical anisotropy and orientation. $H_v$ measures mean-square fluctuations in the anisotropy $\langle \delta^2 \rangle$.

The total scattered intensity, or the invariant, $Q$, is defined as:

$$Q = \int_{q_{\min}}^{q_{\max}} I(q)q^2 dq$$

where $q$ is the scattering vector defined by $q = (4\pi\lambda)\sin(\theta)$ in which $\lambda$ stands for the wavelength, $\theta$ is the scattering angle and $n$ is the refractive index, and $I(q)$ is the intensity of scattered light at $q$. The $H_v$ and $V_v$ invariants can then be generalized as:

$$Q(H_v) \propto \langle \delta^2 \rangle = \phi_i (\delta^2_{cr} \chi_{CS})^2$$

$$Q(V_v) \propto \langle \eta^2 \rangle + Q(H_v) = \phi_i (1 - \phi_i) \langle \delta^2 \rangle + \phi_i (\delta^2_{cr} \chi_{CS})^2$$

where $\phi_i$ is the volume fraction of spherulites, $\chi_{CS}$ is the crystallinity with the spherulites, $\delta^2_{cr}$ is the intrinsic anisotropy of a pure crystal, $P_2$ is the Hermans-type orientation function, $\alpha_2$ is the average polarizability of the crystals and $\alpha_0$ is the average polarizability of the surrounding amorphous phase.

Initially, $Q(H_v)$ and $Q(V_v)$ of pure iPP gradually increase with time. After an induction time, the formation of small crystals causes an increase in density fluctuations during the early stages of crystallization, which is reflected in an increase in $Q(V_v)$. The orientation fluctuations that arise from the optical anisotropy of these small crystals during their later stage of development initiate an increase in $Q(H_v)$ while $Q(V_v)$ continues to rise. The difference in the onset time of $Q(H_v)$ and $Q(V_v)$ is caused by the development of weak anisotropic domains as the precursors of spherulites. These weak anisotropic domains are loosely structured spherulites, which initiated the rise in $Q(V_v)$, but the anisotropy from the crystalline parts of these spherulites is too small to be measurable, thereby no visible increase was seen in the $H_v$ curve. As crystallization continues, the internal structure of these spherulites matures and orientation fluctuations caused by the growing anisotropic entities starts to increase, leading to an increase in $Q(H_v)$. $Q(V_v)$ increases with time as the small crystalline regions grow in size and number and passes through a maximum when the volume fraction of the the spherulites reaches 50%, in agreement with equation (3.8). A subsequent decrease in $Q(V_v)$ is observed during later stages of crystallization when the crystalline phase becomes dominant ($\phi_i > 0.5$). $Q(H_v)$ shows a sigmoidal increase, where the changes in $Q(H_v)$ parallel those in $Q(V_v)$ during the later stages of crystallization. The exact position of the maximum in $Q(V_v)$ corresponding to the sigmoidal increase in $Q(H_v)$ is believed to be polymer specific and depends on the crystallization temperature.
The SALS results are also verified with observations from POM. Fig. 3.4 shows, in combination with the SALS invariants $Q(H_v)$ and $Q(V_v)$ optical micrographs at different times during the crystallization of P$_{1.1}$vol% at 135 °C. The structure development can be observed microscopically, and the maximum in $Q(V_v)$ clearly occurs before the instant of spherulitic impingement, which is in agreement with the observation made by Pogodina et al., 55 Elmoumni et al., 56 and Baert et al. 54 After $Q(V_v)$ passes through a maximum, i.e., when the spherulites occupy 50% of the volume, a subsequent decrease in $Q(V_v)$ is observed during later stages of crystallization. $Q(H_v)$ shows a sigmoidal increase, especially when the crystalline phase becomes dominant ($\phi > 0.5$). The changes in $Q(H_v)$ and $Q(V_v)$ are parallel during the later stages of crystallization.

Fig. 3.4. SALS invariants and POM images showing the structure evolution during the crystallization of P$_{1.1}$ vol% at 135 °C.
As proven by the non-isothermal DSC studies, silica particles act as a good nucleating agent for the iPP matrix. The nucleating ability of silica particles is also evident from the $H_v$ scattering invariants shown in Fig. 3.5a. The onset of crystallization and the time required to reach the maximum $Q(H_v)$ is significantly shortened. With increasing silica content till 1.1 vol%, the onset time needed to reach the maximum in $Q(H_v)$ decreases and then it increases. Fig. 3.5b shows that the addition of silica nanoparticles shifts the maximum value of $Q(V_v)$ to a shorter time first and then to a longer time, while the shortest time occurs to P$_{1.1}$ vol% silica. The maximum in $Q(V_v)$ is a characteristic light scattering time for crystallization. It is thought to occur at at time when amorphous and crystalline regions are of equal volume fraction and thus density fluctuations are at a maximum.\textsuperscript{37,57} This indicates that P$_{1.1}$ vol% silica reaches 50% (volume fraction) of crystalline regions in the shortest time.

3.3.5. Shear-induced crystallization of iPP/silica nanocomposites

It is well known that the crystallization of semi-crystalline polymers can be strongly influenced by flow.\textsuperscript{13,14,45,58,55} Upon shearing, orientation and structure development can be observed. This is typical for shear-induced crystallization. The addition of nanoparticles, which are nuclei for the crystallization of polymers, will affect molecular configurations
affect molecular configurations and the molecules’ ability to organize, align and form nuclei under shear conditions. Therefore, in addition to quiescent experiments from SALS and DSC, shear-induced crystallization experiments were performed via in-situ SAXS.

Under quiescent conditions crystalline structures grow isotropically. This gives a uniform SAXS intensity distribution over the whole azimuthal angular range. When flow is applied, chain orientation occurs at a faster rate relative to quiescent conditions, leading to a faster crystallization rate. Oriented molecules form row nuclei or shishes, and kebabs grow on these row nuclei. The kebab-like crystalline structure shows an intensity distribution in the meridional direction observed as two lobes due to anisotropic growth in one direction (Fig. 3.1). A series of two-dimensional SAXS patterns of iPP/silica nanocomposites acquired at 135 °C with a shear rate of 60 s$^{-1}$ for 3 s are illustrated in Fig. 3.6. The SAXS images at time $t = 3$ s correspond to an amorphous melt. The images consist of weak diffuse scattering, which indicate the absence of any detectable structures or orientations. The intensity of discrete scattering in the following images becomes stronger due to the growth of lamellar structures in the melt. After a certain time, the intensity becomes constant and no significant changes can be observed in the scattering patterns.

![Fig. 3.6. 2-D SAXS patterns of iPP/silica nanocomposites after pre-shear (60 s$^{-1}$ for 3 s). The time (second) is indicated on the left.](image_url)
Chapter 3 Crystallization behavior of iPP/silica nanocomposites

In view of the observed reduction in the viscosity, it is not surprising to find a very specific trend for orientation under flow as a function of filler concentration. Flow orients molecules, especially the high molar mass chains. The adsorption of iPP chains to the nanofiller influences the molar mass distribution in the iPP melts. Therefore, flow-induced orientations are affected. The changes in orientation of the molecules are reflected in the difference of SAXS images (Fig. 3.6).

After the shear was stopped for 30 s, the scattering patterns of P_0 vol% silica and P_0.35 vol% silica show the appearance of meridional maxima. Compared with P_0.9 vol% silica (column 3 in Fig. 3.6), P_0 vol% silica exhibits a stronger and more intense development of the meridional maxima as a function of time. For P_1.1 vol% (column 4 in Fig. 3.6), the intensity shows a uniform scattering pattern as a function of azimuthal angle over the experimental time. The total intensity reaches a plateau after ~180 s and no meridional maxima were observed (column 4 in Fig. 3.6). For P_2.3 vol% silica, the meridional maxima lobes reappear but grow at a slower rate compared to P_0.35 vol% silica and pure iPP. The lobe intensity of P_2.3 vol% silica is much lower than pure iPP.

Generally, flow first orients the high molar mass, creating extra nuclei and accelerating the overall crystallization kinetics. In other words, low molar mass chains orient slower than high molar mass chains. Hence, the later appearance or vanishing of meridional lobes in iPP/silica nanocomposites can be attributed to the selective physisorption of high molar mass iPP chains to the silica surface while low molar mass chains consist of the matrix of iPP/silica nanocomposites. This explains the lower orientation signal or lobe intensity in P_0.9 vol% silica and P_1.1 vol% silica. The appearance of meridional lobes in the P_2.3 vol% silica but with less lobe intensity than P_0 vol% silica may be explained by the formation of the solid-like structure in the iPP matrix of P_2.3 vol% silica (Fig. 2.9a). The formation of the structure produced more nucleation sites and, thus smaller crystals formed in P_2.3 vol% silica when its crystallinity X(t) remains similar as P_0 vol% silica. Therefore, the lobe intensity of P_2.3 vol% silica is much less than pure iPP. Under shear, the polymer chains bridging the two particles and the surface of the particles experience high stress. The lobe intensity in P_2.3 vol% is thus higher than P_0.9 vol% silica and P_1.1 vol% silica.

3.4. Conclusions

The crystallization behavior of iPP/silica nanocomposites was studied under both isothermal and non-isothermal crystallization conditions by using DSC and SALS. The addition of silica nanocomposites increases the crystallization temperature, the crystallization rate and the crystallinity, while no influences on the iPP melt temperatures are observed. The results from the quiescent crystallization behavior confirm that the addition of silica nanoparticles has a dual effect. Depending on its concentration, nanoparticles can either enhance crystallization by providing nucleating surfaces or retard crystallization by suppressing the crystal growth, while the highest crystallization rate occurs to the samples with the lowest viscosity, observed and discussed in Chapter 2. The increases in the crystallization rate can be explained by both selective adsorption and
decreases in entanglement density. Till now, distinguish between the selective adsorption and the loss of entanglements is not yet clear. Nucleating efficiency increases after addition of ~0.4 vol% silica nanoparticles comparing with pure iPP, after which the nucleation efficiency is saturated or slightly decreased.

The 2D-SAXS images after shear suggest the selective adsorption of iPP chains to silica surfaces. After adsorption of high molar mass chains to the silica surfaces, the low molar mass chains in the matrix form small crystals. The formation of the small crystals results in less intensity in the meridional lobes or lead to disappearance of the meridional lobes in 2D-SAXS patterns.

3.5. References

Chapter 3 Crystallization behavior of iPP/silica nanocomposites

34 Stein, R.S.; Wilson, P. R. J. Appl. Phys. 1962, 33: 1914-1922.
Abstract

Recent research suggests that the melt viscosity of polymers can be reduced by using nanoparticles as additives. In this chapter, we show a decrease in the melt viscosity of an aromatic poly(carbonate) (PC) through the addition of a small amount of silica nanoparticles. Two different spherical silica nanoparticles with an average diameter of 13 nm and 45 nm respectively and one cylindrical shape silica nanoparticles with a diameter of 12 nm and a length of 70 nm are used and dispersed in a bisphenol A-based PC via melt blending. Transmission Electron Microscopy (TEM) images show a good dispersion of nanoparticles in PC matrix. The most remarkable result is that ~26% decrease in viscosity comes from the addition of silica nanoparticles to PC. The decrease in viscosity of PC/silica nanocomposites is repeatable using different preparation methods, i.e., master-batch and direct methods on both a mini-extruder and an industrial large-scale extruder.
4.1. Introduction

In the previous chapters, the effect of the addition of silica nanoparticles on the viscoelastic and crystallization behavior of semi-crystalline iPP/silica nanocomposites was discussed. A decrease of the viscosity of iPP/silica nanocomposites was observed. In this chapter, the effect of the addition of silica nanoparticles on the viscoelastic properties of an amorphous polymer, i.e., poly(carbonate) (PC), will be discussed. PC was chosen because of two reasons: 1) PC has a similar molar mass between entanglements, \( M_e \), as iPP, and 2) Comparing with iPP, which is apolar, PC is polar. Considering that the surface of silica nanoparticles is polar, PC has thus a stronger interaction with the surface of the silica nanoparticles than iPP.

PC is one of the most important engineering thermoplastics and is used in a wide variety of applications in its pure form or in combination with fillers, due to the combination of a high toughness, transparency and heat resistance, despite its high melt viscosity, which limits the processing. For a number of PC systems with different fillers a decrease in viscosity was found. For instance, Chen et al. and Lai et al. reported that the addition of micron-sized particles, i.e., glass-beads and barium sulfate, to PC leads to a decrease in viscosity in comparison to unfilled PC. On adding fillers, the viscosity of both systems decreased with increasing filler content. At high filler loadings, a stronger shear-thinning behavior was observed, which was assigned to a ‘ball bearing’ effect. However, the effect of the stringent processing conditions on possible changes of the molar mass distribution due to mechanical degradation was not studied. Wang et al. reported a decrease in viscosity of PC/calcium carbonate (CaCO\(_3\)) nanocomposites. The viscosity showed a continuous decrease on increasing the CaCO\(_3\) content. The viscosity for PC nanocomposites with 1 wt% CaCO\(_3\) measured at 250 °C was comparable with the viscosity of the pure PC at 260 °C. Thus, the effect of adding of 1 wt% CaCO\(_3\) into PC is the same as decreasing the processing temperature by \(-10\) °C. Concomitantly, the glass transition temperature (\( T_g \)) was decreased by approx. 6 °C. They attributed this decrease in viscosity to the excluded free volume induced by the CaCO\(_3\) nanoparticles, the same mechanism as proposed by Mackay and co-workers for a number of systems. However, no investigation on the molar mass variation of PC/CaCO\(_3\) nanocomposites was carried out. In addition, a decrease in viscosity was also observed by adding multiwall carbon nanotubes (MWCNT) to polycarbonate by Jin et al. It was postulated that the decreased viscosity resulted from the increase in the mobility of the PC molecules and the free volume in the PC/MWCNT nanocomposite, which was supported by the decrease in \( T_g \) of the nanocomposites compared to the neat PC.

In this chapter, the effect of the addition of pre-made silica nanoparticles on the viscosity of PC/silica nanocomposites is discussed, prepared by melt-compounding via a master-batch method and a direct mixing method. The state of dispersion of the silica nanoparticles, the effect of particle size, and the effect of silica nanoparticles on the \( T_g \) of the nanocomposites are also discussed in relation to the rheological behavior. The chapter is concluded by a discussion on the possible underlying mechanisms.
Chapter 4 Nanoscale effects on the decrease in viscosity of PC/silica nanocomposites

4.2. Experimental

4.2.1. Materials

A bisphenol-A based PC with a weight-average molar mass ($M_w$) = 30 kg mol$^{-1}$ and polydispersity index (PDI) = 2.6 was supplied by SABIC Innovative Plastics (SIP), the Netherlands. Silica suspensions with an average diameter of both 13 nm and 45 nm were purchased from Nissan Chemical as a 30-31 wt% suspension in methyl ethyl ketone (MEK). A 20-21 wt% silica suspension in MEK with an average diameter of 12 nm and a length of 70 nm was used to study the effect of the geometry of the silica nanoparticles. All materials were used as received.

4.2.2. Preparation of PC/silica nanocomposites

PC powder was dried for 12 hours at 130 °C before compounding. A PC/silica master-batch containing ~1.7 vol% of silica was prepared via melt blending on a twin-screw extruder (ZSK-25, Krupp Werner and Pfleiderer GmbH, Germany) at a screw speed of 300 rpm. The temperature of the extruder was set at approx. 40 °C for the feeder section and up to 300 °C in the melting zone. The PC powder with 0.1 wt% tris(2,4-di-tert-butylphenyl) phosphite as processing stabilizer was wetted by the silica suspension just before extrusion. The silica nanoparticles were used without any further surface modification. Different amounts of PC were added to the master-batch by melt blending on a small-scale twin-screw Haake Rheomix extruder with a screw speed of 100 rpm at 280 °C to obtain nanocomposites with silica contents ranging from 0.1 to 1.1 vol%.

In addition to the master-batch method, also a direct method was used by melt blending the required amount of silica suspension and PC powder on a home-built, recirculating, twin-screw mini-extruder with an internal volume of 5 cm$^3$, at a temperature of 270 °C and a screw speed of 75 rpm for 15 min under a N$_2$ atmosphere. Series of PC/silica nanocomposites with silica contents ranging from 0.3 to 1.7 vol% were obtained. To confirm the repeatability, a similar direct method was performed by using an industrial large-scale extruder, which was the same as used for master-batch method.

4.2.3. Characterization techniques

Rheology. Dynamic shear measurements were performed on a stress-controlled AR-G2 rheometer (TA Instruments) by using an 8 mm parallel plate-plate geometry and disk-shaped specimens (8 mm in diameter; 0.5 mm in thickness). Frequency sweeps in a range of 100-0.01 rad/s were performed at a temperature range of 250 to 165 °C under a N$_2$ atmosphere, with a constant strain of 10%, which was within the linear viscoelastic range. The data for the storage modulus $G'$ and loss modulus $G''$ of PC/silica nanocomposites were used for the determination of the discrete relaxation spectra, which were obtained by using the IRIS software developed by Baumgaertel et al. Based on these relaxation moduli spectra, the absolute value of complex viscosity $|\eta^*|$ and compliance were calculated.

Transmission Electron Microscopy (TEM). Morphological investigations were performed by using a Tecnai 20 transmission electron microscopy (TEM), operated at 200 kV. Ultrathin sections...
(50-70 nm) were obtained at room temperature by using a Leica Ultracut E microtome. Chemical staining of the sections was not required, since the electron density of silica is much higher than that of PC.

**Thermogravimetric Analysis (TGA).** A Q500 TGA (TA Instruments) was used for the quantitative determination of the silica content in the nanocomposites. Samples were heated under a pressed air atmosphere at 10 °C/min from 30 to 900 °C and held at 900 °C for 15 min. The residue was assumed to be only composed of silica. All measurements were repeated at least twice and an average of the results was used.

**Size Exclusion Chromatography (SEC).** The molar mass and polydispersity of PC was determined by using SEC on a Polymer Laboratories PL gel 5 μm MinIMIX-C 250×4.6 mm Column and a UV detector, operated at 254 nm (SABIC IP, the Netherlands). Measurements were performed at room temperature using dichloromethane as the solvent and toluene as a flow marker. Monodisperse PS standards were used for calibration. The molar mass of PC was calculated relative to the PS standards.

**Gas Chromatography - Mass Spectroscopy (GC-MS).** For the qualitative analysis of MEK residues, thermal desorption GC-MS was used. The analysis was performed by using a Gerstel EDS 2 thermodesorption system equipped with a Gerstel TDS-A autosampler and a Gerstel CIS 4 programmable temperature vaporization (PTV) inlet (Gerstel) and an Agilent 6890 gas chromatograph with a 5973 mass-selective detector.

**Differential Scanning Calorimetry (DSC).** The glass transition temperature was determined by a Q1000 DSC (TA Instruments). Each sample with sample mass of 3-5 mg was heated from 30 to 200 °C, cooled down to 30 °C, and heated again to 200 °C, all at a rate of 10 °C/min in standard DSC Tzero pans. The inflection point of the second heating cycle as a function of temperature was taken as the \( T_g \).

**Dynamic Mechanical Thermal Analysis (DMTA).** DMTA was performed on a Q800 Dynamic Analyzer (TA Instruments) in a film-tension mode to determine the mechanical glass transition of PC/silica nanocomposites. Compression-molded rectangular samples (40 × 5 × 1 mm) were measured with a temperature range of 25 to 200 °C at a heating rate of 2 °C/min and a frequency of 1 Hz, with a preload of 0.01 N and a force track of 110%.

### 4.3. Results and discussion

First, the state of dispersion of silica nanoparticles in PC matrix is presented, after which the rheology of the PC/silica nanocomposites is addressed. The possible mechanisms for the observed rheological behavior of the PC/silica nanocomposites are discussed in the last part of this section.

#### 4.3.1. State of dispersion of silica nanoparticles in PC matrix

One of the characteristics of nanocomposites is that the properties may be affected at very low filler loadings due to the very large surface-to-volume ratio of nanofillers. Therefore, a controlled dispersion of the nanoparticles is crucial. Since similar states of dispersion in the nanocomposites prepared via different methods, i.e., master-batches,
direct method via both mini-extruder and industrial extruder, was observed via transmission electron microscopy (TEM), only TEM images of the nanocomposites as a function of the silica concentration using the master-batch preparation method are discussed. The TEM images (Fig. 4.1) show that silica nanoparticles are dispersed in the form of small aggregates with an average diameter of 80 nm. In the (PC + 0.1 vol% silica) nanocomposite, silica nanoparticles disperse nicely in the PC matrix with a diameter in the range of 25-75 nm. With increasing silica content, larger silica nanoparticles aggregates appear in the PC matrix, while nanoparticles form harder aggregates, especially in the (PC + 1.7 vol% silica) nanocomposite. The TEM image of the (PC + 0.8 vol% silica) nanocomposite prepared from master-batch (Fig. 4.1) is different than that of the (PC + 0.8 vol% silica) nanocomposite prepared from the direct method (Fig. 4.3a), the reason of which is not clear to us. However, the observed difference does not affect the observed phenomenon in the viscosity reduction. The (PC + 0.8 vol% silica) nanocomposite, which was prepared by the master-batch and has a state of dispersion as shown in Fig. 4.1, has the lowest viscosity of the studied PC/silica nanocomposites. Similarly, the (PC + 0.8 vol% silica) nanocomposite, which was prepared via the direct method and has a state of dispersion as shown in Fig. 4.3a, has also the lowest viscosity of the investigated PC/silica nanocomposites. The decrease in viscosity for both samples compared with pure PC is similar. Moreover, it is worth noting that the difference in the state of dispersion may be observed using other characterization methods, while similar states of dispersion were observed via TEM.

![Fig. 4.1. TEM images of PC/silica nanocomposites with different silica content (vol%) prepared by the master-batch method.](image-url)
4.3.2. Rheology of PC/silica nanocomposites

4.3.2.1. Einstein’s theory

In his pioneering work, Einstein described the increase in viscosity of a suspension \( \eta \) as a function of volume fraction of rigid spherical fillers \( \phi \), with the help of the following equation:\(^7\)

\[
\eta = \eta_0 (1+2.5\phi)
\]

(4.1)

where \( \eta_0 \) is the matrix viscosity.

The Einstein equation was based on the assumption that the particles were large relative to the molecules making up the medium, so that the medium could be considered as a continuum relative to the particle.\(^8\) Although the law has been verified for large particles at low concentration, e.g. glass spheres,\(^9\) it has not been feasible to test it rigorously for nanoparticles. Both confinement and surface effects provided by the large specific surface area of nanoparticles have been shown to produce conformational changes to polymer molecules, so it is expected that nanoparticles affect the macroscopic viscosity differently than predicted by Einstein’s law.\(^4\)

In addition, Einstein’s law postulated a suspension so dilute that there was no appreciable interaction between the spheres.\(^10\) Guth et al\(^11\) and Vand\(^12\) introduced a filler-interaction term to the Einstein equation (4.1), resulting in the following expression:\(^12\)

\[
\eta = \eta_0 (1+2.5\phi + 7.349\phi^2)
\]

(4.2)

Therefore, the contribution of particle-particle interaction leads to a further increase in the viscosity of the system.

Based on equations (4.1) and (4.2), the viscosity of the (PC + 0.8 vol% silica) nanocomposite should increase by \( \sim 2 \% \) with respect to pure PC. However, our experimental results point to the fact that nano-scale effects of silica nanoparticles in the PC/silica nanocomposite system lead to a decrease in viscosity.

4.3.2.2. Dynamic properties

Generally, the absolute value of the complex viscosity \( |\eta'| \) is used to evaluate the melt viscosity of polymer melts during compounding. Therefore, \( |\eta'| \) of PC/silica nanocomposites prepared by the master-batch method was measured as a function of the angular frequency and the results are plotted in Fig. 4.2a. In the low frequency range, the PC/silica nanocomposites have a Newtonian behavior, while a shear-thinning behavior is observed in the high frequency range. The curve of \( |\eta'| \) versus frequency for PC goes up when frequency is \(< 0.03 \text{ rad/s} \). This might be due to the formation of bubbles during measurements, which comes from the improper drying of PCs. This upturn of the curve at low frequency probably reflects the elastic response of these bubbles. Comparing with pure PC, the onset of shear-thinning for the PC/silica nanocomposites is delayed to higher frequencies, especially for the (PC + 0.8 vol% silica) nanocomposite. The PC/silica nanocomposites have a less pronounced shear-thinning behavior than that of pure PC.
can be observed that with the addition of silica nanoparticles, the $|\eta'|$ at a certain frequency first drops and then increases over the studied silica content range.

The minimum $|\eta'|$ is found at approx. 0.8 vol% silica content, which is illustrated in Fig. 4.2b showing the $|\eta'|$ at a frequency of 1 rad/s as a function of silica content. The 0.8 vol% content of silica nanoparticles reduced the viscosity of pure PC by ~ 47%, calculated based on equation (4.3):

$$\Delta = \frac{|\eta'_i| - |\eta'_0|}{|\eta'_0|} \times 100\%$$

where $|\eta'_i|$ is the complex viscosity of PC/silica nanocomposites at a silica content of $i$, and $|\eta'_0|$ is the complex viscosity of pure PC.

Notice that the decrease in viscosity also occurs at high frequencies. This viscosity reduction was also observed in the steady-state viscosity of the PC/silica nanocomposites, which will be discussed in Chapter 5.

**4.3.2.3. Effect of wall slip or inhomogeneous flow**

Earlier studies showed that when a capillary rheometer was used, the decrease in viscosity could be due to inhomogeneous flow or a slip at the slit wall caused by the nanoparticles. Therefore, all our rheological measurements were performed by using a parallel plate-plate geometry. This method minimizes the possibility of slip at the wall during the measurements. The possible occurrence of wall slip can be determined by...
varying the gap distance between the parallel plates. No significant effect was observed when the gap distance was varied from 300 μm to 600 μm for the (PC + 0.8 vol% silica) nanocomposite, indicating that the decrease in viscosity does not originate from wall slip or inhomogeneous flow.

4.3.2.4. Effect of degradation

The occurrence of strong local flow fields in high particle concentration regions might lead to molar mass decrease. According to the power law which describes the molar mass dependence of the zero-shear viscosity, \( \eta_0 = kM_w^{3.4} \), a slight decrease in molar mass can lead to a significant decrease in viscosity. To ensure that the decrease in viscosity is not due to the degradation of PC, the molar mass of PC/silica nanocomposites after the preparation was characterized by SEC. The results are summarized in Table 4.1 and it can be observed that a small decrease in the molar mass and a corresponding increase of the polydispersity index (PDI) occurs during the extrusion process. This slight change in molar mass might lead to large decrease in viscosity. Therefore, the effect of molar mass variation on the decrease in viscosity of PC/silica nanocomposites was investigated based on the power law. After correcting the viscosity for the change in molar mass using the power law equation, the remaining decrease of the viscosity for the system with the highest viscosity reduction, i.e., ~ 0.8 vol% silica, accounts to ~ 26%. To exclude possible thermo-oxidative degradation reactions, the molar mass of the samples before and after rheological measurements were also measured and negligible molar mass variations were observed. Therefore, hardly any thermal degradation occurs during rheology measurements due to the use of N\(_2\) flow.

<table>
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<tr>
<th>Silica content (vol%)</th>
<th>( M_w ) (kg⋅mol(^{-1}))</th>
<th>( M_n ) (kg⋅mol(^{-1}))</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
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<td>30.1</td>
<td>12.0</td>
<td>2.5</td>
</tr>
<tr>
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<td>29.3</td>
<td>11.6</td>
<td>2.5</td>
</tr>
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<td>11.0</td>
<td>2.6</td>
</tr>
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</tr>
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<tr>
<td>1.7</td>
<td>28.4</td>
<td>11.0</td>
<td>2.6</td>
</tr>
</tbody>
</table>

4.3.2.5. Effect of residual solvent

A small amount of solvent can induce a large decrease in viscosity, since solvent molecules can act as a plasticizer. During the nanocomposite preparation, a suspension of silica particles in MEK was used to wet the PC powder before the extrusion step, which was followed by a drying step in the oven at 130 °C for at least 12 hours under a N\(_2\) flow.
GC-MS was used to measure possible residual traces of MEK after the preparation step for all systems. For comparison, MEK was added to a pure PC powder to obtain a 7 wt% MEK system via the same procedure. The GC-MS data showed that there were negligible amounts of MEK left in the PC/silica nanocomposites after the drying procedure. Furthermore, the effect of MEK on the viscosity was checked by comparing the viscosity of pure PC ($\eta^* = 6900$ Pa*s at 1 rad/s and 250 °C) to PC processed with 7 wt% MEK followed by drying ($\eta^* = 6867$ Pa*s at 1 rad/s and 250 °C). These results confirm that the viscosity decrease cannot be ascribed to traces of residual solvent.

### 4.3.2.6. Effect of preparation methods

It is worth noting that using the master-batch processing method, PC in the (PC + 1.7 vol% silica) nanocomposite was deposited through the extruder twice in comparison with pure PC that was processed only once. This will cause more degradation of PC in the (PC + 1.7 vol% silica) nanocomposite. To ensure that the PC has the same processing and thermal history for all PC/silica nanocomposites, a modified master-batch method was used in which the pure PC was extruded twice. In addition, a direct method via the mini-extruder and industrial large-scale extruder was also used.

<table>
<thead>
<tr>
<th>Method</th>
<th>Viscosity reduction $\Delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Master-batch</td>
<td>$28 \pm 3$</td>
</tr>
<tr>
<td>Modified master-batch</td>
<td>$26 \pm 4$</td>
</tr>
<tr>
<td>Direct method via industrial extruder</td>
<td>$26 \pm 3$</td>
</tr>
<tr>
<td>Direct method via mini-extruder</td>
<td>$27 \pm 2$</td>
</tr>
</tbody>
</table>

### Table 4.3. Molar mass of PC/silica nanocomposites prepared via mini-extruder obtained by SEC.

<table>
<thead>
<tr>
<th>Silica content (vol%)</th>
<th>$M_n$ (kg·mol$^{-1}$)</th>
<th>$M_w$ (kg·mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>30.0</td>
<td>11.6</td>
<td>2.6</td>
</tr>
<tr>
<td>0.3</td>
<td>29.9</td>
<td>11.6</td>
<td>2.6</td>
</tr>
<tr>
<td>0.8</td>
<td>29.6</td>
<td>11.4</td>
<td>2.6</td>
</tr>
<tr>
<td>1.1</td>
<td>29.8</td>
<td>11.5</td>
<td>2.6</td>
</tr>
<tr>
<td>1.7</td>
<td>29.1</td>
<td>11.0</td>
<td>2.6</td>
</tr>
</tbody>
</table>

The state of dispersion of the silica nanoparticles prepared via the modified master-batch and the direct methods is similar as that displayed and discussed in the section of 4.3.1. The absolute value of dynamic complex viscosity $\eta^*$ was measured as a function of the angular frequency for the samples prepared via different methods. The lowest viscosity prepared via different methods occurs to the nanocomposites with the addition of ~ 0.8
vol% silica nanoparticles. The results on the viscosity reduction percentage Δ are listed in Table 4.2. The values reported here are the values after correcting the effect of molar mass. Table 4.2 indicates a great repeatability of the viscosity reduction for our studied PC/silica nanocomposites. In addition, the molar mass of the samples prepared from direct method via mini-extruder was characterized using SEC and the results are presented in Table 4.3. Table 4.3 confirms that no degradation takes place for the samples made from the direct method, independent of the silica concentration.

4.3.2.7. Effect of particle surface area

As stated in the introduction, nanocomposites may offer a substantial improvement of the properties at very low filler loadings due to the large specific area of the nano-sized particles. Therefore, the particle size surface area, i.e., particle geometry, plays a key role in improving nanocomposites’ properties. The effect of particle size on the viscosity reduction of the PC/silica nanocomposites was investigated on materials prepared by the direct method using the mini-extruder, considering that the molar mass of the samples prepared via direct method using mini-extruder is more stable than the molar mass for the samples prepared via the other methods. Silica particles with three different diameters and geometry were used (Table 4.4): two types are spherical particles with an average diameter of 13 nm and 45 nm, while the other type contains cylindrical particles with an average diameter of 12 nm and a length of 70 nm.

Fig. 4.3 shows the state of dispersion of the three different silica particles in the PC matrix as visualized by TEM. The silica particles with an average diameter of 45 nm have a good dispersion with individual or two nanoparticles (Fig. 4.3b), while the silica particles with an average diameter of 13 nm form small aggregates with an average diameter of 80 nm. The image of the cylinder silica nanoparticles in the PC nanocomposites (Fig. 4.3c) does not clearly show the cylindrical shape of the particles. The dispersion of the cylindrical nanoparticles (Fig. 4.3c) is similar as that for the spherical nanoparticles with an average diameter of 13 nm (Fig. 4.3a). The cylindrical silica nanoparticles form aggregates with an average diameter of 100 nm. The reason for the state of dispersion of the cylindrical nanoparticles is might due to the fact that the cylinders are originally soft. These soft cylinders, the images of which were not presented here, have a tendency to form such aggregates to minimize their surface energy.

<table>
<thead>
<tr>
<th>Particle diameter (nm)</th>
<th>Calculated Surface area (m²/g)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>126</td>
<td>Sphere</td>
</tr>
<tr>
<td>45</td>
<td>60</td>
<td>Sphere</td>
</tr>
<tr>
<td>12/70</td>
<td>25.7</td>
<td>Cylinder</td>
</tr>
</tbody>
</table>
Chapter 4 Nanoscale effects on the decrease in viscosity of PC/silica nanocomposites

Fig. 4.3. TEM images of the (PC + 0.8 vol% silica) nanocomposite with different silica particle sizes and geometry prepared via the direct method using the mini-extruder: (a) 13 nm, (b) 45 nm and (c) 12/70 nm.

Fig. 4.4a shows the absolute value of complex viscosity $|\eta^*|$ ($\omega = 1$ rad/s) as a function of silica content for the (PC + 45 nm silica) nanocomposites. The $|\eta^*|$ first drops, then increases, reaching a minimum at $\sim 0.8$ vol% silica content for the (PC + 45 nm silica) system. The same trend was also observed for both the (PC + 13 nm silica) and the (PC + 12/70 nm silica) systems, in which the lowest viscosity occurs to the samples with $\sim 0.8$ vol% silica. It is unclear to us why the lowest $|\eta^*|$ of the PC/silica nanocomposites with three different nanoparticles occurs at similar silica content ($\sim 0.8$ vol%). One of the possible reasons comes from the state of dispersion of these three different nanoparticles.

Both Fig. 4.4b and Table 4.5 show the effects of nanoparticle size on the viscosity reduction of the studied systems. The effects of the nanoparticle size on the viscosity reduction can be observed in Fig. 4.4b. The smaller the nanoparticles (13 nm), the higher is the surface area and thus the large viscosity reduction was induced by the addition of $\sim 0.8$ vol% nanoparticles. The numbers in Table 4.5 were calculated based on complex viscosity at $\omega = 1$ rad/s at 250 °C after correcting for the degradation. The percentage of viscosity reduction indicates that both the size and the geometry of silica particles...
influence the rheological behavior (Fig. 4.4b). The roles of the size and the geometry of nanoparticles on the percentage of the viscosity reduction (Table 4.5), however, are not shown clearly in our systems. The most plausible reason is that the state of dispersion for these three different systems is comparable (Fig. 4.3). Therefore, a similar surface area of the silica nanoparticles is in contact with the PC chains, which may explain why the lowest $|\eta^*|$ occurred at similar silica content for all studied PC/silica nanocomposites with similar viscosity reduction $\Delta$.

Table 4.5. Comparison of the maximum decrease in viscosity of PC/silica nanocomposites with different types of silica nanoparticles prepared from direct method via the mini-extruder. The maximum viscosity reduction $\Delta$ indicates here is for the (PC + 0.8 vol% silica) nanocomposite.

<table>
<thead>
<tr>
<th>System name</th>
<th>Viscosity reduction $\Delta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC + 13 nm silica</td>
<td>27 ± 2</td>
</tr>
<tr>
<td>PC + 45 nm silica</td>
<td>21 ± 1</td>
</tr>
<tr>
<td>PC + 12/70 nm silica</td>
<td>24 ± 2</td>
</tr>
</tbody>
</table>

4.3.2.8. Relaxation time of PC/silica nanocomposites

The absolute value of complex viscosity $|\eta^*|$ at frequency 1 rad/s was taken as $\eta_0$. We expect that $|\eta^*|$ approaches to $\eta_0$ at a very low shear rate when the viscosity is independent of the shear rate. The limiting low shear-rate value of the viscosity is referred to as the zero-shear viscosity, $\eta_0$. This material constant plays an important role in polymer rheology, as an indicator of molar mass ($\eta_0 = kM^m_w$). The direct measurement of $\eta_0$ is often practically impossible. This is because standard rheometers often produce unreliable data at very low shear rates.$^{20}$ It is important to note that there are some empirical equations that can be used to obtain $\eta_0$ via extrapolating the viscosity function $|\eta^*(\dot{\gamma})|$. Here the Cross model (equation (4.4)) is used to get an estimate of the $\eta_0$ variation with silica content.

$$\eta(\dot{\gamma}) = \eta_0\left[1 + (\dot{\gamma})^m\right]^{-\frac{1}{m}}$$  \hspace{1cm} (4.4)

where $\dot{\gamma}$ is the shear rate, $\eta_0$ is the zero-shear viscosity, $\tau$ is a material constant with the units of time, and $m$ is a dimensionless material constant. $m$ is a measure of the degree of dependence of viscosity on shear rate in the shear-thinning region. A value of zero for $m$ indicates Newtonian behavior, while increasing the value of $m$ indicates an enhanced shear-thinning behavior. Fig. 4.2a shows the fitting data and experimental data at 250 °C, while the fitted zero-shear viscosity $\eta_0$ with varying silica content is shown in Fig. 4.2b. Fig. 4.2a demonstrates that the Cross model can be used for our experimental data. Fig. 4.2b shows the zero-shear viscosity $\eta_0$ variation with increasing silica contents, while a minimum $\eta_0$ occurs at silica content ~ 0.8 vol%.

In addition to the zero-shear viscosity $\eta_0$, the material constant $m$ and the changes of $\tau$ (Fig. 4.5a) can be derived by using the Cross model. With increasing silica content from 0
Chapter 4 Nanoscale effects on the decrease in viscosity of PC/silica nanocomposites

vol% to 0.1 vol%, \( m \) decreases, after which \( m \) stays constant with increasing silica content. This indicates that PC/silica nanocomposites have less pronounced shear-thinning behavior than that of pure PC. The reciprocal value of the frequency at which \( |\eta^*| \) starts to decrease from a constant number is referred to as the characteristic time \( \tau \) (Fig. 4.5a). Fig. 4.5a indicates that with increasing silica content, the characteristic time \( \tau \) decreases first and then increases again, while for the (PC + 0.8 vol% silica) nanocomposite, \( \tau \) decreases considerably (~ 44%) in comparison to pure PC. Comparing both Fig. 4.2b and Fig. 4.5a, the correlations between the characteristic time \( \tau \) obtained from the Cross model and the absolute value of complex viscosity \( |\eta^*| \) can be observed. Fig. 4.5b shows the correlations between \( \tau \) and \( |\eta^*| \), which yields a straight line. The variation of \( |\eta^*| \) implies a change in the reptation time, which can be demonstrated via the changes in the characteristic time \( \tau \) in the Cross model.

4.3.3. Possible mechanisms for the decrease in viscosity of PC/silica nanocomposites

4.3.3.1. ‘Ball-bearing’ effect

In our studied PC/silica nanocomposites, a viscosity reduction of approx. 26% can be obtained. Four different mechanisms for the decrease in viscosity of nanocomposites have been reported. The first mechanism is the so-called ‘ball-bearing’ effect. If spherical particle-filled polymers are forced to shear, an extremely high local shear is developed in the narrow gaps between the nearby rotating spheres, which induces the polymer chains to disentangle. This phenomenon has been reported by many research groups. Shenoy described the ball-bearing effect as the reduction of the friction between the polymer chains by small amounts of particles when the polymer matrix exhibit a near-Newtonian behaviour. The ‘ball-bearing’ effect is enhanced by increasing the shear rate, which manifests itself by a stronger shear-thinning. The ‘ball-bearing’ effect on the viscosity reduction of PC/silica nanocomposites was thus studied via investigating the shear-thinning behavior by comparing the slope of absolute value of complex viscosity \( |\eta^*| \) versus frequency \( \omega \) (Fig. 4.6). A higher the slope implies a more pronounced shear-thinning behavior. Fig. 4.6a shows that the slope for the (PC + 0.8 vol% silica)
nanocomposite is 0.67, while the slope for pure PC is 0.75. Our results (Fig. 4.6a) indicate thus less pronounced shear-thinning for the (PC + 0.8 vol% silica) nanocomposite than for pure PC. Therefore, we can conclude that the viscosity reduction in the studied PC/silica nanocomposites cannot be attributed to the ‘ball-bearing’ effect.

4.3.3.2. Excluded free volume

The second mechanism is the concept of excluded free volume induced by nanoparticles, which was put forward by Mackay and co-workers\textsuperscript{4,18} to explain the decrease in viscosity of nanoparticle-filled polymer melts. According to Mackay et al., the confinement of polymer chains near the surfaces of nanoparticles induces conformational changes to polymer molecules, which increases the free volume of the nanocomposites.\textsuperscript{4} The increased free volume leads to fast relaxation of polymer chains in the nanocomposites. The systems display thus a decrease in viscosity simultaneous with a depression of the $T_g$.

<table>
<thead>
<tr>
<th>Silica content (vol%)</th>
<th>$T_g$ (°C) \textsuperscript{a)</th>
<th>$T_g$ (°C) \textsuperscript{b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>151</td>
<td>152</td>
</tr>
<tr>
<td>0.1</td>
<td>151</td>
<td>152</td>
</tr>
<tr>
<td>0.3</td>
<td>151</td>
<td>152</td>
</tr>
<tr>
<td>0.5</td>
<td>149</td>
<td>151</td>
</tr>
<tr>
<td>0.8</td>
<td>150</td>
<td>151</td>
</tr>
<tr>
<td>1.1</td>
<td>149</td>
<td>151</td>
</tr>
<tr>
<td>1.7</td>
<td>149</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 4.6. $T_g$s for PC/silica nanocomposites as a function of silica content.

\textsuperscript{a) The $T_g$ was measured by DSC; b) The $T_g$ was obtained via the loss modulus peak measured by DMTA.}

The $T_g$s of the studied PC/silica nanocomposites were characterized via both DSC and DMTA. The results are listed in Table 4.6. For all prepared PC/silica nanocomposites, the $T_g$ was found to be constant with increasing silica content, while a difference in $T_g$ of approximate 1 °C between pure PC and PC/silica nanocomposite with the lowest complex viscosity (0.8 vol% silica content) was found. To check the relevance of this 1 °C difference in $T_g$ on the viscosity, time-temperature superposition (TTS) was applied. Mastercurves of the different nanocomposites at a reference temperature of $T_r$ = 190 °C were obtained via the TTS and used to calculate the $[\eta]$ of pure PC and the (PC + 0.8 vol% silica) nanocomposite at 250 °C and at the same distance from $T_r$, e.g. $T = (T_r + 50)$ °C (Fig. 4.6). The decrease of $[\eta]$ for the (PC + 0.8 vol% silica) nanocomposite compared to $[\eta]$ of pure PC at 250 °C and at the same distance from $T_r$, e.g. $T = (T_r + 50)$ °C, is 47% and 45% respectively, confirming that the 1 °C difference in $T_g$ has a negligible effect on the viscosity in comparison to the effect of the nanoparticles. Furthermore, the shape of derivative of heat capacity of PC/silica nanocomposites was compared with pure PC. Fig.
4.7 demonstrates that the addition of silica nanoparticles does not influence the shape of the curve of derivative of heat capacity versus temperature. This indicates that the addition of silica nanoparticles to PC has a global effect on PC.

Fig. 4.6. The absolute value of complex viscosity $|\eta^*|$ versus frequency $\omega$ of PC and (PC + 0.8 vol% silica) nanocomposites: (a) at 250 °C and (b) at $T = (T_g + 50)$ °C (reference temperature $T_r = 190$ °C).

Fig. 4.7. Derivative of the heat capacity versus temperature for PC/silica nanocomposites characterized via DSC.

4.3.3.3. Selective adsorption

The third mechanism for a decrease in viscosity of nanocomposites is the selective physisorption of polymer chains on the nanoparticle surface, postulated by a.o. Jain et al. According to this concept, the polymer chains with the highest molar mass are adsorbed on the nanoparticle surface, while the polymer chains with low molar mass constitute the surrounding matrix. One way to test this hypothesis is via time-dependent fractionation of molar mass as described by Jain et al. The molar mass of the PC in the PC/silica nanocomposites was determined using SEC. The nanocomposites were dissolved in dichloromethane. If chains are adsorbed on the silica surface, only free chains will dissolve initially, and subsequently, more and more
adsorbed chains will desorb and dissolve in the solvent. Therefore, PC/silica nanocomposites were dissolved in dichloromethane at room temperature for different times, and the dissolved PC was separated and its molar mass was characterized. Fig. 4.8 gives the fractionation results after the PC/silica nanocomposites were dissolved in dichloromethane for 5, 10, 30 min, and 24 hours respectively, and shows no variation of the measured molar mass distribution with time. These results indicate that the ‘selective adsorption’ mechanism cannot be used to explain the experimental results. On the other hand, dichloromethane is a very good solvent for PC; within 5 min all PC chains were dissolved, so the method used may not be discriminating enough.

In addition to solution fractionation of the chains with different molar masses, the steady-state compliance can also give insight in the possibility of ‘selective adsorption’. If a fraction of high molar mass chains is adsorbed to nanoparticles, a lower compliance should be observed. Fig. 4.9 shows the storage compliance \( J' \) and loss compliance \( J'' \) versus frequency for the PC and (PC + 0.8 vol% silica) nanocomposite. The low-frequency limiting value of \( J' \) is the steady-state compliance. At 0.01 rad/s, both materials have nearly the same \( J' \), where \( J'' \) is clearly different. The fact that both systems have a similar \( J' \) suggests that a fraction of high molar mass chains is not selectively adsorbed on the nanoparticles. Furthermore, a similar \( J' \) means that high molar mass tail of the molar mass distribution is not affected by addition of silica nanoparticles. The difference in \( J'' \) comes from the decrease in viscosity for the (PC + 0.8 vol% silica) nanocomposite.

Both results from fractionation of molar mass and compliance indicate that ‘selective adsorption’ can not explain the viscosity reduction in the studied PC/silica nanocomposites.

In summary, we tested three different possibilities, i.e., the ‘ball-bearing’ effect, the excluded free volume and the selective physisorption, to explain the decrease in viscosity of PC/silica nanocomposites. The results in this chapter show that the decrease in viscosity phenomenon can not be explained by these three mechanisms. The most logical explanation is that the addition of silica nanoparticles into PC induces a decrease of the
entanglement density, which reduces thus the friction between polymer chains under deformation. Therefore, the decrease in viscosity of PC/silica nanocomposites is observed.

4.4. Conclusions

PC/silica nanocomposites were made via melt processing by a master-batch and direct method using both an industrial large-scale extruder and a mini-extruder. TEM images demonstrate that silica particles have a good dispersion in the PC matrix while 13 nm particles have aggregates of 25-80 nm and 45 nm particles have mostly individual dispersed particles inside the PC matrix.

The decrease in viscosity of PC with the addition of pre-made silica in a narrow concentration window was observed. The results indicate that the $[\eta']$ first drops and then increases, with a minimum at silica content ~ 0.8 vol% and with a decrease of ~ 26%. The effect of particle size on the viscosity reduction of the studied PC/silica nanocomposites was investigated via the direct method by using of the mini-extruder. The results show that surface area and particle geometry play a role to the viscosity reduction with the effective surface area as the most important parameter. However, our results show that the lowest viscosity for these three different PC/silica nanocomposites occurs at a similar silica content (~ 0.8 vol%) with a comparable viscosity reduction $\Delta$ which points to the fact that a similar silica surface area are exposed to PC chains in these three PC/silica nanocomposites.

The Cross model was used to fit the experimental data to obtain the zero-shear viscosity $\eta_0$, relaxation time $\tau$ and the Cross rate constant $m$. The results indicate that relaxation time $\tau$ decreases and then increases with increasing silica content, with a minimum number at silica content ~ 0.8 vol%. The decrease of $m$ for the (PC + 0.8 vol% silica) nanocomposites shows that the (PC + 0.8 vol% silica) nanocomposite has less tendency for shear-thinning at high shear rates than that pure PC.

After discussing the effect of wall slip or inhomogeneous flow, molar mass and residual solvent on the viscosity reduction of PC/silica nanocomposites, three possibilities, i.e., the ‘ball-bearing’ effect, extra free volume, and selective adsorption, were considered to try to explain the viscosity reduction in the studied PC/silica nanocomposites. Our results confirm that firstly ‘ball-bearing effect’ is not important for our systems. Secondly, glass transition temperature $T_g$ is constant after the addition of silica nanocomposites, suggesting that no extra free volume plays a role in the decrease of the viscosity. Thirdly, fractionation of molar mass experiments and the investigations of compliance show no evidence of ‘selective adsorption’.

4.5. References

Oh, H.; Green, P.F. Nat. Mater. 2009, 8: 139-143.
CHAPTER 5

Abstract

The influence of silica nanoparticles on the viscoelastic properties of PC/silica nanocomposites has been investigated. The addition of silica to PC induces a decrease in viscosity. The decrease is dependent on PC molar mass and silica content, while the measurement temperature is irrelevant for the viscosity reduction of the studied systems. Moreover, the time-temperature superposition (TTS) principle does not fail with the addition of silica nanoparticles to PC. The terminal relaxation time $\tau_p$, the WLF constants, the rubbery plateau modulus $G''_\infty$ and the entanglement molar mass $M_\text{e}$, illustrate the effect of silica on the viscoelastic properties of PC/silica nanocomposites. The viscoelastic behavior in the terminal zone from the mastercurves and the calculation results confirm that there is no solid-like viscoelastic behavior in the investigated PC/silica nanocomposites.

Viscoelastic properties of poly(carbonate) (PC)/silica nanocomposites
5.1. Introduction

The rheological behavior of polymer nanocomposites has attracted significant interest in recent years. This is because rheological measurements can provide not only an assessment of processability but also give insights of the relation between the molecular structure and chain dynamics of polymers. Experimentally, polymer nanocomposites exhibit a typical solid-like viscoelastic behavior at particle volume fractions much smaller than predicted for conventional composites. Explanations range from the close packing of a highly anisotropic particulate phase to the creation of a polymer-mediated particle network. Generally, the addition of nanoparticles to polymers increases the viscosity of the nanocomposite. The rheological behavior depends on the molecular structures, the state of the filler dispersion, the shape and the orientation of the filler, the interaction between the filler and the polymer, as well as the filler-filler interactions. In Chapter 4, a decrease in the zero-shear viscosity of the PC/silica nanocomposites was described. With the addition of silica nanoparticles, the viscosity of the PC/silica nanocomposites decreases first and then increases with the lowest viscosity of the studied PC/silica nanocomposites at 0.8 vol% silica. The effect of the state of silica dispersion, the particle size (geometry) on the viscosity reduction was also discussed. However, the effect on the viscoelastic properties of the PC/silica nanocomposites, especially the viscoelastic behavior in the terminal zone, needs further investigation.

A considerable portion of polymer matrix is affected by the nanofillers in nanocomposites due to polymer-filler interactions. Simulations suggest that changes in monomer packing near the polymer-particle interface lead to local segmental dynamics that differ from that of the homopolymer. In the case of attractive polymer-particle interactions, the dynamics can be highly heterogeneous, particularly at high loading fractions. These dynamic heterogeneities, which arise due to the presence of nanofillers, have been suggested to explain the differences in viscoelastic properties between nanocomposites and the pure polymer matrix. The decrease in viscosity observed in the studied PC/silica nanocomposites, which is different from the expectation based on Einstein’s equation, is thus attributed to the interaction between PC and silica nanoparticles.

In this chapter, a detailed study on the viscoelastic properties of the PC/silica nanocomposites is, therefore, presented. The transition from linear-to-nonlinear behavior of the PC/silica nanocomposites is first discussed. This is followed by a comparison of the steady-state and dynamic viscoelastic properties. The remainder of the chapter will focus on the effect of silica on the time-temperature superposition (TTS) principle and the related viscoelastic properties. Special attention is given to the effect of the silica nanoparticles on the rubbery plateau modulus $G_N$ and the entanglement molar mass $M_e$, which will be used as input for Chapter 6.
5.2. Experimental

5.2.1. Materials

Three different bisphenol-A based poly(carbonates) (PC), supplied by SABIC Innovative Plastics (SIP), were used. The molar mass information is listed in Table 5.1. The PCs used are coded as PC\textsubscript{x}, where x stands for the weight-average molar mass $M_w$ of the used PC. A 30-31 wt% suspension of silica nanoparticles (an average diameter of 13 nm) in methyl ethyl ketone (MEK) was purchased from Nissan Chemical. All the materials were used as received.

<table>
<thead>
<tr>
<th>PC</th>
<th>$M_w$ (kg mol$^{-1}$)</th>
<th>$M_n$ (kg mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC\textsubscript{30}</td>
<td>30.0</td>
<td>11.6</td>
<td>2.6</td>
</tr>
<tr>
<td>PC\textsubscript{35}</td>
<td>34.6</td>
<td>12.4</td>
<td>2.8</td>
</tr>
<tr>
<td>PC\textsubscript{40}</td>
<td>40.8</td>
<td>14.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

5.2.2. Preparation of PC/silica nanocomposites

PC powder was first dried in a vacuum oven for 12 hours at 130 °C under N\textsubscript{2} flow. Approx. 0.1 wt% processing stabilizer tris(2,4-di-tert-butylphenyl) phosphite was added to the PC powder before further processing. A series of PC/silica nanocomposites with silica content ranging from 0.3 to 1.7 vol% was produced by melt blending the required amount of silica suspension and PC powder at 270 °C in a home-built, recirculating, twin-screw mini-extruder (internal volume of 5 cm$^3$) with a screw speed of 75 rpm for 15 minutes under N\textsubscript{2} atmosphere.

PC/silica nanocomposite sheets with a thickness of ~ 0.5 mm were prepared by using compression molding at 260 °C for 10 minutes under a pressure of 50 bars. Samples for the rheological characterization (8 mm in diameter, 0.5 mm in thickness) were cut from this sheet.

5.2.3. Characterization techniques

Rheological measurements were performed under N\textsubscript{2} atmosphere on a stress-controlled AR-G2 rheometer (TA Instruments) using an 8 mm parallel plate-plate geometry and disk-shaped specimen. Strain sweep experiments were performed with a strain ranging from 1.0 - 8000 % at 250 °C and 0.1 rad/s. Steady-state measurements were carried out at 250 °C with a shear rate ranging from 0.01 s$^{-1}$ to 10 s$^{-1}$. Frequency sweeps ranging from 100 - 0.01 rad/s were performed in a temperature range of 250 - 165 °C and with a constant strain of 10%, which was within the linear viscoelastic regime.

The data for storage modulus $G'$ and loss modulus $G''$ was used to determine the discrete relaxation spectra, obtained by using the IRIS software developed by Baumgaertel et al.\textsuperscript{10}
5.3. Results and discussion

The linear-to-nonlinear viscoelastic behavior of the PC/silica nanocomposites is first discussed. Second, the steady-state and the dynamic viscosity of PC/silica nanocomposites are compared. In this part, the focus is on the dynamic viscoelastic properties of PC/silica nanocomposites. The viscosity reduction data presented in Chapter 4 are discussed here more extensively. The effect of molar mass and temperature on the viscosity reduction of PC/silica nanocomposites are demonstrated and discussed. The time-temperature superposition (TTS) principle of PC/silica nanocomposites is examined, based on which the viscoelastic properties of PC/silica nanocomposites, i.e., terminal relaxation time $\tau_d$, WLF constant, rubbery plateau modulus $G_N^0$, molar mass between entanglements $M_e$ and viscoelastic behavior in the terminal zone, are discussed.

5.3.1. Linear-to-nonlinear viscoelastic behavior of PC/silica nanocomposites

To study the viscoelastic properties of polymers, it is important to define the linear deformation range. In the small strain regime, the response of a polymer follows the deformation linearly. If the deformation is above a critical value, the polymer deforms nonlinearly, where the stress depends on the magnitude, the rate and the kinematics of the deformation. In the linear-to-nonlinear transition range, the modulus decreases with increasing deformation. By investigating the transition from linear-to-nonlinear viscoelastic behaviour, insights into the relation between molecular structure and polymer chain dynamics, the network formation of nanoparticles, and the network between polymer and nanoparticles, can be obtained.

![Fig. 5.1. (a) Storage modulus $G'$ and (b) loss modulus $G''$ versus strain at 250 °C and 0.1 rad/s for the PC$_{30}$/silica nanocomposites.](image)

The strain sweep of the PC/silica nanocomposites was performed at 250 °C at a frequency of 0.1 rad/s. The variation of the storage modulus $G'$ and the loss modulus $G''$ for PC$_{30}$/silica nanocomposites with increasing strain is shown in Fig. 5.1. It has to be noted that the data at low strains may be inconsistent due to the limiting torque. Fig. 5.1a demonstrates that the $G'$ of the pure PC$_{30}$ remains constant over the entire strain range. With the addition of silica, $G'$ of the nanocomposites shows a different behavior. At small
deformations, \( G' \) for PC\(_{30}\)/silica nanocomposites is constant, while under large deformation (> 50% strain) a transition from a linear to nonlinear behavior occurs. The stability of the measurements, specifically at high strains (~ 300%), was verified by applying a Lissajous analysis,\(^{12}\) which evaluates the variations of the displacement with the oscillation torque during strain sweep measurements (Fig. 5.2). Fig. 5.2 demonstrates that during measurements, the shape of Lissajous-plots is in a nice elliptical form, which indicates that the strain sweep measurements at strains of ~ 300% were stable. In addition, the stability of strain sweep measurements can be checked by overlapping several circles as displayed in Fig. 5.2 for one sample. In our measurements (the results of which are not presented here), several circles were found to overlap nicely to each other for each sample. Therefore, the stability of the strain sweep measurements in our experiments was confirmed.

![Fig. 5.2. Displacement versus oscillation (osc.) torque for PC\(_{30}\)/silica nanocomposites at 0.1 rad/s, 300% strain at 250 °C.](image)

This linear-to-nonlinear transition in the melt state is referred to as strain thinning. For a small strain, the entangling and disentangling rates of PC\(_{30}\) chains are equal.\(^{13}\) Therefore, the \( G' \) and the \( G'' \) are constant in this equilibrium state. If the strain amplitude increases further, the PC chains release the entanglements and align in the flow direction, resulting in a change of the network. The release of network causes the moduli to decrease. Fig. 5.1a illustrates that the strain thinning of the PC\(_{30}\)/silica nanocomposites occurs much earlier, which results in lower critical strain values. A similar critical strain value is observed for the nanocomposites with silica content from 0.3 vol% to 1.1 vol% (Fig. 5.1a). However, the critical strain amplitude for the (PC\(_{30}\) + 1.7 vol% silica) nanocomposite is shifted to a higher value. Sternstein et al.\(^{14}\) postulated that the reduction of \( G' \) and \( G'' \) with increasing applied strain is related to filler-polymer interactions including the aspects of trapped topological entanglements. In a nanocomposite with a high silica content, there are many trapped entanglements near the silica surfaces,\(^{15}\) which cause a local drag during deformation, namely, the trapped entanglements hamper the disentangling procedure under deformation, and in turn leads to a higher critical strain value.

In addition, Fig. 5.1b shows that within the linear range, up to 0.8 vol% of silica, \( G'' \) decreases. If the silica content exceeds ~ 0.8 vol%, \( G'' \) increases with increasing silica concentration. However, a reverse trend for \( G' \) is found in Fig. 5.1a. These variations
correspond directly to the viscosity changes consistent with the definition of complex viscosity:

$$|\eta'| = \sqrt{G''(\omega)^2 + G'(\omega)^2}$$

(5.1)

In Chapter 4, we observed similar trends for $|\eta'|$ as it is shown here for $G''$ as a function of silica content. These trends suggest that the addition of silica has a larger impact on decreasing $G'$ than on increasing $G''$, especially for the (PC$_{30}$ + 0.8 vol% silica) nanocomposite. Furthermore, the increase of $G'$ and the decrease of $G''$ reduces the loss factor ($G''/G'$) dramatically within the linear deformation range as visualized in Fig. 5.3a. Fig. 5.3b presents the loss modulus $G''$ and the storage modulus $G'$ at small amplitude with different silica contents. It can be seen that the (PC$_{30}$ + 0.8 vol% silica) nanocomposite has a high $G'$ and the lowest $G''$, which implies that ~0.8 vol% silica nanoparticles leads to a high elastic modulus and the lowest energy dissipation. Fig. 5.3a shows that the (PC$_{30}$ + 1.7 vol% silica) nanocomposite has the lowest loss factor, which is constant over the entire experimental strain range. This is attributed to the possible filler network via polymer matrix at the highest studied silica concentration. The constant factor implies that there is no change of the filler network with increasing strain. In contrast to earlier reports, no clear peak for the loss modulus $G''$ was observed for PC$_{30}$/silica nanocomposites (Fig. 5.1b). Aranguren et al. observed that the appearance of a peak in $G''$ was related to the energy dissipation produced by the breakdown of silica aggregates. TEM images show a similar silica dispersion for the PC$_{30}$/silica nanocomposites with different silica contents before and after strain sweep. The absence of the loss modulus $G''$ peak combined with the observations from TEM suggests that no breakdown of silica aggregates occurs during the strain sweep measurements.

![Fig. 5.3. (a) Loss factor $G''/G'$ versus strain at 250 °C and 0.1 rad/s for PC$_{30}$/silica nanocomposites; (b) $G'_s$ and $G''_s$ versus silica content at 250 °C and 0.1 rad/s, $G''_s$ is the loss modulus and $G'_s$ is the storage modulus at small amplitude (ca. 4%).](image)

The results from the strain sweep measurements demonstrate that the linear-to-nonlinear transition and strain-dependent viscoelastic behavior of the PC$_{30}$/silica nanocomposites are affected by the addition of silica. This is due to the fact that the large
surface-to-volume ratio of nanoparticles affects a considerable portion of polymer chains which are attached to the filler surface even at very low filler loadings.

In summary, the strain sweep results indicate that silica nanoparticles have a larger influence on the decrease of loss modulus than on the increase of storage modulus, especially for the (PC + 0.8 vol% silica) nanocomposite (Fig. 5.3). All results illustrate the importance of silica addition for the viscoelastic properties of PC/silica nanocomposites, which will be further demonstrated in both steady-state and dynamic measurements.

5.3.2. Steady-state and dynamic viscoelastic properties of PC/silica nanocomposites

5.3.2.1. Steady-state properties

In the rheological characterization of nanocomposites, the steady shear response provides useful information on the materials' processability. Therefore, the steady-state viscosities of the PC/silica nanocomposites were measured at 250 °C with shear rates ranging from 0.01 s$^{-1}$ to 10 s$^{-1}$. As an example, the results of the PC$_{35}$/silica nanocomposites are presented in Fig. 5.4a. The pure PC$_{35}$ matrix exhibits a Newtonian behavior, i.e., the steady-state viscosity is independent of the shear rate within the measurement range. The behavior of both the (PC$_{35}$ + 0.3 vol% silica) and the (PC$_{35}$ + 0.7 vol% silica) nanocomposites are similar to pure PC$_{35}$, while PC$_{35}$ has higher steady-state viscosity. With increasing shear rate, a decrease of the steady-state viscosity was observed for both the (PC$_{35}$ + 0.9 vol% silica) and (PC$_{35}$ + 1.1 vol% silica) nanocomposites (Fig. 5.4a). The steady-state viscoelastic behavior of the PC$_{35}$/silica nanocomposites is thereby dependent on the silica content. In addition, the steady-state viscosity at a certain shear rate depends on the silica concentrations. The steady-state viscosity at a certain shear rate decreases considerably for the (PC$_{35}$ + 0.9 vol% silica) nanocomposite, but then increases when silica content is ≥1.1 vol%. Similar trends are found in the dynamic measurements. The comparison of the steady-state viscosity and the dynamic viscosity for the PC$_{35}$ and the (PC$_{35}$ + 0.9 vol% silica) nanocomposite is plotted in Fig. 5.4b.

Fig. 5.4. (a) Steady-state viscosity versus shear rate and (b) comparison between steady-state and dynamic viscosity of PC$_{35}$/silica nanocomposites at 250 °C.
As demonstrated in Fig. 5.4b for pure PC₃₅, the shear rate dependence of the steady-state viscosity $|\eta'_{s}|$ is similar to the frequency dependence of the dynamic viscosity $|\eta'(\omega)|$, which is defined by the Cox-Merz rule.¹⁸ Therefore, the Cox-Merz rule works for pure PC, which indicates that the measurements were performed correctly. It is worth noting that the dynamic complex viscosity versus frequency curve for pure PC₃₅ goes up at low frequency range (< 0.03 rad/s) compared with that for the steady-state curve (Fig. 5.4b). This might be due to the formation of bubbles during measurements, which comes from the improper drying of PCs, therefore, this upturn of the curve at low frequency probably reflects the elastic response of these bubbles. On the contrary, the (PC₃₅ + 0.9 vol% silica) nanocomposite does not obey the Cox-Merz rule (Fig. 5.4b). This deviation is typical for suspensions of solid spherical particles. Otsuka et al.¹⁹ and Jain et al.²⁰ observed a similar behavior. Fig. 5.4b indicates that at very low frequencies (< 10⁻² rad/s or < 10⁻² s⁻¹), the absolute value of the complex viscosity $|\eta'(\omega)|$ and the steady-state viscosity $|\eta'_{s}|$ will eventually be the same. This suggests that at low shear rate or low frequency, the (PC₃₅ + 0.9 vol% silica) nanocomposite has a Newtonian behavior.¹³

Although the steady-state studies provide us information on the viscoelastic behavior of polymer nanocomposites, steady shear flow properties do not provide reliable results for highly concentrated and agglomerated composite systems. Therefore, the stability of steady-state measurements was checked. First, the normal force was found to be very low for PC/silica nanocomposites during our steady-state experiments. Second, the investigated shear rate range for the (PC₃₅ + 0.9 vol% silica) nanocomposite is the same as that for pure PC. Third, the steady-state viscosity for PC/silica nanocomposites, especially for the (PC₃₅ + 0.9 vol% silica) nanocomposite is lower than pure PC (Fig. 5.4b). Therefore, the possibility to produce large normal force difference to form heterogeneous structures and melt fracture, especially at the edge of the sample is low. In addition, at the end of measurements, the shape of samples was always checked. The shape of samples was good after each measurements, which indicates the measurements of steady-state measurements for PC/silica nanocomposites were stable. The stability of steady-state measurements is confirmed and the data listed in Fig. 5.4 are reliable.

5.3.2.2. Dynamic properties

Reliable rheological data can be obtained by using dynamic oscillatory shear measurements, which offer insights into the effect of filler dispersion, volume fraction, and particle-matrix interaction on the dynamic mechanical properties. Therefore, the dynamic properties of the PC/silica nanocomposites were measured for a variety of silica contents.

Fig. 5.5 shows $|\eta'|$ of PC₃₀/silica and PC₃₅/silica nanocomposites as a function of frequency. At low frequencies, $|\eta'|$ is independent of frequency, i.e., a Newtonian behavior, but $|\eta'|$ declines in the range of high frequencies. A decrease in $|\eta'|$ was observed for both PC₃₀/silica and PC₃₅/silica nanocomposites after the addition of silica nanoparticles. The molar mass difference between PC₃₀ (30.0 kg·mol⁻¹) and PC₃₅ (34.6 kg·mol⁻¹) does not affect the viscosity variations in these two systems. It is worth noting that the complex
Chapter 5 Viscoelastic properties of PC/silica nanocomposites

viscosity versus frequency curves for both pure PCs go up at low frequency rang (< 0.03 rad/s). As mentioned earlier, this might be due to the formation of bubbles during measurements, which comes from the improper drying of PCs.

![Fig. 5.5. Dynamic viscosity versus frequency at 10% strain and 250 °C for (a) PC_{30}/silica and (b) PC_{35}/silica nanocomposites.](image)

5.3.2.3. Effect of molar mass on the viscosity reduction of PC/silica nanocomposites

Molar mass or radius of gyration $R_g$ of PC does affect the viscosity reduction of PC/silica nanocomposites if molar mass difference is above a certain threshold. To describe the viscosity reduction more clearly, we define viscosity reduction percentage $\Delta$ as:

$$
\Delta = \frac{|\eta_i^*| - |\eta_0^*|}{|\eta_0^*|} \times 100\% 
$$

(5.2)

where $|\eta_i^*|$ is the complex viscosity of PC/silica nanocomposites at a silica content of $i$, and $|\eta_0^*|$ is the complex viscosity of pure PC. In Fig. 5.6a, the viscosity reduction percentage $\Delta$, induced by the addition of ~ 0.9 vol% silica nanoparticles to PCs with different molar mass (PC_{30}, PC_{35} and PC_{40}), as a function of $(T-T_g)$ is presented. Here, $T$ is the temperature where $|\eta^*|$ was measured, and $T_g$ is the glass transition temperature. It can be seen that there are negligible differences in the viscosity reduction between PC_{30} and PC_{35} systems. Similarly, the viscosity reduction was also observed in PC_{40} systems. But the viscosity reduction $\Delta$ for PC_{40} (40.8 kg/mol), which has a higher molar mass than PC_{30} and PC_{35}, is smaller. The effect of molar mass on the viscosity reduction can be schematically illustrated in Fig. 5.6b. With increasing molar mass, the viscosity reduction $\Delta$ decreases while the silica content with the lowest viscosity (marked as * in Fig. 5.6b) is shifted to a lower value.

In the nanocomposites, the interparticle distance $\Lambda$ can be calculated based on the following equation:

$$
\Lambda/D = (\phi_0/\phi)^{1/3} - 1
$$

(5.3)

where $D$ is the particle diameter, $\phi$ is the volume fraction and $\phi_m \approx 0.638$ is the maximum random packing volume fraction. Bridging of chains between particles in
nanocomposites occur when one polymer coil starts to touch two nanoparticles, namely, $\Lambda \approx 2R_g$. With increasing molar mass, $R_g$ of PC chains increases. Therefore, $\Lambda$ for bridging increases. Based on equation (5.3), a lower volume fraction of silica nanoparticles is needed to obtain $\Lambda \approx 2R_g$. If the lowest viscosity point for the PC/silica nanocomposites occurs at a concentration when $\Lambda < 2R_g$, the concentration for high molar mass PC is lower than that for low molar mass PC (the point marked as * is shifted to a lower value, as demonstrated in Fig. 5.6b).

5.3.2.4. Effect of temperature on the viscosity reduction of PC/silica nanocomposites

Fig. 5.6a also demonstrates the temperature influences on the viscosity reduction. The graph shows a similar decrease in viscosity over a broad temperature range ($T-T_g = 50 \, ^\circ\text{C}$-$130 \, ^\circ\text{C}$). Generally, temperature not only affects the rheological properties of the matrix, it can also affect the state of dispersion of the nanocomposites via changes in particle-particle and polymer-particle interactions. However, our results indicate that temperature is irrelevant to the viscosity reduction percentage $\Delta$ of the studied PC/silica nanocomposites.

5.3.3. Time-temperature superposition

5.3.3.1. Time-temperature superposition (TTS) principle

The time-temperature superposition (TTS) law for glassy polymer systems deals with a precise situation: the viscoelastic modulus as a function of frequency at any given temperature is equal to the one at a different temperature, provided that the frequencies are multiplied by a constant shift factor. It has been reported that certain polymer nanocomposites exhibit gradients of the glass transition temperature induced by
Chapter 5 Viscoelastic properties of PC/silica nanocomposites

When a rheological measurement is performed, the entire sample is submitted to an oscillatory strain under a same frequency. However, if its glass transition temperature varies with position, a change in temperature does not correspond to a constant frequency shift. The distribution of the elastic modulus in these samples also does not shift homogeneously with changes in temperature. To continue using the TTS law for characterization of these nanocomposites, it is necessary to use approximations otherwise the law fails. In practice, there are many conceivable reasons as to why the principle may fail, such as the occurrence of more than one relaxation mechanism with a distinct temperature dependence. As a result, materials that change chemically or physically during rheological measurements will not obey the TTS law.

From investigating the TTS behavior, the relaxation mechanism of polymer nanocomposites can be found. Therefore, the effect of silica on the relaxation of PC chains was determined by examining the dynamic moduli in the linear viscoelastic region via frequency sweeps performed in the temperature range of 250 - 165 °C. Logarithmic plots of storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ taken at temperature $T$ were superimposed on those taken at temperature $T_r$ by a translation of $\alpha T$ along the frequency axis. No vertical shift along the modulus axis was necessary. TTS in this case can be expressed by:

$$G'(\omega, T) = G'(\omega \cdot \alpha, T_r)$$  \hspace{1cm} (5.4)
where # represents one or two primes. In this study, the reference temperature $T_r$ was chosen as 210 °C.

Fig. 5.7 shows the mastercurves of the studied PC/silica nanocomposites with different molar masses at $T_r = 210$ °C. The data extend over ca. 9 decades of frequencies. The PC matrix (Fig. 5.7) has a predominantly viscous behavior ($G'(\omega) < G''(\omega)$) at low frequencies with a transition towards a rubber-like regime ($G'(\omega) > G''(\omega)$) at intermediate frequencies. Further increasing the frequency induces another transition regime ($G'(\omega) < G''(\omega)$). The nanocomposites demonstrate a similar rheological behavior as that displayed by the PC matrix. The results confirm that the PC/silica nanocomposites obeyed the TTS principle.

Whether the TTS principle holds can also be conveniently read from a $G_d$-$\delta$ plot. A $G_d$-$\delta$ plot is a plot of the phase angle $\delta$ versus the absolute value of the complex modulus $G'$. The plot eliminates the effect of shifting along the frequency axis and yields temperature-independent curves where TTS holds. Fig. 5.8a gives the $G_d$-$\delta$ plot at $T_r = 210$ °C for PC$_{30}$/silica nanocomposites as an example. The figure illustrates that the $G_d$-$\delta$ plots of the PC$_{30}$/silica nanocomposites overlap nicely with that of the pure PC$_{30}$, thereby confirming that TTS law is obeyed for each sample. Additionally, the overlap of the plots implies that there are no relaxation spectra changes with addition of silica nanoparticles, e.g. no selective adsorption occurs in the system. The addition of silica nanoparticles has a global effect on the PC/silica nanocomposites.

The fact that TTS holds implies that PC/silica nanocomposites are homogeneous, i.e., no micro- or macrophase separations, no agglomerates of silica, and no microstructural changes during measurements. Han plots, which plot the storage modulus $G'(\omega)$ versus the loss modulus $G''(\omega)$ with frequency as a parameter, can be used to elucidate structure differences between the polymer matrix and the filled systems at a fixed temperature. Han plots for PC$_{30}$/silica nanocomposites are presented in Fig 5.8b. The storage moduli $G'(\omega)$, for a given loss moduli $G''(\omega)$, are similar with increasing silica content. The negligible changes in the shift and the slope of $G'(\omega)$ versus $G''(\omega)$ curves indicate that the microstructure of the PC/silica nanocomposites does not change significantly with the addition of silica nanoparticles during measurements.

Fig. 5.8. (a) $G_d$-$\delta$ plot and (b) Han plot for PC$_{30}$/silica nanocomposites at $T_r = 210$ °C.
Analogous to the Han plots, Cole-Cole plots can also be used in the detection of TTS or structural features. Here, the imaginary viscosity $\eta''$ is depicted as a function of real viscosity $\eta'$ (Fig. 5.9). A standard semi-arc is obtained if the deformation behavior of the material can be described by a single relaxation time or with a narrow relaxation time distribution. In complex polymeric systems, more than one relaxation time can occur, leading to the distortion of the arc or to the appearance of a second arc. Therefore, Cole-Cole plots were used to investigate the microstructures or molecular architectures of homopolymers or materials with a wide relaxation time distribution such as heterogeneous polymeric systems, polymer composites, block copolymers and polymer blends. Fig. 5.9 gives the Cole-Cole plots for PC$_{30}$/silica nanocomposites at $T_r = 210^\circ$C.

Standard semi-arc trends were produced from all PC$_{30}$/silica nanocomposites Cole-Cole plots (Fig 5.9). This confirms that the time and temperature effects are superimposable in the studied PC/silica systems. The regular semi-arc curves indicate that these silica nanoparticles filled polymeric systems exhibit a single relaxation time or a narrow relaxation time distribution. With increasing silica concentration, the diameter of the semi-arc becomes smaller while a small tail appears at lower frequencies. At low frequency (or zero frequency) and $\eta'' = 0$, the corresponding real viscosity $\eta'$ is equal to the zero-shear viscosity. In Fig. 5.9, it is evident that this zero-viscosity value changes with silica content, which is similar to the viscosity variation discussed in Chapter 4. The appearance of the tail within low frequency range might be due to the formation of bubbles during measurements, which comes from the improper drying of PCs. Furthermore, the frequency where $\eta''$ is maximum varies with silica concentration. These changes allow us to calculate the systems’ relaxation times. For example, the maximum value of $\eta''$ for the (PC$_{30}$ + 0.8 vol% silica) nanocomposite corresponds to the highest frequency value in the studied PC$_{30}$/silica nanocomposites, suggesting that the (PC$_{30}$ + 0.8 vol% silica) nanocomposite relaxes the fastest.

In summary, TTS was found to be satisfactory and applicable for PC/silica nanocomposites within the investigated temperature range. The viscoelastic spectra shown in Fig. 5.7 demonstrate that nanocomposites form entangled melts similar to pure polymer. In contrast to the heterogeneity, the rheological measurements suggest that the silica effect on polymer melt dynamics may be described homogeneously. Therefore, based on
PC/silica nanocomposites’ mastercurves and their differences, their viscoelastic properties including relaxation time $\tau_d$, WLF constants, plateau modulus $G_N$, and molar mass between entanglements $M_e$ can be calculated. For clarity, only two samples for each system are listed in Figs. 5.7 b and c.

5.3.3.2. Relaxation time $\tau_d$ and shift of the mastercurves

For entangled homopolymers, the reciprocal of the first crossover frequency obtained from $G'(\omega)$ and $G''(\omega)$ (on a log - log plot, listed in Fig. 5.7) corresponds to the reptation disengagement time, $\tau_d^{32}$ namely the terminal relaxation time. When the mastercurves for PC and the (PC + 0.9 vol% silica) nanocomposites are superimposed, it can be observed that the first $G'(\omega) = G''(\omega)$ crossover points of the (PC + 0.9 vol% silica) nanocomposites are shifted to a higher $\omega$ (Fig. 5.7). It is evident (Fig. 5.7b, dashed line) that the first crossover frequency of the (PC$_{35}$ + 0.9 vol% silica) nanocomposite shifts to a higher frequency, indicating a shorter relaxation time than that of the unfilled PC$_{35}$. Table 5.3 lists $\tau_d$ for PC$_{30}$/silica nanocomposites calculated from the reciprocal of the first crossover frequency. The number points out that with increasing silica contents, $\tau_d$ decreases until the concentration of silica increased > 0.8 vol%, while an increase in $\tau_d$ for the (PC$_{30}$ + 1.7 vol% silica) nanocomposite was observed. This implies that the addition of silica nanoparticles in PC matrix induces changes in the relaxation time of PC chains. This is expected, since the decrease in viscosity observed in the (PC + 0.9 vol% silica) nanocomposites indicates a faster terminal relaxation time $\tau_d$.

Fig. 5.10. WLF functions’ plot of shift factor $\alpha_T$ for the (PC$_{30}$ + 0 vol% silica) and the (PC$_{30}$ + 0.8 vol% silica) nanocomposites.

5.3.3.3. WLF constants and effect of free volume

The TTS shift factor $\alpha_T(T)$, can be described by the WLF equation,\(^{13}\) which is derived on the basis of temperature dependent free volume:

$$\log \alpha_T = -C_1^T (T - T_g) / (C_2^T + (T - T_g))$$

(5.5)
Here, \( C_1^g = \frac{B}{2.303} f_g \) and \( C_2^g = \frac{f_g}{\alpha f} \), where \( f_g \) is the fractional free volume at \( T_g \), \( \alpha f \) is the temperature coefficient of the fractional free volume, and \( B \) is a constant generally assumed to be unity. If the reference temperature \( T_r \) is different from the glass transition temperature, the WLF equation will be rewritten as:

\[
\log \alpha_r = -C_1^r (T - T_r) / (C_2^r + (T - T_r))
\]

(5.6)

where \( C_1^r = \frac{B}{2.303} f_r \), \( C_2^r = \frac{f_r}{\alpha f} \), and \( f_r \) is the fractional free volume at reference temperature \( T_r \).

Inspection of the equation (5.6) reveals that plots of \( 1/\log (\alpha T) \) as a function of \( 1/(T - T_r) \) should be linear, if the expression holds, and the parameters may be determined from the plots’ slopes and intercepts. For the nanocomposites studied, the \( 1/\log (\alpha T) \) plots were noted to have a linear relationship, indicating the validity of the above equations. An example is given in Fig 5.10. From the slopes and intercepts, \( C_1^r \), \( C_2^r \), and \( f_r \) were determined for each sample. The values of \( f_g \) can be calculated via the equation:

\[
f_g = B(C_2^g + T_g - T_r) / (2.303C_1^g)
\]

(5.7)

The calculated values for the PC_{30}/silica nanocomposites are tabulated in Table 5.2.

Table 5.2: Viscoelastic properties of PC/silica nanocomposites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( C_1^r )</th>
<th>( C_2^r )</th>
<th>( f_r/B )</th>
<th>( f_g/B )</th>
<th>( \alpha f/B )</th>
<th>( T_g(°C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC_{30} + 0 vol% silica</td>
<td>3.5</td>
<td>86.8</td>
<td>0.1</td>
<td>0.04</td>
<td>1.4\times10^{-3}</td>
<td>152</td>
</tr>
<tr>
<td>PC_{30} + 0.3 vol% silica</td>
<td>3.9</td>
<td>97.2</td>
<td>0.1</td>
<td>0.04</td>
<td>1.1\times10^{-3}</td>
<td>152</td>
</tr>
<tr>
<td>PC_{30} + 0.8 vol% silica</td>
<td>3.9</td>
<td>98.9</td>
<td>0.1</td>
<td>0.04</td>
<td>1.1\times10^{-3}</td>
<td>151</td>
</tr>
<tr>
<td>PC_{30} + 1.1 vol% silica</td>
<td>3.8</td>
<td>93.4</td>
<td>0.1</td>
<td>0.04</td>
<td>1.2\times10^{-3}</td>
<td>151</td>
</tr>
<tr>
<td>PC_{30} + 1.7 vol% silica</td>
<td>3.5</td>
<td>91.9</td>
<td>0.1</td>
<td>0.04</td>
<td>1.3\times10^{-3}</td>
<td>150</td>
</tr>
</tbody>
</table>

Table 5.2 shows that the addition of silica to PC_{30} slightly increases \( C_1^r \) and \( C_2^r \) with increasing silica content. The fractional free volume at the reference temperature \( f_r \) and the fractional free volume at the glass transition temperature \( f_g \) keep constant with increasing silica content. The constant value of \( f_r \) implies that the addition of silica nanoparticles does not vary the free volume of the nanocomposites. The invariable value of \( f_g \) indicates that in the PC/silica nanocomposite systems, the glass transition is essentially an iso-free volume condition, and the long-range molecular motion occurs only when the free volume reaches the same critical level regardless of system composition. However, the thermal expansivity \( \alpha f \) decreases with the addition of silica nanoparticles, and then it increases again, with a minimum value for the (PC_{30} + 0.8 vol% silica) nanocomposites. It is not clear to us whether the trend of \( \alpha f \) with increasing silica content is significant.

5.3.3.4. Rubbery plateau \( G_N^0 \) and \( M_f \)

The slightly confined PC chains around silica surfaces are expected to have an influence on the viscoelastic properties of PC/silica nanocomposites. One of the
The viscoelastic properties, the plateau modulus $G'^0$, was shown in Fig. 5.7. To quantify $G'^0$, the ‘tan δ minimum criterion’ is utilized, wherein $G'^0$ is set to equal the storage modulus $G'$ at the frequency where tan δ has its minimum:

$$G'^0 = G'_\text{min}$$  \hspace{1cm} (5.8)

Table 5.3 illustrates that the addition of silica nanoparticles influences the $G'^0$ of PC/silica nanocomposites. With increasing silica content, $G'^0$ decreases continuously. It is worth noting this method to calculate $G'^0$ based on equation (5.8) is different from the standard method. According to the standard method, the value for $G'^0$ is chosen where $G''$ reaches its minimum. This method was not applied in this work, since the minimum of $G''$ is not clearly displayed (Fig. 5.7) in the studied PC/silica nanocomposites.

The relationship of $G'^0$ to the molar mass between entanglements $M_e$ is:

$$M_e = \frac{4\rho RT}{5G'^0}$$  \hspace{1cm} (5.9)

where $R$ is the universal gas constant (8.314 J mol$^{-1}$K$^{-1}$), $\rho$ is density, and $T$ is the absolute temperature. The density $\rho$ of PC can be expressed as:

$$\rho = \frac{10^3}{\exp(-0.307 + 1.86 \times 10^{-5}T^{1/2})}$$  \hspace{1cm} (5.10)

Table 5.3. Rheological properties of PC/silica nanocomposites.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$G'^0$ (MPa)</th>
<th>$M_e$ (kg/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$N$</th>
<th>$\eta_0$ (Pa*s)</th>
<th>$\omega$ (rad/s)</th>
<th>$\tau_d$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{30} + 0$ vol% silica</td>
<td>2.4</td>
<td>30.0</td>
<td>1580</td>
<td>19</td>
<td>6.87E+03</td>
<td>22.7</td>
<td>0.28</td>
</tr>
<tr>
<td>PC$_{30} + 0.3$ vol% silica</td>
<td>2.1</td>
<td>29.9</td>
<td>1806</td>
<td>17</td>
<td>5.59E+03</td>
<td>23.9</td>
<td>0.26</td>
</tr>
<tr>
<td>PC$_{30} + 0.8$ vol% silica</td>
<td>2.1</td>
<td>29.6</td>
<td>1806</td>
<td>16</td>
<td>4.69E+03</td>
<td>32.1</td>
<td>0.20</td>
</tr>
<tr>
<td>PC$_{30} + 1.1$ vol% silica</td>
<td>2.0</td>
<td>29.7</td>
<td>1896</td>
<td>16</td>
<td>4.90E+03</td>
<td>30.6</td>
<td>0.21</td>
</tr>
<tr>
<td>PC$_{30} + 1.7$ vol% silica</td>
<td>1.6</td>
<td>29.4</td>
<td>2355</td>
<td>12</td>
<td>5.30E+03</td>
<td>27.0</td>
<td>0.23</td>
</tr>
</tbody>
</table>

By combining equations (5.8), (5.9) & (5.10), $M_e$ of PC/silica nanocomposites at $T = 250$ °C can be calculated and is listed in Table 5.3. Note that this is only a crude calculation which deviates from the usual value reported in the literature. The comparison must be treated with caution considering the uncertainty in estimating $M_e$ in the bulk. The main point is that $M_e$ in the (PC + 0.8 vol% silica) nanocomposite is larger than for pure PC (see also Chapter 6). It can also be seen that the $M_e$ increases with the addition of silica nanoparticles. Therefore, the number of entanglements per chain $N = M_w/M_e$ (Table 5.3) decreases with silica content. This may be one of the reasons for
reduction in viscosity of PC/silica systems after the addition of ~ 0.8 vol% silica. Fewer entanglements are present, which requires less activation energy to flow. The results in Table 5.3 indicate a relation between $N$ and the viscosity reduction.

5.3.3.5. Behavior in the terminal zone

In the terminal zone, the slope of log $G'$ versus log $\omega$ for an ideal polymeric liquid is 1, while the slope of log $G'$ versus log $\omega$ is 2. Therefore, an ideal polymeric liquid has a slope of 2 for log $G'$ versus log $G''$. In general, highly concentrated composites show a yield stress and non-terminal solid-like behavior at lower frequency ranges due to the increase of chain entanglements and interactions between particles and polymer matrix as well as between particles. Subsequently, the slopes of log $G''$ versus log $\omega$ and log $G'$ versus log $\omega$ decrease. Fig. 5.8b shows the logarithmic plot of $G'$ and $G''$ for PC$_{30}$/silica nanocomposites. Slopes for PC$_{30}$ and (PC$_{30}$ + 1.1 vol% silica) nanocomposite from the Han plots are ~ 1.7, while their terminal zone slopes from the mastercurves (Fig. 5.7a) are both ~ 1.5. The results show negligible solid-like response of PC$_{30}$ chains after the addition of silica nanoparticles.

Generally, the critical silica content where the solid-like response appears is the content when the bridging effects occur, i.e., when the interparticle distance $\Lambda$ reaches the polymer chain size $2R_g$. The highest silica ($D = 13$ nm) volume fraction investigated is $\phi_m \approx 0.011$. From equation (5.3), $\Lambda = 35$ nm can be obtained. In addition, the radius of gyration of a polymer chain can be calculated based on:

$$R_g = \sqrt[3]{\frac{2n}{3}b} \quad (5.11)$$

where $b$ is the segmental length and $n$ is the number of monomer unit per chain. $R_g$ of PC$_{30}$ is ~ 10.4 nm. Therefore, $\Lambda = 35$ nm $> 2R_g = 20.8$ nm. This suggests that the effect associated with bridging of two particles via a polymer chain may be eliminated for PC$_{30}$.

The mastercurves (Fig. 5.7) do not show obvious changes of the slopes for PC/silica nanocomposites in the terminal zone. Data points for $G' < 30$ Pa were deleted during data analysis considering the measurement accuracy. Therefore, the slope divergence, if there was any, was eliminated. However, the $G'$ variations at 10% strain from strain sweep were measured at 0.1 rad/s, which is in the terminal zone (Fig. 5.1a). The results indicate structural changes in the PC/silica nanocomposites during measurements. These structures may be due to an early stage particle-particle interaction via polymer matrix. The oscillation of one particle A can be transferred via polymer matrix to another particle B, which thus feels the existence of particle A. These structures do not have solid-like behavior. Therefore, no changes in the slopes in the terminal zone were clearly observed.

5.4. Conclusions

The influences of the addition of silica nanoparticles on the viscoelastic properties of PC have been described in this chapter. Strain sweep measurements show that silica
addition affects the linear-to-nonlinear transition of PC/silica nanocomposites. Both the steady-state and dynamic results demonstrate a viscosity drop for the (PC + 0.9 vol% silica) nanocomposite. The viscosity reduction is dependent on PCs’ molar mass. With increasing molar mass, the silica content for the lowest viscosity point is expected to occur at lower silica content.

The studied nanocomposites were confirmed to obey the TTS principle based on Gδ plots, Han Plots, Cole-Cole plots and mastercurves. The addition of silica nanoparticles shifted the mastercurves of the PC/silica nanocomposites to a higher frequency range. The TTS shift factors, namely, the plot of 1/log(αT) as a function of 1/(T−Tg) is linear. The terminal relaxation time τd decrease with the addition of silica first, followed by increase, with minimum values at the silica contents, where the lowest complex viscosity occurs to the (PC + 0.8 vol% silica) nanocomposite. The WLF results demonstrate that the fractional free volume fr keeps constant with the addition of silica nanoparticles, and the thermal expansivity αf decreases and then increases with increasing the silica content while the lowest value of αf occurs to the (PC + 0.8 vol% silica) nanocomposite. Results from calculation show changes in the molar mass between entanglements Mε with addition of silica.

5.5. References

21 Oh, H.; Green, P.F. Nat. Mater. 2009, 8: 139-143.
Chapter 5 Viscoelastic properties of PC/silica nanocomposites

Abstract

A model, which is based on the reptation theory and takes into account of tube length fluctuations and constraint releases, is used to predict the linear viscoelastic properties of PC/silica nanocomposites. A time-marching algorithm is applied in this model, while no artificial time scale separation between fluctuations and reptation is imposed but rather allow both relaxation processes to proceed simultaneously. The model accurately predicts the behavior of both PC and PC/silica nanocomposites. Fitting of the modeled/experimental results demonstrates an increase in the molar mass between entanglements $M_e$ of PC/silica nanocomposites compared to that of pure PC. The increase in $M_e$ leads to a decrease in the entanglement number per chain $N$, and, thus, friction reduction, which offers an explanation for the viscosity reduction of the PC/silica nanocomposites observed in our systems.

Mechanism of the viscosity reduction of poly(carbonate) (PC)/silica nanocomposites

We acknowledge dr. E. van Ruymbeke for the help with modeling described in this chapter. One publication based on the results of this chapter is in preparation: J.G.P. Goossens; C.X. Sun; E. van Ruymbeke; C. Bailly A decrease in viscosity of poly(carbonate)/silica nanocomposites elucidated via reptation models.
6.1. Introduction

To predict and control the rheology/property balance of poly(carbonate)(PC)/silica nanocomposites, it is essential to understand the mechanism of the observed viscosity reduction as discussed in Chapters 4 and 5. Possible mechanisms to fully explain the experimental findings were discussed in Chapter 4, i.e., the ‘ball-bearing’ effect, extra free volume, and selective adsorption of the high molar mass chains, proved to be inadequate. The hypothesis was put forward that the observed viscosity reduction of PC/silica nanocomposites originates from a change in entanglement density.

One of the physical models used to predict polymer melt viscoelasticity was developed by Edwards and Doi and is based on the scaling and reptation concepts of de Gennes. However, this model only offers qualitative predictions of the linear viscoelasticity of linear polymers. Limitations of this model are that pure reptation oversimplifies the true dynamics of linear chains in the melt, since other relaxation mechanisms, such as tube length fluctuations and constraint release, play an important role. Further, the polydisperse character of many polymers implies that a certain mixing rule has to be applied, which takes into account the contributions from various chain lengths and their mutual interactions. A linear mixing rule fails due to the coupling of relaxation functions from chains with different lengths, because short chains accelerate the relaxation of longer chains and vice versa. Double reptation accounts for these effects in a very natural manner and is frequently used, although other complementary approaches were reported. Recently, generalized mixing rules derived from double reptation have been proposed.

Quantitative predictions of the linear viscoelasticity of a number of polymers including PC taking into molar mass distribution information are now available. Utilizing a classical description of reptation, fluctuations, and constraint release processes, van Ruymbeke et al. built a new model to predict the linear viscoelastic behavior of mixtures of (asymmetric) star and linear polymers, assuming their molecular structure is known. In this chapter, this model is used to fit the PC/silica nanocomposites viscoelastic experimental data and to elucidate the mechanism for the observed viscosity reduction in the PC/silica nanocomposites.

First, the related theories of pure polymer melts will be described. This is followed by a comparison between the experimental data and the fits of the model for pure PC and PC/silica nanocomposites. In the last part of this chapter, both experimental data and modeling data are used to explain the viscosity reduction in PC/silica nanocomposites.

6.2. Theory

Relaxation processes. When a small strain is imposed on an entangled polymer, chain segments can orient along the flow direction. When the strain is first imposed on the polymer, the polymer chain remains relaxed as if it was in a diluted solution for a very short time, defined as the Rouse process. This short relaxing motion is thus termed as Rouse motion. The Rouse process describes the relaxation process of a Kuhn length prior to the relaxation of entanglements. For entangled polymers, relaxation processes at times
much shorter than the reptation time are also dominated by the Rouse mechanism. After the Rouse motions, the chain begins to feel the topological constraints from the entanglements. This is modeled by the concept of a tube and a primitive chain (Fig. 6.1), which is essentially a coarse grained representation of the true situation.

Upon deformation, the tube and the primitive chain progressively loses its orientation memory by three relaxation processes: reptation, tube length fluctuations and constraint release. The relative importance and corresponding rates of these three relaxation processes depend on the details of the molecular architecture and can be captured in the following equation:

$$ G(t) = G_0 \left[ \sum_i \phi_i \left( p_{\text{rept}}(x_i, t) p_{\text{fluc}}(x_i, t) p_{\text{envir}}(x_i, t) dx_i \right) \right] $$

Equation (6.1) can be used to calculate the relaxation modulus $G(t)$. The bracketed expression corresponds to the relaxation function $F(t)$, which is the unrelaxed fraction of the polymer melt at time $t$; $\phi_i$ is the volumetric fraction of chain $i$, $x_i$ is describing the position of a primitive chain segment along chain $i$, and ranges from 0 (at the end of the chain) to 1 (at the center); $p_{\text{rept}}$, $p_{\text{fluc}}$, and $p_{\text{envir}}$ represent the probabilities that the segment survives, i.e., remains oriented, amidst the effects of reptation, tube length fluctuations or influences of the environment (constraint release), because a given segment only contributes to the modulus, if it has not relaxed as a result of the three possible relaxation mechanisms. However, it is not necessary to divide the different relaxation mechanisms into three different time regions corresponding to the relaxation state of each molecule.

Reptation. Reptation is the main relaxation mechanism for linear chains. According to the basic reptation theory, the chain is confined in a tube formed by the entanglements of the neighboring chains (Fig. 6.1). In order to relax, the chain has to move out of its original tube. The dominant motion of this chain is a ‘sliding’ motion due to the geometric constraints of the tube (Fig. 6.1), and hence the name ‘reptation’ is given. As a result, the memory of the orientation is lost and the chain returns to the equilibrium coil conformation.

$$ p_{\text{rept}}(x_i, t) = \sum_{p_{\text{slit}}} \frac{4}{p_{\text{slit}}} \sin \left( \frac{p_{\text{slit}} \pi x_i}{2} \right) e^{- \frac{p_{\text{slit}}^2 t}{2 \tau_{\text{slit}}}} $$

Fig. 6.1. Reptation process of a polymer chain.
Equation (6.2) describes the reptation probability \( p_{\text{rept}} \) which been determined by Doi and Edwards.\(^1\) In this equation, \( \tau_{\text{rept}} \) is the reptation time of the chain, \( x_i \) describes the position of a primitive chain segment along chain \( i \), and ranges from 0 (at the end of the chain) to 1 (at the center), \( t \) is the time and \( p \) is the probability. For linear chains, \( \tau_{\text{rept}} \) is only a function of the molar mass \( M \) and the entanglement relaxation time \( \tau_e \):

\[
\tau_{\text{rept},0}(M) = 3\tau \left( \frac{M}{M_e(0)} \right)^3
\]

(6.3)

where \( M_e(0) \) is the molar mass between two effective entanglements. The effect of dynamic dilutions can be rescaled in the following way:

\[
\tau_{\text{rept},0}(t) = \tau_{\text{rept},0}(\Phi(t))
\]

(6.4)

where \( \tau_{\text{rept},0} \) is the reptation time at time \( t=0 \), \( \Phi(t) \) is the unrelaxed polymer fraction at time \( t \) and the exponent \( \alpha \) is the dilution exponent.

**Fluctuations.** Fast Rouse motions of chain segments in the vicinity of the chain ends allow the chain to extend to some regions outside the original tube, especially for a low degree of entanglements. This results in tube length fluctuations (Fig. 6.1) around its equilibrium value.\(^1\)\(^1\)

The equilibrium length of the tube \( L_{eq} \) corresponds to the minimum potential energy \( U \) resulting from the balance of the entropic spring force and of tube constraint (Fig. 6.2) where:

\[
U(x) = \frac{3kT}{2Nb^2}(L_{eq}x^2) + \text{constant}
\]

(6.5)

in which \( N \) is the number of monomer per chain, \( b \) is the monomer equivalent length. The \( L_{eq} \), around which the true tube length fluctuates, is only the most probable one. Any fluctuations shortening the tube will relax the external segments.

**Entropical force**

![Entropical force diagram]

**Topological force**

![Topological force diagram]

**Fig. 6.2. Tube length fluctuations via entropic force and topological force.**

For segments close to the chain end, the ‘early’ fluctuations are not controlled by the potential, but by unconstrained Rouse motions of the chain end:

\[
\tau_{\text{early}}(x_i) = \frac{9\pi^2}{16} \left( \frac{M_e}{M_{\text{arm}}} \right)^2 \tau_{R,\text{chain}} x_i^6
\]

(6.6)

where \( \tau_{R,\text{chain}} \) is the Rouse time of the chain and \( M_e \) is the molar mass of the ‘arm’ (i.e., half the molar mass of the chain). Deeper fluctuation is described by exponentially increasing times:
A characteristic waiting time. Since the relaxation time scale increases exponentially with segment depth \( x_i \), external segments can be fully relaxed when internal ones remain oriented. Consequently, the relaxed external segments can be considered as a solvent for the unrelaxed internal segments.\(^{12}\)

The transition \( x_{\text{trans}} \) between the ‘early’ fluctuations and those controlled by the potential occurs at the transition segment where the potential is equal to \( kT \).

The fluctuations time for any depth \( x_i \) can be used to find the survival probability of chains under fluctuations:

\[
\tau_{\text{fluc}}(x_i) = \tau_0 \exp\left( \frac{U(x_i)}{kT} \right) \quad (6.7)
\]

where \( \tau_0 \) is a characteristic waiting time. Since the relaxation time scale increases exponentially with segment depth \( x_i \), external segments can be fully relaxed when internal ones remain oriented. Consequently, the relaxed external segments can be considered as a solvent for the unrelaxed internal segments.\(^{12}\)

The transition \( x_{\text{trans}} \) between the ‘early’ fluctuations and those controlled by the potential occurs at the transition segment where the potential is equal to \( kT \).

The fluctuations time for any depth \( x_i \) can be used to find the survival probability of chains under fluctuations:

\[
p_{\text{surv}}(x_i) = \exp \left( \frac{-\Delta U(x_i \rightarrow \text{trans})}{kT} \right) \quad (6.8)
\]

The transition \( x_{\text{trans}} \) between the ‘early’ fluctuations and those controlled by the potential occurs at the transition segment where the potential is equal to \( kT \).

The fluctuations time for any depth \( x_i \) can be used to find the survival probability of chains under fluctuations:

\[
p_{\text{surv}}(x_i) = \exp \left( \frac{-\Delta U(x_i \rightarrow \text{trans})}{kT} \right) \quad (6.9)
\]

Based on the dynamic dilution mechanism,\(^{12}\) the effective molar mass between entanglements becomes an increasing function of fluctuations depth:

\[
M_e(x_i) = \frac{M_e(0)}{\alpha(x_i)} \quad (6.10)
\]

where \( \alpha(x_i) \) is the unrelaxed polymer fraction if the fluctuation depth of the chain \( i \) is \( x_i \). If the polymer melt is partly relaxed by reptation or fluctuations, only a fraction of the topological constraints remains active and each chain segment can be seen as if it was confined in a widened tube limited by the entanglements (Fig. 6.3). This is modeled by ‘tube dilation’ or ‘dynamic dilution’ concepts pioneered by Marrucci et al.\(^{13}\) and Ball et al.\(^{12}\) When \( \Phi(t) \) is the remaining portion of unrelaxed tube segments, \( L_{eq}, \) tube diameter \( a \) and \( M_e \) have to be renormalized:

\[
L_{eq}(t) = L_{eq}(0)(\Phi(t))^{\frac{1}{2}}, \quad a(t) = \frac{a(0)}{(\Phi(t))^{\frac{3}{2}}}, \quad M_e(t) = \frac{M_e(0)}{\Phi(t)} \quad (6.11)
\]

\( \Phi(t) \) is usually referred to as ‘the solvent’ because it dilutes the entanglements. The molar mass between those entanglements which play an active role in the orientation of the molecules increases with solvent concentration. Tube
dilation speeds up reptation and fluctuations, but it also relaxes the orientation of internal segments by reducing the number of entanglements. It is thus a constraint release mechanism, which can be modeled either by ‘tube Rouse motions’ or ‘double reptation’ concepts. The latter, although only a ‘mean field’ approximation of the real constraint release mechanism, works well in a wide variety of cases and is easy to implement in numerical or analytical schemes.

**Constraint release.** In addition to relaxation by reptation and fluctuations, accelerated or not by tube dilation, a global thermal constraint release mechanism must be considered, i.e., ‘relaxation by the environment’. It is convenient and reasonably accurate to consider that the probability to loose an entanglement is identical for all segments in the melt. Therefore, the probability \( p_{\text{envir}} \) is equal to the probability that a segment, taken at random in the polymer, is still oriented and not relaxed by reptation nor fluctuations. The general expression for \( p_{\text{envir}} \) is:

\[
P_{\text{envir}}(x,t) = \left[ \sum_k \int_0^{x_{\text{trans}}(x_i,t)} p_{\text{rept}}(x_i',t) p_{\text{fluc}}(x_i',t) dx_i' + \int_{x_{\text{trans}}(x_i,t)}^1 p_{\text{rept}}(x_i',t) dx_i' \right]^{x(t)}
\]

(6.12)

This equation implies that all the segments between the center of any molecule \( x_i = 1 \) and a fractional distance \( x_{\text{trans}} \) are not relaxed by fluctuations.

**Time-marching algorithm.** A time-marching algorithm was used to calculate the survival probabilities (equation (6.13)). For a given relaxation mechanism, the survival probability at \( t_k \) is the product of the survival probability at \( t_{k-1} \) and the survival probability during the \( \Delta t \) interval comprised between \( t_{k-1} \) and \( t_k \).

\[
P_{\text{fluc}}(x_i,t) = p_{\text{fluc}}(x_i,t_{k-1}) p_{\text{fluc}}(x_i,T_{k-1} + \Delta t), \quad p_{\text{rept}}(x_i,t) = p_{\text{rept}}(x_i,t_{k-1}) p_{\text{rept}}(x_i,T_{k-1} + \Delta t)
\]

(6.13)

The survival probability during the time interval \( \Delta t \) can be calculated from the corresponding relaxation time at \( t_k \), assuming that \( \Delta t \) is small enough to neglect the variation of the relaxation time during the interval:

\[
P_{\text{survival}}(x_i,T_{k-1} + \Delta t) = \exp \left( \frac{-\Delta t}{T_{\text{relax}}(x_i,t_k)} \right)
\]

(6.14)

At any given time, the relaxation fraction of the polymer acts as a solvent for the relaxation of oriented segments, thereby modifying their characteristic reptation and fluctuations times. Since the solvent fraction increases with time, reptation and fluctuations times change continuously. Due to the arbitrary nature of the polymer (mixture), there is no way to describe these changes analytically. Therefore, a time-marching algorithm was used to calculate \( F(t) \).
Chapter 6 Mechanism of the viscosity reduction of PC/silica nanocomposites

6.3. Experimental

6.3.1. Materials

A Bisphenol-A based PC with a weight-average molar mass of \( M_w = 30.0 \text{ kg mol}^{-1} \) and polydispersity index (PDI) \( \approx 2.6 \) was used, which was supplied by SABIC Innovative Plastics (SIP), the Netherlands. Silica nanoparticles suspended in methyl ethyl ketone (MEK) with an average diameter of 13 nm and a solid content of 30-31 wt% were purchased from Nissan Chemical. All materials were used as received.

6.3.2. Preparation of PC/silica nanocomposites

The PC powder was first dried for 12 hours at 150 °C under \( \text{N}_2 \) flow in a vacuum oven followed by the addition of \( \approx 0.1 \text{ wt%} \) processing stabilizer tris(2,4-di-tert-butylphenyl) phosphite (from SIP). A series of PC/silica nanocomposites with silica contents ranging from 0.3 to 1.7 vol% were obtained by melt compounding as described in Chapter 4. The required amount of silica suspension and PC powder were blended at 270 °C for 15 minutes under \( \text{N}_2 \) atmosphere by using a home-built, recirculating, twin-screw mini-extruder with an internal volume of 5 cm\(^3\) with a screw speed of 75 rpm. Samples for the rheology measurements with a diameter of 8 mm were cut from a compression-molded sheet with a thickness \( \approx 0.5 \text{ mm} \).

6.3.3. Characterization techniques

Rheology. Dynamic measurements were performed on a stress-controlled AR-G2 rheometer (TA Instruments) by using a 8 mm parallel plate-plate geometry and disk-shaped specimen. Frequency sweeps in a range of 100 - 0.01 rad/s were performed with a temperature range of 250 - 165 °C under \( \text{N}_2 \) atmosphere, with a constant strain of 10%, which was within the linear viscoelastic range (see Chapter 5). The data for the storage (\( G' \)) and loss (\( G'' \)) moduli were used to obtain the mastercurves by using the IRIS software.\(^{15} \)

Numerical Modeling. A model based on the theory which was described in theory section was built and implemented in MatLab to predict the relaxation function \( G(t) \). The function \( G(t) \) is then inverted to obtain the dynamic moduli \( G' \) and \( G'' \) by using the well-known Schwarz's relations.\(^{16} \) This model provided excellent results as shown in the work of van Ruymbeke et al.,\(^{8,9,17} \) except at the lowest frequencies due to the series truncation issue.\(^{18} \) In all cases, a Gaussian distribution was used for describing the molar mass distribution. For each sample, optimization of material parameters was performed by minimizing the discrepancy between model prediction and experimental data.

In the model, only three materials parameters are required: the plateau modulus, \( G_0 \), the Rouse time of a segment, \( \tau_e \), and the molar mass between entanglements, \( M_e \). Theoretically, \( G_0 \) and \( M_e \) are linked via the following equation:  

\[
M_e = \frac{4\rho RT}{5G_0} \quad (6.15)
\]

In this case, however, it is necessary to slightly relax this restriction and treat the two parameters as independent (within reasonable boundaries). The dilution exponent \( \alpha \) can be considered as an
additional fitting parameter within strict bounds. In the work of van Ruymbeke et al.,\textsuperscript{9,17} a fixed value of $\alpha$ at 1 is used.

6.4. Results and discussion

6.4.1. Comparison between experimental and modeling data

The model described in the work of van Ruymbeke et al.\textsuperscript{8,9} was used to fit the experimental data of the pure PC and the PC/silica nanocomposites. One of the model’s limitations is that all the samples must have the same glass transition $T_g$, i.e., the same second crossover point in the mastercurves. Considering the fact that there is a slight difference in the second crossover frequency for PC and PC/silica nanocomposites (see Chapters 4 & 5), the experimental data of the PC/silica nanocomposites were horizontally shifted along the frequency axis to the second crossover point of PC while no vertically shift was carried out. The comparison in Fig. 6.4 shows that the first crossover point of the mastercurves for pure PC is located at a lower frequency than for the (PC + 0.8 vol\% silica) nanocomposite. This shift of the relaxation spectrum means that the addition of silica changes $\tau_{rept}$ and indicates that the addition of silica nanoparticles to the PC matrix causes global changes in the polymer relaxation times.\textsuperscript{15} On the other hand, a comparable plateau modulus $G_n^\infty$ for both PC and PC/silica can be observed in Fig. 6.4.

![Fig. 6.4. Comparison of the mastercurves of PC and the (PC + 0.8 vol\% silica) nanocomposite after shifting the nanocomposites' mastercurves to the second crossover frequency of pure PC.](image)

For pure PC, the parameters used to fit the experimental data with a high accuracy are $G_n^\infty = 3.2$ MPa, $\tau_e = 7 \mu$s and $M_e = 1000$ g/mol. The comparison between the fit data and the experimental data for pure PC are plotted in Fig. 6.5a. The fitting curves are in good agreement with the experimental data. Similarly, the model was used to fit the mastercurves of the PC/silica nanocomposites by using $G_n^\infty = 3.2$ MPa and $\tau_e = 7 \mu$s. The results for the (PC + 0.8 vol\% silica) nanocomposites are plotted in Fig. 6.5b. To get the best fit for the PC/silica nanocomposites, modified values for $M_e$ were used and the resulting fit data are listed in Table 6.1.
The fitting parameters for PC/silica nanocomposites (Table 6.1) demonstrate that the $M_e$ is influenced upon the addition of silica nanoparticles. The fitting result $M_e$ based on the same $G_N^0$ is 1000 g/mol for pure PC, while a value of 1200 g/mol is found for the (PC + 0.8 vol% silica) nanocomposite. The $M_e$'s for the PC/silica nanocomposites show clearly that $M_e$ increases with increasing silica content up to ~ 1.7 vol%, followed by a decrease in $M_e$ for the (PC + 2.0 vol% silica) nanocomposites up to a value of pure PC.

The best fit value for $G_N^0 = 3.2$ MPa is on the high side of $G_N^0$ for PC, but it is in the acceptable range. The values for the plateau modulus $G_N^0$ of PC have been reported between 1.2 and 4.1 MPa.\textsuperscript{9,10,20}

In addition, to confirm the effect of the addition of silica nanoparticles on the variations of $M_e$, Fig. 6.6 compares the fitting for the (PC + 0.8 vol% silica) nanocomposite using $M_e = 1000$ g/mol and $M_e = 1200$ g/mol respectively while keeping $G_N^0 = 3.2$ MPa and $\tau_e = 7 \mu$s constant. Fig. 6.6 demonstrates that using $M_e = 1000$ g/mol (Fig. 6.6, the line with cross), the experimental data cannot be fitted for the (PC + 0.8 vol% silica) nanocomposite while a better fit was obtained by using $M_e = 1200$ g/mol (Fig. 6.6, the solid line). The fitting difference in Fig. 6.6 confirms thus that the effect of the addition of silica nanoparticles on the variation of $M_e$.

\textit{Table 6.1. Parameters used to fit the experimental data of PC/silica nanocomposites.}

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$G_N^0$ (MPa)</th>
<th>$\tau_e$ (s)</th>
<th>$M_e$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC + 0 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1000</td>
</tr>
<tr>
<td>PC + 0.1 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1100</td>
</tr>
<tr>
<td>PC + 0.3 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1150</td>
</tr>
<tr>
<td>PC + 0.7 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1175</td>
</tr>
<tr>
<td>PC + 0.8 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1200</td>
</tr>
<tr>
<td>PC + 1.7 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1200</td>
</tr>
<tr>
<td>PC + 2.0 vol% silica</td>
<td>3.2</td>
<td>$7 \times 10^5$</td>
<td>1050</td>
</tr>
</tbody>
</table>
In short, the model used in the work of van Ruymbeke et al.\textsuperscript{8,9} can satisfactorily fit the mastercurves of the used PC and PC/silica nanocomposites. The fitting results show that the addition of silica nanoparticles changes the $M_e$ of the PC/silica nanocomposites.

6.4.2. A hypothesis based on entanglement density variations to explain the viscosity reduction

In a polymer melt, polymer chains are considered as ideal Gaussian chains which represent random walks.\textsuperscript{21} The natural length scale for ideal chains is the root-mean-squared end-to-end distance, $R_{ee}$, which depends on the molar mass $M$ of the polymer as $R_{ee} \sim M^{1/2}$. Due to random thermal motions, a polymer chain explores a pervade volume in the polymer melt, $V_p \sim R_{ee}^3$. Within this volume, there are many other polymers and, thus, many interactions between a specific polymer chain and other chains. A fraction of these interactions restrict the mobility of this polymer chain, resulting in entanglements, which can be thought of as knots or crossings in the system. According to the basic reptation theory, the chain is confined in a tube formed by the entanglements of the neighboring chain segments. Entanglements are the origin of many remarkable polymeric properties, such as the high melt viscosity, transient rubberlike behavior, and toughness.\textsuperscript{21}

The nature of entanglements in confined systems is not yet understood,\textsuperscript{22} but there are reports published on variations of the entanglement density in confined systems. Chain conformations and chain packing densities are modified near a free surface or an interface. Thus, concomitant changes in the entanglement density can be expected relative to the bulk case.\textsuperscript{23}

In a confined system, when the confined layer thickness $h$ is decreased below the length scale of a molecule, $h < R_{ee}$, the volume, which is pervaded by a single molecule, decreases. With increasing confinement, segments next to the studied single chain are increasingly excluded from the pervaded volume, which leads to a reduced entanglement density.\textsuperscript{22} If the polymer segment-to-surface interactions in the interfaces are weak and dispersive, i.e., nonadsorption or physisorption, the ideal chains are only perturbed in the direction normal to the interface, while the random walk in the direction parallel to the
Simulations on primitive paths of a chain near a free surface, modeled as a repulsive wall, reveal a depletion of interchain entanglements in a region with a thickness about one or two times the radius of gyration in the bulk. The deformation behavior of thin glassy free-standing polystyrene films supports a reduced entanglement density if the film thickness is comparable to the chain dimensions.

Theoretical studies qualitatively demonstrated that the density of entanglements decreased in the vicinity of a wall. This topic has been studied through mesoscopic self-consistent field and entanglement network simulations. Daoulas et al. found an oscillatory behavior of the density profile between the polymer/solid interface. As a test case, a thin film of a poly(ethylene) (PE) melt confined between a semi-infinite graphite sheet on the one side and vacuum on the other was considered. Near the graphite surface, the density profile exhibits a characteristic oscillatory behavior, in which at least three peaks can be discerned at distances equal to 4, 8.5, and 13 Å from the graphite plane; a fourth peak at 18 Å was also observed, but with a considerably smaller height. This oscillatory profile is displayed in Fig. 6.7 and illustrates that ~ 4 Å from the highly attractive graphite surface, the local mass density is the strongest. In the bulk, there is a lower local mass density, and thus less friction and a lower viscosity can be expected. Furthermore, the studies on the overall conformation in the melt showed that the chain conformation (the chain coil) was compressed in the direction perpendicular to the bulk and elongated parallel to the surface. Therefore, the chain coil was squeezed in the direction perpendicular to the surface, while it was elongated parallel to the surface. This implies that there is a higher probability to form entanglements in the direction parallel to the surface, and the probability to form entanglements in the perpendicular direction to the surface will be lower. Therefore, a low entanglement density may be observed in the bulk. It has been reported that the entanglement density is reduced in confined systems if the thickness of the confined layer is comparable to chain dimensions, $2R_g$.  

![Fig. 6.7. Local mass density distribution along the z-axis (perpendicular to the interface) for all simulated systems by Daoulas et al.](image)

In our studied PC/silica nanocomposites, the lowest viscosity was found in the (PC + 0.8 vol% silica) nanocomposite. The silica nanoparticle, with an average diameter of 13 nm, has a volume 1150 nm³. When the volume fraction is ~ 0.8 vol%, there are ~ 7 x 10¹⁵ particles per cm³. This amount of silica nanoparticles has a surface area ~ 4.0 x 10¹⁸ nm². Theoretically, such an amount of silica surface can adsorb ~ 100% polymer chains in the
matrix, with the thickness surrounding the silica nanoparticles is comparable to the chain dimension, \(2R_g = 20.8\) nm. Combining with the result that the (PC + 0.8 vol\% silica) nanocomposite has a lower viscosity compared with the pure PCs, the entanglement density of PC chains in the vicinity of the chain dimension is thus reduced with the addition of silica nanoparticles.

6.5. Conclusions and open questions

A model based on reptation theory was used to fit the experimental data for PC and PC/silica nanocomposites. The results show that this model can provide quantitative fitting for both pure PC and PC/silica nanocomposites. The fitting parameters show that the addition of silica leads to an increase of the \(M_e\) of the PC, while the highest \(M_e\) value occurs for the (PC + 0.8 vol\% silica) nanocomposite, which has the minimum viscosity for the studied PC/silica nanocomposites. The addition of silica nanoparticles to the PC matrix might induce a deformation of the PC chains. This deformation leads to an increase in \(M_e\) of PC/silica nanocomposites, and thus a lower entanglement density. The decrease in the entanglement density indicates less friction in PC/silica nanocomposites during rheological measurements. Therefore, a decrease in the viscosity of PC/silica nanocomposites is observed.

At this moment, there are several parameters that need to be further investigated to verify our hypothesis:

1) Effect of \(M_e\): The viscosity reduction phenomenon is observed in iPP/silica and PC/silica nanocomposites, which have low \(M_es\), while for the systems with high \(M_es\), e.g. poly(methyl methacrylate) (PMMA)/silica nanocomposites, no viscosity reduction was observed in our studies.\(^{31}\) The question is what the high limit \(M_e\) value is for the viscosity reduction.

2) Effect of the (particle) curvature: what are the effects of the ratio of nanoparticles’ diameter \(D\) to polymer coil size \(2R_g\) on the viscosity reduction in nanocomposites? In other words, what is the effect of the curvature of nanoparticles on the decrease in viscosity? In the part of iPP/silica nanoparticles (Chapter 2), the used silica nanoparticles sizes are in the range of \(D << 2R_g\) or \(D < 2R_g\). The pronounced viscosity reduction is examined when \(D < 2R_g\). Due to the difficulties to disperse small silica nanoparticles (e.g. 7 nm) nicely in iPP matrix, negligible viscosity reduction is obtained in iPP/silica nanocomposites when the diameter of nanoparticles is the range of \(D << 2R_g\). In PC/silica nanoparticles (Chapter 4), the viscosity reduction is observed in systems where the used size of silica nanoparticles is in the vicinity of the studied PC chain coil size (\(2R_g\)), i.e., \(2R_g = D\). Moreover, the addition of \(\sim 0.8\) vol\% silica nanoparticles with \(D = 12\) nm induces \(\sim 62\%\) viscosity reduction in iPP/silica nanocomposites (Chapter 2), while the addition of \(\sim 0.8\) vol\% silica nanoparticles with \(D = 13\) nm results in \(\sim 26\%\) viscosity reduction in PC/silica nanocomposites (Chapter 4). Considering the difference in characteristic ratio \(C_n\) of PC (\(C_n = 1.8\))\(^{32}\) and iPP (\(C_n = 6.4\)),\(^{33}\) is the curvature/flexibility of polymer chains playing also an important role?
3) Generalized mechanism: It has been shown that the addition of silica nanoparticles to the studied amorphous PC induces entanglement density variations. Does this also partially occur in semi-crystalline polymer nanocomposites? The study in iPP/silica nanocomposites indicates there is negligible shift in the relaxation spectrum (Fig. 2.9b). The crystallization behavior observed in iPP/silica nanocomposites can be explained both by the selective adsorption and the loss of entanglements. Till now it is difficult to distinguish the effects of selective adsorption and loss of entanglements in iPP/silica nanocomposites.

4) Effect of interaction: Generally, the polymer-nanoparticle interaction differences lead to the difference in the relation of relaxation time and temperature. In this thesis, the results demonstrate that the viscosity reduction is different between iPP/silica nanocomposites and PC/silica nanocomposites, which might be attributed to the interaction difference between polymer and nanoparticles. In iPP/silica nanocomposites, there are apolar iPP and polar silica nanoparticle surface, in which van der Waals interaction plays an important role (physisorption). In PC/silica nanocomposites, there are polar PC and polar silica nanoparticle surface. Therefore, the interaction between PC and silica surface is stronger than that between iPP and silica surface. In the case of PMMA/silica nanocomposites, the interaction between PMMA and silica is much stronger than that for both iPP/silica and PC/silica. Our experiments on PMMA/silica nanocomposites showed no viscosity reduction. Furthermore, our results on the PC/brominated PC (PC_Br)/silica nanocomposites, which will be discussed in Chapter 7, show that the addition of ~0.8 vol% silica into the blends of PC/PC_Br with weight ratio 50/50 induces a much higher viscosity reduction than for PC/silica nanocomposites. Therefore, the interaction between polymer and nanoparticle surface is a key parameter. To obtain a (required) viscosity reduction, a suitable interaction between polymer and nanofiller need to be applied. This suitable interaction can induce a slight deformation of polymer chains, and thus change the entanglement density. The effect of the interaction between PC and silica surface on the decrease in viscosity of PC/silica nanocomposites is going to be presented in Chapter 7.

6.6. References

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33 Unpublished data.
CHAPTER 7

Effect of the interaction between poly(carbonate) (PC) and silica surface on the decrease in viscosity of PC/silica nanocomposites

Abstract

Brominated poly(carbonate) (PC_{Br}) was introduced into PC/silica nanocomposites to investigate the effect of the interaction between PC and silica surface on the viscosity reduction of the PC/silica nanocomposites. The viscosity reduction is dependent on the weight ratio of PC/PC_{Br}, while a negligible viscosity reduction was observed in the pure PC_{Br}/silica nanocomposites. The largest viscosity reduction occurs to the system with 50/50 weight ratio of PC/PC_{Br}. After taking into account molar mass variations and glass transition temperature changes, ~49% viscosity reduction was observed for the ((PC/PC_{Br})(50/50) + 0.8 vol% silica) nanocomposite. The viscosity reduction depends on the particle size and geometry. The interaction between Br groups and silica surfaces is confirmed via using silicon atomic force microscopy (AFM) tip to mimic silica surfaces.
7.1. Introduction

In Chapters 4 and 5, the effect of silica nanoparticles on the viscosity of poly(carbonate) (PC) was discussed and it was shown that the viscosity of the PC/silica nanocomposites first decreased to a minimum at 0.8 vol% followed by an increase upon further increasing the concentration of the silica nanoparticles. Possible mechanisms to explain the viscosity reduction, i.e., the ‘ball-bearing’ effect, extra free volume and selective adsorption, were discussed. In Chapter 6, a model based on the reptation theory was used to fit the experimental data observed in the PC/silica nanocomposites, from which it was postulated that the viscosity reduction observed in the PC/silica nanocomposites was attributed to the entanglement density variations induced by the addition of silica nanoparticles. Next to the size and geometry of silica nanoparticles, as discussed in Chapter 4, and the molar mass of PC and temperature, as discussed in Chapter 5, the interaction between the PC and the silica surface is another very important parameter to influence the decrease in viscosity.

It was reported that in a nanocomposite, the number of the adsorbed units \( N_a \) along a linear polymer chain to nanoparticle surface depends on both the interaction between the polymer and the nanoparticle surface, and the molar mass of the linear chain, \( n \), according to equation:

\[
N_a = N^n \tag{7.1}
\]

where \( N \) is the number of monomer units in a chain, and \( n \) depends on the interaction between the particles and the polymer chains.

Further, it is well established by experiment\(^4\) and simulation\(^5\) that strong attractive interactions increase the glass transition temperature of the polymer near to the interface. It has also been reported that the surface interaction is not confined to a surface-bound layer, but is rather a far-field effect that is at least as large, or larger, than one radius of gyration of the polymer \( R_g \). Dionne et al.\(^7\) investigated the structure and dynamics of a poly(ethylene) melt composed of linear monodisperse chains containing homogeneously distributed spherical nanoparticles via using a coarse-grained model and a Monte Carlo algorithm. They demonstrated that the structure within the polymer melt varied as a function of the distance from the nanoparticle surface, but there was no relation to the polymer-nanoparticle interaction energy. On the other hand, it was also observed that \( R_g \) is essentially similar for the polymer nanocomposites and the pure melt, indicating that the overall chain dimensions are independent on the polymer-nanoparticle interaction, the specific interfacial area, and the nanoparticle volume, or even the presence of a nanoparticle.\(^10\) Sternstein et al.\(^11\) reported on the non-linear viscoelastic properties for poly(vinyl acetate) (PVA) nanocomposites of fumed silica with various surface treatments and different molar masses as well as with a copolymer of vinyl acetate and vinyl alcohol. The increase in the composite storage and loss moduli measured at low strains and their relative rates of decrease with strain are found to depend on the filler surface treatment. Sternstein et al. put the idea forward that the polymer-nanoparticle interaction strength changes the entanglement density and distribution in the matrix. The viscoelastic properties of the polymer matrix are thus strongly perturbed by the nanoparticles and
depend upon the polymer-nanoparticle interactions.\textsuperscript{10-13} Strong interactions between polymer and nanoparticles slow down the mobility of polymer chains, and thus the viscosity is significantly higher than that of the pure melt. The nanocomposites with repulsive or weak attractive interaction between polymer-nanoparticles, e.g. our studied PC/silica nanocomposites, exhibit a reduced viscosity relative to the pure melt, due to the increased polymer dynamics induced by the addition of nanoparticles.

The objective of this chapter is to study the effect of the interaction between PC and silica surfaces on the viscosity reduction of the PC/silica nanocomposites. To do that, a bromide (Br) group substituted PC, i.e., PC\textsubscript{Br} (Fig. 7.1a) was used. The variation of the interaction was obtained by varying the amount of Br groups inside the PC/PC\textsubscript{Br}/silica systems, i.e., varying the weight ratio of PC/PC\textsubscript{Br}. The results of the viscosity of the different PC/PC\textsubscript{Br}/silica systems are first discussed in this chapter. Then, the focus of this chapter is on the viscoelastic behavior of the (PC/PC\textsubscript{Br})(50/50)/silica nanocomposites. The last part of this chapter is dedicated to the characterization of the interaction difference between PC/silica and PC\textsubscript{Br}/silica via atomic force microscopy (AFM).

7.2. Experimental

7.2.1. Materials

A bisphenol-A (BPA) based PC with a weight-average molar mass ($M_w$) = 35 kg mol$^{-1}$ and polydispersity index (PDI) = 2.8 was supplied by SABIC Innovative Plastics (SABIC IP), the Netherlands. A brominated PC copolymer (PC\textsubscript{Br}) with $M_w = 23$ kg mol$^{-1}$ and PDI of 2.3 was also provided by SABIC IP. The PC\textsubscript{Br}, whose structure is depicted in Fig. 7.1a, is a copolymer of BPA-based PC and tetra-bromo-BPA based-PC (TB\_BPA\_PC) with a weight ratio of 1:1. The bromine content is ~ 26 wt%.

Silica suspensions with an average diameter of 13 nm (S) and 45 nm (L) were purchased from Nissan Chemical as a 30 - 31 wt% suspension in methyl ethyl ketone (MEK). A 20 - 21 wt% silica (UP) suspension in MEK with an average diameter of 12 nm and a length of 70 nm was used to study the effect of geometry. In addition, a polymer with tetra-bromo-BPA as the repeat unit (TB\_BPA\_PC, Fig. 7.1b) was used to check interaction between Br and a silica surface.
7.2.2. Preparation of PC/PC_Br/silica nanocomposites

The PC and PC_Br powder, blended to weight ratios of 25/75, 50/50 and 75/25 respectively, were dried at 120 °C overnight in an oven under N₂ flow. The PC/PC_Br/silica nanocomposites with volume fraction of 0.3 - 1.7 vol% were obtained by melt compounding the required amount of silica suspension and PC/PC_Br powder with ~ 0.1 wt% tris(2,4-di-tert-butylphenyl) phosphate as processing stabilizer at 280 °C on a home-built twin-screw mini-extruder under N₂ atmosphere with a screw speed of 75 rpm for 15 min. For comparison, PC/silica and PC_Br/silica nanocomposites were also prepared in a similar way.

7.2.3. Characterization techniques

Rheology. Rheological measurements were performed on a stress-controlled AR-G2 rheometer (TA Instruments) by using a parallel plate-plate geometry. Disk-shaped specimen (8 mm in diameter; 0.5 mm in thickness) were measured. The rheometer was connected with N₂ flow during measurements to prevent thermal degradation of polymer. Frequency sweep in a range of 100 - 0.01 rad/s was carried out within a temperature range of 250 - 165 °C and with a constant strain of 10%, which was within the linear viscoelastic range.

Storage modulus G' and loss modulus G'' of PC/silica nanocomposites were used to determine their discrete relaxation spectra using the IRIS software.\textsuperscript{14}

Transmission Electron Microscopy (TEM). Morphological investigations were performed by using a Tecnai 20 transmission electron microscopy (TEM), operated at 200 kV. Sections, with a thickness of 50 - 70 nm, were obtained at room temperature by using a Leica Ultracut E microtome. Chemical staining of the sections was not required, since the electron density of silica is much higher than that of PC.

Thermogravimetric Analysis (TGA). A Q500 TGA (TA Instruments) was used for the quantitative determination of the silica content in the PC/silica nanocomposites. Samples were heated under pressed air at 10 °C/min to 900 °C and held for 15 min. The residue was assumed to be only composed of silica. All measurements were repeated at least twice and an average of the results was used.

Size Exclusion Chromatography (SEC). The molar mass and polydispersity index of PC was determined using SEC in the laboratory of SABIC IP, the Netherlands. PL gel 5 μm MinIMIX-C, 250 x 4.6 mm Columns and a UV detector, operating at 254 nm were used. Measurements were performed at room temperature, using dichloromethane as the solvent and toluene as a flow marker. Monodisperse PS standards were used to set up the calibration curve. The molar mass of PC was calculated based on the PS standards.

Differential Scanning Calorimetry (DSC). The glass transition temperature T_g was determined by using a Q1000 DSC (TA Instruments). Each sample (with sample mass of 3 - 5 mg) was heated from 30 to 200 °C, cooled down to 30 °C and heated up again to 200 °C at a rate of 10 °C/min in standard DSC Tzero pans. The inflection point of the second heating cycle as a function of temperature was taken as the T_g.
Atomic Force Microscopy (AFM). The AFM investigations were performed by using a Smena P47H (NT-MDT Ltd, Moscow, Russia). The AFM was operated in contact mode under an air atmosphere using a silicon cantilever (CSG 11 NT-MDT), which was coated with a gold layer for a higher laser beam reflectivity. The vertical cantilever deflection was measured by an optical registration system and converted into an electrical signal DFL. In contact mode, the DFL signal was used to characterize the interaction force between the tip and the sample surface. An AFM silicon tip was used to mimic a silica surface to touch the sample films, which were prepared via spin-coating. The attractive force upon moving the tip away from sample was recorded, via which the interaction between PC/silica and PC\textsubscript{Br}/silica was qualitatively compared.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA was performed on a Q800 Dynamic Mechanical Analyzer (TA Instruments) in a film-tension mode to determine the mechanical glass transition of the PC/silica nanocomposites. Compression-molded rectangular samples (40 × 5 × 1 mm) were measured with a temperature range of 25 to 200 °C at a heating rate of 2 °C/min and a frequency of 1 Hz, with a preload of 0.01 N and a force track of 110%.

7.3. Results and discussion

In this section, the miscibility between PC and PC\textsubscript{Br} is first presented. This is followed by a discussion on the effect of the addition of silica nanoparticles on the viscosity of the PC/PC\textsubscript{Br}/silica nanocomposites with the main focus on the (PC/PC\textsubscript{Br})\textsubscript{(50/50)}/silica system. Finally, the interaction of PC and PC\textsubscript{Br} with silica nanoparticles is evaluated.

7.3.1. Rheology of PC/PC\textsubscript{Br}/silica nanocomposites

![Graphs showing the effects of temperature and complex viscosity on the rheology of PC/PC\textsubscript{Br}/silica nanocomposites.](image)

Fig. 7.2. (a) $G_\omega$ plot and (b) the absolute value of complex viscosity $|\eta^*|$ versus frequency $\omega$ of PC/PC\textsubscript{Br} blends.

It has been reported that the actual interaction (the constant $n$ in equation (7.1)) between the particles and the polymer chains as well as the molar mass of the polymer influences the number of the adsorbed units $N_a$. In order to differentiate the effect of the molar mass and the polymer-particle interaction, a brominated PC (PC\textsubscript{Br}) resin
including polar Br groups and with a \( T_g \) around 180 °C was used. Considering the fact that homogeneity of the blend of PC and PC\(_{Br}\) is important for the rheological behavior, the miscibility was first studied via a plot of the phase angle \( \delta \) versus the absolute value of the complex modulus \( G^* \), the so-called \( G_d-\delta \) plot (Fig. 7.2a). The reasons to use rheology to study the miscibility are due to the sensitivity and convenience. Fig. 7.2a demonstrates that the \( G_d-\delta \) plots for the PC/PC\(_{Br}\) blends at a reference temperature \( T_r = 210 \) °C overlap perfectly with that for PC and PC\(_{Br}\). This implies a similar relaxation spectrum between the blends and the pure polymers, which is a strong indication that the system is fully miscible. In addition, the Fox equation \(^{15}\) was used to check the mixing rule between PC and PC\(_{Br}\):

\[
\frac{1}{T_g} = \frac{W_{PC}}{T_{gPC}} + \frac{W_{PC_{Br}}}{T_{gPC_{Br}}} \tag{7.2}
\]

in which \( T_g, T_{gPC} \) and \( T_{gPC_{Br}} \) are the glass transition temperature of the mixture, PC and PC\(_{Br}\) respectively; \( W_{PC} \) and \( W_{PC_{Br}} \) are the weight fraction of PC and PC\(_{Br}\). DSC results (not presented here) showed that with varying the weight ratio of PC/PC\(_{Br}\), \( T_g \) of the mixtures follow equation (7.2).

The interaction between PC bulk and the silica surface was varied by changing the weight of ratio of PC/PC\(_{Br}\). In this study, weight ratios of 25/75, 50/50 and 75/50 were used and the molar mass information is listed in Table 7.1. The absolute value of complex viscosity \( |\eta^*| \) of the PC/PC\(_{Br}\) blends with different weight ratios is plotted in Fig. 7.2b. PC, PC\(_{Br}\) and the PC/PC\(_{Br}\) blends have a Newtonian behavior at low frequency. At high frequencies, a shear thinning behavior is observed. \( |\eta^*| \) increases with increasing weight ratio of PC\(_{Br}\) due to the higher \( T_g \) of the PC\(_{Br}\). The \( |\eta^*| \) versus frequency curves slightly go up for the PC and the (PC/PC\(_{Br}\))(75/25) in the terminal region (\( \omega < 0.3 \) rad/s), which might be due to the formation of bubbles during measurements, which comes from the improper drying of PCs, therefore, this upturn of the curve at low frequency probably reflects the elastic response of these bubbles.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>( M_w ) (kg m(^{-1}))</th>
<th>( M_n ) (kg m(^{-1}))</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>34.6</td>
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<td>2.8</td>
</tr>
<tr>
<td>(PC/PC(_{Br})) 75/25</td>
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<td>11.2</td>
<td>2.9</td>
</tr>
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<tr>
<td>PC(_{Br})</td>
<td>22.9</td>
<td>9.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The addtions of ~0.8 vol% silica nanoparticles induces the viscosity reduction, after which the viscosity

Table 7.1. Molar mass of the studied PC/PC\(_{Br}\) blends.

The effect of the PC-silica interaction, which is related to the amount of Br groups, on the rheological behavior of the PC/PC\(_{Br}\)/silica nanocomposites is demonstrated in Fig. 7.3, in which the absolute value of complex viscosity \( |\eta^*| \) versus frequency at 250 °C is presented. Interestingly, the rheological behavior of PC/PC\(_{Br}\)/silica nanocomposites (Figs. 7.3b and 7.3c) is similar as the PC/silica nanocomposites (Fig. 7.3a). The addition of ~0.8 vol% silica nanoparticles induces the viscosity reduction, after which the viscosity
increases again with the silica nanoparticles content. However, there is negligible viscosity reduction for the PC_Br/silica nanocomposites (Fig. 7.3d).

Fig. 7.3 presents that the viscosity of the PC/PC_Br/silica nanocomposites varies with silica content as well as Br content. Table 7.2 lists the highest viscosity reduction percentage $\Delta$ (for definition see Chapter 5) and the corresponding silica content for each system. The values of $\Delta$ listed in the table are the values after taking into account the influence of molar mass variation and $T_g$. The molar mass of the studied PC/PC_Br/silica nanocomposites was characterized via SEC. Based on the measured molar mass and the power law which describes the molar mass ($M_w$) dependence of the zero-shear rate viscosity, $\eta_0 = kM_w^{3.4}$, the effect of the molar mass variation on the viscosity reduction of the system was established.

Fig. 7.3 and Table 7.2 demonstrate that the extent of the $|\eta^*|$ reduction changes with varying the ratio of PC/PC_Br, indicating that the interaction plays an important role on the viscoelastic properties of the nanocomposites. The largest viscosity reduction ($\Delta \sim 49\%$) occurs for the (PC/PC_Br)(50/50) system. The difference in the state of dispersion ($\sim 0.9$ vol%) in the PC_Br and PC/PC_Br blends is presented in Fig. 7.4. The TEM images show the presence of silica aggregates of $\sim 50$ nm, while a comparable state of dispersion is observed for the PC_Br/silica and the (PC/PC_Br)(50/50)/silica
nanocomposites. Therefore, the Δ difference between the PC_Br/silica system (~ 0%) and 
the (PC/PC_Br)(50/50)/silica nanocomposites (~ 49%) cannot be attributed to the state of 
dispersion.

Table 7.2. An overview of the viscosity reduction for PC/PC_Br/silica nanocomposites 
and the silica content corresponding to the lowest viscosity.

<table>
<thead>
<tr>
<th>System name</th>
<th>Br groups (wt%)</th>
<th>Δ (%)</th>
<th>Silica content (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>0</td>
<td>28</td>
<td>0.9</td>
</tr>
<tr>
<td>(PC/ PC_Br ) (75/25)</td>
<td>6.5</td>
<td>24</td>
<td>0.7</td>
</tr>
<tr>
<td>(PC/ PC_Br ) 50/50</td>
<td>13</td>
<td>49</td>
<td>0.8</td>
</tr>
<tr>
<td>(PC/ PC_Br ) (25/75)</td>
<td>19.5</td>
<td>32</td>
<td>0.4</td>
</tr>
<tr>
<td>PC_Br</td>
<td>26</td>
<td>0</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Fig. 7.4. TEM images of nanocomposites with approx. 0.9 vol% silica in (a) PC_Br, 
(b)(PC/PC_Br)(50/50) and (c) (PC/PC_Br)(75/25).

In addition, the Δ for the ((PC/PC_Br)(50/50) + 0.8 vol% silica) nanocomposite is ~ 55% in Fig. 7.3c, which is much higher than pure PC reported in Chapter 4 & 5. It is 
intriguing to investigate further on the parameters that can induce the viscosity reduction 
in this system. As it was discussed in Chapter 4, the PC/silica nanocomposites prepared
via mini-extruder did not show degradation, which is also applicable for the 
(PC/PC_Br)(50/50)/silica nanocomposites. Negligible effect (~ 4%) of the molar mass on 
the viscosity reduction was observed. Δ of ~ 51% is therefore the result of the addition of 
silica nanoparticles.

The glass transition temperatures of the (PC/PC_Br)(50/50)/silica nanocomposites 
were characterized by both DSC and DMTA and the results are listed in Table 7.3. With 
the addition of silica nanoparticles, the T_g slightly decreases (Table 7.3), viz. 3 °C 
difference between the T_g of the ((PC/PC_Br)(50/50) + 0 vol% silica) and the 
((PC/PC_Br)(50/50) + 0.8 vol% silica) system. Generally, T_g-induced viscosity changes 
can be evaluated via mastercurves. From the mastercurves (Fig. 7.5), the [η] at a certain 
distance from T_g, e.g. at T = (T_g + 50) °C (Table 7.4), can be compared. The results 
indicate that the ~ 3 °C difference in T_g leads to ~ 2% decrease in viscosity.
Chapter 7 Effect of the interaction between PC and silica surface on the decrease in viscosity of PC/silica nanocomposites

Table 7.3. $T_g$ of (PC/PC$_{Br}$(50/50))/silica nanocomposites with increasing silica content.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>$T_g$ (°C) $^a$</th>
<th>$T_g$ (°C) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PC/PC$_{Br}$(50/50) + 0 vol% silica)</td>
<td>164</td>
<td>167</td>
</tr>
<tr>
<td>(PC/PC$_{Br}$(50/50) + 0.1 vol% silica)</td>
<td>163</td>
<td>166</td>
</tr>
<tr>
<td>(PC/PC$_{Br}$(50/50) + 0.4 vol% silica)</td>
<td>162</td>
<td>163</td>
</tr>
<tr>
<td>(PC/PC$_{Br}$(50/50) + 0.8 vol% silica)</td>
<td>161</td>
<td>164</td>
</tr>
<tr>
<td>(PC/PC$_{Br}$(50/50) + 1.7 vol% silica)</td>
<td>161</td>
<td>163</td>
</tr>
</tbody>
</table>

$^a$ The $T_g$ was measured by DSC; $^b$ The $T_g$ was obtained via loss modulus peak measured by DMTA.

Fig. 7.5. Mastercurves of the (PC/PC$_{Br}$(50/50)) and the ((PC/PC$_{Br}$(50/50) + 0.8 vol% silica) nanocomposite at $T_r$ = 210 °C.

Table 7.4. Comparison of $|\eta'|$ for (PC/PC$_{Br}$(50/50))/silica nanocomposites at 250 °C and $T = (T_g + 50)$ °C at 0.01 rad/s.

| Silica content (vol%) | $|\eta'|$ (Pa*s) $T = 250$ °C at 0.01rad/s | $|\eta'|$ (Pa*s) $T = (T_g + 50)$ °C at 0.01rad/s |
|-----------------------|------------------------------------------|------------------------------------------|
| 0                     | $1.89*10^4$                              | $5.50*10^5$                              |
| 0.8                   | $8.59*10^3$                              | $2.59*10^5$                              |
| Viscosity reduction   | 55%                                      | 53%                                      |

The investigation on the effect of $T_g$ on the viscosity reduction is based on the fact that TTS can be applied. Whether TTS principle holds can be evaluated from the $G_d$-δ plot (Fig. 7.6a).$^{17}$ For clarity, only two curves are plotted in Fig. 7.6a. The figure illustrates that the $G_d$-δ plot of the ((PC/PC$_{Br}$(50/50) + 0.8 vol% silica) nanocomposite overlaps with that of the pure (PC/PC$_{Br}$(50/50) blends, thereby confirming that TTS law is obeyed. Additionally, the overlap of the plots implies that the addition of silica nanoparticles has a global effect on the PC/silica nanocomposites.$^{18}$

As it was found in the Chapter 4-6, the addition of silica nanoparticles to the PC matrix induces the variations of the molar mass between entanglements $M_e$ in the PC/silica nanocomposites. It is thus interesting to check the effect of silica nanoparticles on the $M_e$. 
of the (PC/PC\_Br)(50/50)/silica nanocomposites. Considering equation (5.9), it is necessary to investigate the effect of silica nanoparticles on the plateau modulus $G_N^0$ of the (PC/PC\_Br)(50/50)/silica nanocomposites. The $G_\gamma$-\(\delta\) plot is one of the possibilities for the determination of $G_N^0$.\(^{19}\) This definition can be expressed in terms of $|G^*(\delta)|$:

$$G_N^0 = \lim_{\delta \to 0} G'(\delta)$$  \(\text{(7.3)}\)

In addition,

$$G' = \left( (G^*)^2 + (G^*)^2 \right)^{1/2}$$  \(\text{(7.4)}\)

$$G_N^0 = G'(\delta \to 0, \delta \to 0)$$  \(\text{(7.5)}\)

If tan $\delta \to 0$, $G'$ dominates over $G''$ and finally disappears, $|G^*|$ approaches $G'$ (equation 7.4). From equation (7.5), the conclusion that $|G^*|$ at the minimum phase angle $\delta$ equals $G_N^0$ can be obtained.\(^{20}\) The $|G^*|$ when $\delta \to 0$, i.e., $G_N^0$, for both the pure (PC/PC\_Br) (50/50) blend and the ((PC/PC\_Br) (50/50) + 0.8 vol\% silica) nanocomposite is marked by the dashed line in Fig. 7.6a. The figure shows that the addition of ~ 0.8 vol\% silica does not affect the $G_N^0$, which is ~ 2.0 MPa. Fig. 7.5 presents the mastercurves for both the pure (PC/PC\_Br) (50/50) blend and the ((PC/PC\_Br) (50/50) + 0.8 vol\% silica) nanocomposite. With the addition of ~ 0.8 vol\% silica, the mastercurves of the ((PC/PC\_Br) (50/50) + 0.8 vol\% silica) nanocomposite shift horizontally to a higher frequency. Using the model built up in Chapter 6 for the PC/silica nanocomposites, an increase in $M_e$ of ((PC/PC\_Br) (50/50) + 0.8 vol\% silica) nanocomposite was obtained, which can explain the viscosity reduction of the ((PC/PC\_Br) (50/50) + 0.8 vol\% silica) nanocomposite compared to the pure (PC/PC\_Br) (50/50) blend. The fitting results are presented in Fig. 7.7. The fitting results show that with adding ~ 0.8 vol\% silica nanoparticles, $M_e$ increases from 1000 g/mol to 1200 g/mol. Compared with the results listed in Table 6.1 for PC/silica nanocomposites, the addition of ~ 0.8 vol\% silica nanoparticles into PC or (PC/PC\_Br)(50/50) induces a similar $M_e$ variation, while the viscosity reduction for (PC/PC\_Br)(50/50)/silica nanocomposites is much higher than that for PC/silica nanocomposites. This indicates that the interaction between PC\_Br and silica nanoparticles surfaces plays also a significant role.

Cole-Cole figures plot the imaginary viscosity $\eta''$ as a function of real viscosity $\eta'$ (Fig. 7.6b)\(^{21}\) and can be used to investigate the microstructure or molecular architecture of homopolymers or materials with a wide distribution of relaxation times, such as polymer composites, block copolymers and polymer blends.\(^{22,23}\) Fig. 7.6b depicts the Cole-Cole plots for (PC/PC\_Br)(50/50)/silica nanocomposites at 250 °C. Semi-arc curves are observed for all (PC/PC\_Br)(50/50)/silica nanocomposites (Fig. 7.6b). The regular semi-arc curves indicate that these silica nanoparticles-filled polymeric systems exhibit a single relaxation time or a narrow relaxation time distribution.\(^{21}\) With increasing silica concentration, the size of the semi-arc becomes smaller. At low frequencies (or zero frequency) and $\eta'' = 0$, the corresponding real viscosity $\eta'$ is equal to the zero-shear viscosity. From Fig. 7.6b, it is evident that these zero-viscosity changes with silica content, which is similar to the viscosity variation reported in Fig. 7.3c. Furthermore, the frequency at which $\eta''$ is maximum varies with silica concentration. These changes allow us to calculate the relaxation times of the systems. For example, the maximum value of $\eta''$ for
Chapter 7 Effect of the interaction between PC and silica surface on the decrease in viscosity of PC/silica nanocomposites

((PC/PC_Br)(50/50) + 0.8 vol% silica) nanocomposite corresponds to the highest frequency for the studied (PC/PC_Br)(50/50)/silica nanocomposites, suggesting that the ((PC/PC_Br)(50/50) + 0.8 vol% silica) nanocomposite relaxes the fastest.

Fig. 7.6. (a) G_δ-δ plot at Tr = 210 °C and (b) Cole-Cole plot at 250 °C for the (PC/PC_Br)(50/50)/silica nanocomposites.

Fig. 7.7. Comparison between the experimental (circle and square) and the fitted (—) dynamic moduli for (PC/PC_Br)(50/50)/silica nanocomposites.

In summary, the addition of silica to PC/PC_Br induces a viscosity reduction, but the extent depends on the Br content. The results of the (PC/PC_Br)(50-50) systems demonstrate that the viscosity reduction is not due to the molar mass degradation nor from a decrease of T_g, but attributed to the entanglement density variations induced by the addition of silica nanoparticles.

7.3.2. Effect of particle size on the viscosity reduction of (PC/PC_Br)(50/50)/silica nanocomposites

As stated before, nanocomposites may offer a substantial improvement of some of the properties at very low filler loadings because of the large specific surface area of nanoparticles. It was shown that the surface area, i.e., particle size and geometry, plays an
Therefore, the effect of particle size and geometry on the viscosity reduction of the PC/PC\textsubscript{Br}/silica nanocomposites was investigated. Three different silica particles were used (for details see Table 4.4): two fillers are spherical silica particles with an average diameter of 13 nm (coded as S), and 45 nm (coded as L), while the other silica particles are cylindrical with an average diameter of 12 nm and a length of 70 nm (coded as UP).

The state of dispersion in the (PC/PC\textsubscript{Br})(50/50) matrix is given in Fig. 7.8 and illustrates that well-dispersed silica nanoparticles can be obtained. Small particles ($D = 13 \text{ nm}$) formed small aggregates of $\sim 50 \text{ nm}$, while large nanoparticles ($45 \text{ nm}$) dispersed individually or in clusters of a few particles. The cylindrically-shaped particles dispersed individually or with aggregates $\sim 100 \text{ nm}$ (Fig. 7.8).

The different states of dispersion of the three silica nanoparticles result in different amount of the effective surface area of the silica nanoparticles to the polymer matrix. Therefore, the addition of these nanoparticles to the (PC/PC\textsubscript{Br})(50/50) matrix influence the viscoelastic behavior differently. In addition to Fig. 7.3c, Fig. 7.9 shows the absolute value of complex viscosity $|\eta^*|$ versus frequency for (PC/PC\textsubscript{Br})(50/50) systems with large and cylinder shape nanoparticles. The addition of both nanoparticles also induces a viscosity reduction for the (PC/PC\textsubscript{Br})(50/50) matrix. Within the investigated silica concentration, the minimum $|\eta^*|$ occurs for ((PC/PC\textsubscript{Br})(50/50)\textsubscript{L} + 0.9 vol\% silica) nanocomposites, while 2.0 vol\% UP silica nanoparticles are needed to obtain the minimum value of $|\eta^*|$.

It is evident that the size and geometry affects on the extent of the viscosity reduction of the (PC/PC\textsubscript{Br})(50/50) systems (Table 7.5). The addition of $\sim 0.8 \text{ vol}\%$ small nanoparticles induced a reduction of approx. 49\%, while the addition of $\sim 0.9 \text{ vol}\%$ large particles leads to a reduction of approx. 33\%. The increase in particle size decreases the particles’ surface area (Table 4.4). Therefore, the effective silica surface area to PC/PC\textsubscript{Br} matrix is decreased, which leads to a decrease in $\Delta$ (Table 7.5).
Chapter 7 Effect of the interaction between PC and silica surface on the decrease in viscosity of PC/silica nanocomposites

Fig. 7.9. The absolute value of complex viscosity $|\eta^*|$ versus frequency $\omega$ for (PC/PC$_{Br}$(50/50) with (a) large (L) and (b) cylinder shape (UP) nanoparticles at 10% strain and at 250 °C.

Table 7.5. An overview of the effect of particle size on the decrease in viscosity of (PC/PC$_{Br}$(50/50)/silica nanocomposites.

<table>
<thead>
<tr>
<th>System name</th>
<th>$\Delta$ (%)</th>
<th>Silica content (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PC/PC$_{Br}$) (50/50)$_S$</td>
<td>49</td>
<td>0.8</td>
</tr>
<tr>
<td>(PC/PC$_{Br}$) (50/50)$_L$</td>
<td>33</td>
<td>0.9</td>
</tr>
<tr>
<td>(PC/PC$<em>{Br}$) (50/50)$</em>{UP}$</td>
<td>29</td>
<td>2.0</td>
</tr>
</tbody>
</table>

When comparing Table 7.5 and Table 4.5, we see that the addition of silica to (PC/PC$_{Br}$(50/50) induces larger viscosity reduction than for pure PC systems. The reasons may come from the interaction difference between PC/silica and PC$_{Br}$ silica, which will be characterization in the next section via atomic force microscopy (AFM).

7.3.3. Interaction of PC/silica versus PC$_{Br}$/silica

Atomic force microscopy (AFM) is a widely used technique to measure interaction forces between surfaces of materials and the tip. In idealized experimental conditions, e.g. in ultrahigh vacuum, when the cantilever tip approaches a sample surface, van der Waals forces start to act. They are sufficiently far-ranging and are felt at a distance of a few tens of Ångstroms. Then, at the distance of several Ångstroms repulsive forces start to act. In our measurements, the interaction difference between pure PC with silica and PC$_{Br}$ with silica was checked by using an AFM silicon tip to mimic silica nanoparticle surface. During mapping, the tip was allowed to touch the surface of the sample, which was prepared via spin-coating. The attractive force, when the tip was retracted from the surface of the sample, was measured. The vertical cantilever deflection was measured by means of the optical registration system and converted into electrical signal DFL, which is a
parameter characterizing the interaction force between the tip and the surface in contact mode. There is a linear relationship between the DFL value and the force.

Table 7.6. DFL results from pure PC with different Br concentrations.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>DFL (pA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>- 545 ± 15</td>
</tr>
<tr>
<td>PC_Br</td>
<td>- 584 ± 40</td>
</tr>
<tr>
<td>TB_BPA_PC</td>
<td>- 806 ± 50</td>
</tr>
</tbody>
</table>

Average DFL values from ~ 12 different positions for PC film and PC_Br film were listed in Table 7.6 and indicate a slightly higher interaction of PC_Br with the silica surface. However, PC_Br is a 1:1 (by weight) copolymer of BPA-based PC and TB_BPA_PC, which has ~ 26 wt% of PC_Br, ~ 2.7 mol% Br groups. It is thus difficult to check the Br interaction with silica. To further confirm the Br interaction with the silicon tip, a pure polymer with tetra-bromo-BPA as repeating unit, i.e., TB_BPA_PC (Fig. 7.1b) was used. The results are also presented in Table 7.6. Although under real conditions (in ambient air) practically always some water is present and a water layer may be adsorbed on the sample and tip surfaces, our results show a clear difference of approx. 220 pA. Furthermore, all samples were made via a similar procedure and under similar conditions, from which we assume that there was similar amount of humidity on each sample. Therefore, the results from AFM confirm that Br groups have higher interaction with silica surface.

7.4. Conclusions

The viscoelastic behavior of PC/PC_Br/silica nanocomposites was studied. The addition of silica to PC/PC_Br blends induced a viscosity reduction, while no viscosity reduction was found in PC_Br/silica nanocomposites. The ratio and the molar mass of PC/PC_Br play an important role on the viscoelastic behavior of the system. The addition of ~ 0.8 vol% silica to (PC/PC_Br)(50/50) blends leads to ~ 49% viscosity reduction, which does not come from the changes of the T_g nor from the molar mass variations. The fitting results based on the reptation model imply that the addition of silica nanoparticles induces the entanglement density variations in (PC/PC_Br)(50/50) blends, which can explain the observed viscosity changes. The results confirmed the importance of the Br groups, which has a higher interaction with silica surface as shown by AFM, on the viscosity reduction.

7.5. References

Chapter 7 Effect of the interaction between PC and silica surface on the decrease in viscosity of PC/silica nanocomposites

10 Cassagnau, Ph. Polymer 2008, 49: 2183-2196.
22 Oh, H.; Green, P.F. Nature Mater. 2009, 8: 139-143.
Mechanical properties of poly(carbonate) (PC)/silica nanocomposites

Abstract

In this chapter, the mechanical properties of PC/silica nanocomposites are presented. The results from the uniaxial compression tests demonstrate that the addition of silica nanoparticles slightly increases the modulus and the yield stress of PC/silica nanocomposites. With increasing annealing time and silica content, an increase in the yield stress is observed, which is confirmed by the uniaxial compression and tensile tests. A similar softening and strain hardening modulus are found from the true stress-strain curves of PC/silica nanocomposites. The mechanical properties of PC/silica nanocomposites were not deteriorated by the addition of silica nanoparticles, which induced the viscosity reduction of the system.
8.1. Introduction

In the previous chapters, the viscoelastic behavior of the PC/silica nanocomposites was discussed. With the addition of silica nanoparticles, the absolute value of complex viscosity $|\eta^*|$ first dropped with a minimum $|\eta^*|$ at approx. 0.8 vol% silica content followed by an increase over the studied silica content range. The effect of the particle size and the state of dispersion of the nanoparticles was discussed in Chapter 4 and it was shown that the state of dispersion played an important role on the viscosity reduction of the PC/silica nanocomposites. Aggregates with an average diameter of ~ 80 nm were observed in the system of the PC/silica (13 nm) nanocomposites, while in the PC/silica (45 nm) nanocomposites individual or on average two silica nanoparticles were observed in the PC matrix. Therefore, comparable effective surface area of the nanoparticles interacted with the PC matrix, resulting in the comparable viscosity reduction with addition of ~ 0.8 vol% silica (Chapter 4). The effect of the molar mass of the PC was presented in Chapter 5. It was observed that upon adding a similar amount of silica nanoparticles (~ 0.8 vol%), the extent of the viscosity reduction decreases on increasing molar mass. In Chapter 6, a mechanism was proposed to explain the decrease in viscosity of the PC/silica nanocomposites. Based on the results of the experimental data and the fitting results of a modified reptation model, a novel concept of the entanglement density variations was introduced. Although there are still open questions on the exact details of the mechanism, the viscosity reduction of the PC/silica nanocomposites was experimentally verified. However, the improved processability by the addition of nanoparticles does not make sense if the mechanical properties of the nanocomposites are deteriorated. To be able to control the rheology/property balance of PC, the effect of the addition of silica nanoparticles on the mechanical properties was investigated and will be discussed in this chapter.

Numerous studies addressed the effect of nanofillers on the mechanical properties.\(^1\)\(^-\)\(^5\) In comparison with the conventional (micrometer) fillers, nanoparticles have some unique features. First, nanoparticles with a high specific surface area delocalize stress when samples are under deformation, and thus improve the mechanical properties of nanocomposites. It was reported that nanoparticles can enhance the Young’s modulus of the polymers more dramatically than micro-fillers.\(^6\)\(^,\)\(^7\) Secondly, the required loadings of nanoparticles in a polymer matrix (< 5 vol%) are usually considerably lower than micro-fillers (typically 10 - 40 vol%).\(^8\) This signifies that many intrinsic merits of neat polymers, such as low weight, ductility, and good processability, will be retained after the addition of nanoparticles. Additionally, the mechanical properties of polymer nanocomposites can be tailored by changing the volume fraction (i.e., interparticle distance), shape, and size of the filler particles.\(^9\)

It was demonstrated that compounding of PC with nanoclay can be a feasible approach for enhancing the tensile strength and Young’s modulus of PC, although the addition of clay may decrease the impact strength of PC.\(^10\)\(^-\)\(^14\) In addition to nanoclay, other inorganic fillers, such as polyhedral oligomeric silsesquioxane (POSS) and calcium carbonate (CaCO\(_3\)), have been used to improve the mechanical properties of PC. Zhao et al.\(^15\) studied the mechanical properties of PC/POSS composites and observed slight improvements in
the tensile and dynamic mechanical modulus with increasing the loading of trisilanolphenyl-POSS at the expense of a decreasing ductility. Wang et al.\textsuperscript{16} reported an enhancement in mechanical properties of PC/CaCO\textsubscript{3} nanocomposites. Upon incorporation of 1 wt\% CaCO\textsubscript{3}, the tensile and bending modulus together with the bending strength of PC were improved, while the tensile strength and elongation at break were reduced. The slight decrease of the tensile strength was illustrative for the weak interaction between the CaCO\textsubscript{3} nanoparticles and PC. It is worth noting that the viscosity of the PC/CaCO\textsubscript{3} nanocomposites showed a continuous decrease on increasing the CaCO\textsubscript{3} content. Concomitantly, the glass transition temperature (T\textsubscript{g}) was decreased by approx. 6 °C.

The final properties of a polymer are not only determined by product composition, but also processing or shaping step, which, in many cases, is underestimated or even neglected. During the shaping process, polymers are subjected to complex flow fields with large temperature and pressure gradients in short time, resulting in large variations (heterogeneity) in properties throughout the entire product. The heterogeneity of the products may become worse due to non-uniform cooling during processing. Moreover, because of its high melt viscosity and poor resistance to abrasion and chemicals, PC is not suitable for certain applications.\textsuperscript{17} Furthermore, PC undergoes relatively rapid physical aging just below its T\textsubscript{g}, which can lead to embrittlement.\textsuperscript{18} One approach to reduce the embrittlement is to incorporate an impact modifier that can increase the toughness when the matrix loses its inherent ductility due to physical aging.\textsuperscript{19} Dan et al.\textsuperscript{20} added poly(acrylate)/TiO\textsubscript{2} composite particles to PC to slow down the aging rate. For nanocomposites, the adsorption of polymer chains to nanoparticle surfaces affects their relaxation time, which result in different microstructures (heterogeneity) and lead to different properties during aging process. Priestly et al.\textsuperscript{21} reported that the physical aging rate of poly(methyl methacrylate) (PMMA) was reduced by more than a factor of 20 in 0.4 vol\% silica-PMMA nanocomposites. This comes from that the reduced strength of the β process results from hydrogen bonding between PMMA ester side groups and hydroxyl units on the surface of silica nanoparticles.

In this chapter, the mechanical properties of PC/silica nanocomposites characterized by compression and tensile tests are discussed. Generally, it is difficult to predict the macroscopic properties of polymers from its molecular structure. This can be partly ascribed to the influence of the thermomechanical history on the mechanical response, but more important reasons are the different length-scales and time-scales involved. By measuring the intrinsic properties via the application of a homogeneous deformation, localization of strain may be avoided. Homogeneous deformation experiments can be performed by uniaxial compression tests,\textsuperscript{22, 23} which typically results in true stress-strain curves with an initial (visco-) elastic region, a yield stress point, strain softening (also known as yield-drop), and strain hardening (or network hardening). Therefore, uniaxial compression tests were performed to study the effect of the addition of silica nanoparticles on the intrinsic behavior of the PC/silica nanocomposites. In addition, the interaction with the silica surface may influence the relaxation behavior of PC chains. Therefore, different aging behavior as a function of time may be expected.\textsuperscript{24} Physical aging occurs because the polymer chains attempt to reach an equilibrium state with minimal internal enthalpy. This
equilibrium process proceeds by local ordering, which is reflected in the changes of the energy landscape of the polymer. The energy landscape reflects the freedom of mobility of chain segments at a specific position in space, and it is constantly changing towards its state of lowest internal energy. Normally, physical aging is marked by an increase in yield stress and increased strain softening. The effect of aging on the mechanical properties of the PC/silica nanocomposites will also be studied.

8.2. Experimental

8.2.1. Materials

A bisphenol-A based PC with a weight-average molar mass ($M_w$) = 30 kg·mol$^{-1}$ and polydispersity index (PDI) = 2.6 was supplied by SABIC Innovative Plastics (SIP). Silica nanoparticles suspended in methyl ethyl ketone (MEK) with an average diameter of 13 nm and a solid content of 30 - 31 wt% were purchased from Nissan Chemical. All materials were used as received.

8.2.2. Preparation of PC/silica nanocomposites

The PC powder was first dried for 12 hours at 120 °C under N$_2$ flow. A series of PC/silica nanocomposites containing silica content from 0 to 1.7 vol% was prepared via melt blending on a twin-screw extruder (ZSK-25, Krupp Werner and Pfleiderer GmbH, Germany) at a screw speed of 300 rpm. The temperature of the extruder was set to ~ 40 °C for the feeder section and up to ~ 300 °C in the melting zone. The PC powder with ~ 0.1 wt% processing stabilizer tris(2,4-di-tert-butylphenyl) phosphate (from SIP) was mixed together with the required amount of silica suspension just before extrusion.

8.2.3. Characterization techniques

Compression Testing. Uniaxial compression tests were performed on a servo-hydraulic MTS 831 Elastomer Testing System. Cylindrically shaped specimens with a diameter and height of ~ 5 mm were compressed using true-strain control, at a constant true strain rate of $10^{-3}$ s$^{-1}$ between two parallel flat steel plates. In order to prevent any bulging of the sample, friction was reduced by applying a lubricating PTFE spray on the polished steel plates. Moreover, a layer of PTFE skived film tape (3M 5480) was placed between the sample and the lubricated plates. The stiffness of the testing equipment was measured and corrected in a real-time feedback loop to ensure accurate strain measurement and control. All experiments, including sample preparation, were performed at room temperature. From the recorded force and true strain signals, the true stress was calculated assuming isochoric deformation.

Annealing was performed at 120 °C for 24 hours under N$_2$ flow in an oven. To ensure that the cylindrical shape of the compression test samples were maintained, the annealing procedure was executed prior to machine the samples into cylindrical specimens.
Tensile Testing. Tensile tests were performed on a Zwick/Roell 2010 tensile testing machine with a constant rate of $10^{-2} \text{ s}^{-1}$ at room temperature. Rectangular bars of 84 x 10 x 1 mm$^3$ with a gauge section of 54 x 5 x 1 mm$^3$ were cut from 1 mm thick plates.

Annealing was performed in an oven under N$_2$ flow at $T = 120 \degree C$ for 1 hr, 3 hrs, 10 hrs, 1 day, 3 days, 10 days and 30 days respectively. Dumb-bell shapes samples were cut after the annealing procedure was completed to maintain the shape of the measured bars.

All tensile yield stresses listed in the results section are engineering yield stresses. The results were taken as the mean value of ~4 measurements.

Transmission Electron Microscopy (TEM). Morphological investigations were performed by using a Tecnai 20 transmission electron microscopy (TEM), operated at 200 kV. Sections of 50 - 70 nm were obtained at room temperature by using a Leica Ultracut E microtome. Chemical staining of the sections was not required, since the electron density of silica is much higher than that of PC.

8.3. Results and discussion

First, the effect of the addition of silica nanoparticles on the macroscopic stress-strain response of the PC/silica nanocomposites measured via uniaxial compression texts is discussed. Based on the true stress-strain curves of the PC/silica nanocomposites, the effect of the silica nanoparticles on the modulus, the yield stress, the strain softening, and the strain hardening is discussed. In addition, the stability of the state of dispersion of the silica nanoparticles in the PC/silica nanocomposites after deformation is presented. In addition, the effect of physical aging on the mechanical properties, especially on the yield stress, of the PC/silica nanocomposites is investigated via both compression and tensile tests.

8.3.1. Macroscopic stress-strain response of PC/silica nanocomposites measured via compression tests

Fig. 8.1a shows the true stress-strain curves of PC and PC/silica nanocomposites from the uniaxial compression tests. All the PC/silica nanocomposites exhibit elastic plastic deformation behavior, including an initial viscoelastic region followed by yielding, strain softening and strain hardening regardless of the silica content. The curves (Fig. 8.1a) demonstrate no deterioration of the mechanical properties in the studied PC/silica nanocomposites, while the processing properties are improved. With increasing silica content, the modulus, the yield stress, and the strain hardening modulus of the PC/silica nanocomposites increase. The property improvements will be discussed in more detail further.

It has been reported that the addition of nanoparticles to polymer matrix can suppress physical aging, which may be a major advantage associated with the long-term stability of polymer nanocomposites. The PC/silica nanocomposites were thus annealed in an oven at 120 °C for 24 hours to investigate the effect of the silica nanoparticles on the physical aging of the PC/silica nanocomposites and the mechanical properties were measured afterwards via compression tests. Fig. 8.1b presents the true stress-strain curves of the
annealed PC and PC/silica nanocomposites after 24 hours at 120 °C, while Fig. 8.2 gives the comparison of the curves before and after annealing for pure PC and PC with 0.8 vol% silica. The mechanical properties calculated from the stress-strain curves are listed in Table 8.1 as a function of silica content.

Fig. 8.1. Stress-strain curves of the PC/silica nanocomposites measured via uniaxial compression tests before (as-molded) and after annealing (annealed) at 120 °C for 24 hours.

### 8.3.1.1. Effect of silica nanoparticles on the modulus and the yield stress of PC/silica nanocomposites

Table 8.1 demonstrates that the yield stress increases steadily with silica content for the samples as-molded and after annealing. The yield stress of PC at room temperature is associated with the segmental motions, i.e., the mechanical glass transition temperature.

Upon physical aging, a local densification or a local attraction of individual atoms to their neighbors will occur, which induces changes of energy landscape or a change in free volume distribution. In order to induce molecular mobility, this local order has to be destroyed. If the segmental mobility is not triggered by temperature but by force, an increase in the yield stress should be observed. Fig. 8.2, Fig. 8.3 and Table 8.1 demonstrate that the yield stresses for both pure PC and PC/silica nanocomposites increase after annealed at 120 °C for 24 hours.
Fig. 8.2. Stress-strain curves for pure PC and the (PC + 0.8 vol% silica) nanocomposite before (as-molded) and after annealing (annealed) at 120 °C for 24 hours.

Table 8.1: Mechanical properties of PC/silica nanocomposites as-molded and after annealing (annealed) at 120 °C for 24 hours measured via uniaxial compression tests.

<table>
<thead>
<tr>
<th></th>
<th>PC + 0 vol% silica</th>
<th>PC + 0.8 vol% silica</th>
<th>PC + 1.7 vol% silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-molded</td>
<td>1.6</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>annealed</td>
<td>1.7</td>
<td>1.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Δ*</td>
<td>0.1</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Yield stress (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-molded</td>
<td>64.7 ± 0.3</td>
<td>65.6 ± 0.6</td>
<td>66.9 ± 0.2</td>
</tr>
<tr>
<td>annealed</td>
<td>72.5 ± 0.2</td>
<td>72.7 ± 0.1</td>
<td>74.6 ± 0.2</td>
</tr>
<tr>
<td>Δ</td>
<td>7.7 ± 0.2</td>
<td>7.1 ± 0.6</td>
<td>7.7 ± 0.2</td>
</tr>
<tr>
<td>Softening (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-molded</td>
<td>11.7 ± 0.3</td>
<td>10.9 ± 0.6</td>
<td>11.5 ± 0.2</td>
</tr>
<tr>
<td>annealed</td>
<td>16.4 ± 0.3</td>
<td>16.2 ± 0.7</td>
<td>16.4 ± 0.1</td>
</tr>
<tr>
<td>Δ</td>
<td>4.7 ± 0.3</td>
<td>5.3 ± 0.7</td>
<td>4.9 ± 0.2</td>
</tr>
<tr>
<td>Strain hardening (MPa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-molded</td>
<td>51.4 ± 1.4</td>
<td>51.8 ± 0.4</td>
<td>53.0 ± 0.2</td>
</tr>
<tr>
<td>annealed</td>
<td>49.9 ± 0.2</td>
<td>49.8 ± 1.1</td>
<td>49.0 ± 0.9</td>
</tr>
<tr>
<td>Δ</td>
<td>-1.5 ± 1.4</td>
<td>-2.0 ± 1.1</td>
<td>-4.0 ± 0.9</td>
</tr>
</tbody>
</table>

Δ stands for the difference between as-molded values and annealed values.

For as-molded samples, the yield-stress increases linearly with silica content, but after annealing the yield stress increases slightly up to approx. 0.8 vol% silica followed by a relative faster increase with increasing silica to 1.7 vol%. Therefore, the effect of silica nanoparticles on the yield stress of the PC/silica nanocomposites might be different for the samples before and after annealing (Fig. 8.3). Fig. 8.1 and Fig. 8.2 show that the yielding takes place at a true strain of $\varepsilon = \sim 0.1$, with no change in the state of dispersion of the
silica nanoparticles was observed before and after annealing (see Section 8.3.2). Therefore, the effect of annealing on the yield stress of the PC/silica nanocomposites (Fig. 8.3) is not due to the variation of the state of silica dispersion. To further investigate the effects of annealing on the yield stress of PC/silica nanocomposites, tensile tests were performed. The results will be discussed in more detail in this chapter (see Section 8.3.3).

![Fig. 8.3. Effect of silica nanoparticles on the yield stress of PC/silica nanocomposites for the samples as-molded and after annealed at 120 °C for 24 hours.](image)

### 8.3.1.2. Effect of silica nanoparticles on the strain softening and the strain hardening of PC/silica nanocomposites

In addition to the yield point, the combination of softening and strain hardening proves to be a key issue in understanding the intrinsic mechanical properties of polymers. The strain softening behavior of the PC/silica nanocomposites was studied and the results are listed in Table 8.1. The data for both the as-molded samples and the samples annealed at 120 °C for 24 hours show that the addition of silica does not influence the strain softening significantly. A slight decrease in the strain softening was observed for the as-molded (PC + 0.8 vol% silica) nanocomposite compared to pure PC, while after annealing at 120 °C for 24 hours the difference in the strain softening between the (PC + 0.8 vol% silica) and pure PC is marginal. Comparing the softening for one sample, e.g. for the (PC + 0.8 vol% silica) nanocomposite, before and after annealing, softening increases for the PC/silica nanocomposites samples (Table 8.1) after annealing. With increasing silica content, similar variations $\Delta$ of softening of the PC/silica nanocomposites before and after annealing were observed (Table 8.1), implying that the addition of silica does not hinder the embrittlement process.

Once the critical stress is surpassed, the stress to further yield should be constant, until the entanglement network starts to orient, manifesting itself in strain hardening. The strain hardening moduli for the PC/silica nanocomposites is also listed in Table 8.1 and it can be observed that the addition of silica nanoparticles slightly increases the strain hardening modulus. Annealing at 120 °C for 24 hours slightly decreases the strain hardening modulus of the PC/silica nanocomposites while negligible changes in the strain hardening modulus was observed for pure PC. A similar observation was reported for pure...
PC by Meijer et al. They compared the intrinsic response of an annealed and a quenched PC sample. Annealing results in an increase of both modulus and yield stress, but upon plastic deformation the differences between both stress-strain curves disappear and they fully coincide at a strain of ~0.3. The influence of the thermal history is erased at that strain and both samples are transformed to a similar mechanically rejuvenated state.

8.3.2. Stability of state of dispersion in PC/silica nanocomposites

It is well established that the state of dispersion of nanoparticles is a crucial factor in determining the final properties of nanocomposites. Changes in the state of dispersion after aging or deformation may lead to different mechanical properties. Therefore, it is important to study the stability of the state of silica dispersion in PC matrix after annealing or after deformation. Transmission electron microscopy (TEM) was used to study the morphology of the (PC + 1.7 vol% silica) nanocomposite, which has the highest silica content in our studied systems, and thus the largest variations in the state of the dispersion, if there are any, are expected. Samples subjected to a true strain $\varepsilon = ~0.25$ and $\varepsilon = ~1.0$ in compression tests were used for comparison.

Figs. 8.4a and 8.4c depict the state of dispersion of the (PC + 1.7 vol% silica) nanocomposite before annealing, while Figs. 8.4b and 8.4d are measured after annealing. Comparing Figs. 8.4a and 8.4b for $\varepsilon = ~0.25$, a similar state of dispersion was observed, indicating a stable silica dispersion. Upon increasing the deformation, oriented silica
aggregates can be observed in the sample before annealing (Fig. 8.4c), which are not present in the sample after annealing (Fig. 8.4d). The orientation of the silica aggregates at high true strain $\varepsilon = \sim 1.0$ in Fig. 8.4c can contribute to the increased strain hardening. Therefore, a higher straining hardening modulus is observed for the (PC + 1.7 vol% silica) before annealing in comparison to after annealing (Table 8.1).

### 8.3.3. Effect of physical aging on the yield stress of PC/silica nanocomposites studied via tensile tests

Below $T_g$, amorphous polymers are in non-equilibrium state, and, as a result, their physical and mechanical properties are subject to change in time. This is called physical aging. To investigate the effect of physical aging on the yield stress of the PC/silica nanocomposites, annealing was carried out at 120 °C for different times. The yield stress was calculated based on the stress-strain curves (Fig. 8.5) from the tensile test measurements.

![Stress-strain curves for the PC/silica nanocomposites measured at room temperature after annealing at 120 °C for 0 s and 30 days.](image1)

![Yield stress versus annealing time (annealed at $T_a = 120 °C$) measured at room temperature for the PC/silica nanocomposites.](image2)

Fig. 8.5 shows that the yield stress of the PC/silica nanocomposites measured at room temperature increases slightly with increasing annealing time, while the shape of stress-strain curves is similar, even after annealing at 120 °C for 30 days. The evolution of yield
stress as a function of time for the pure PC and the PC/silica nanocomposites is presented in Fig. 8.6. The yield stresses for the studied PC/silica nanocomposites increase with increasing annealing time \( t_a \). There is no plateau of the yield stress versus time displayed in Fig. 8.6 even after \( t_a = 30 \) days. This indicates that no equilibrium was reached for the studied PC/silica nanocomposites after annealed at 120 °C for 30 days.

From these results it is evident that the yield stress of the PC/silica nanocomposites increases slightly by the addition of silica nanoparticles (Fig. 8.6). The addition of silica nanoparticles to the PC matrix does not reduce the physical aging rate of the nanocomposites (Fig. 8.6).

8.4. Conclusions

The mechanical properties of the PC/silica nanocomposites have been characterized and discussed. The intrinsic properties, obtained from the uniaxial compression tests, were not deteriorated by the addition of silica nanoparticles, while the addition of silica nanoparticles slightly increased the modulus of the PC matrix. Further, the yield stress increased with silica contents. Annealing or physical aging varies the mechanical properties of the PC/silica nanocomposites. After annealing, the yield stress of the (PC + 1.7 vol% silica) nanocomposite increases faster than the as-molded samples. The softening and strain hardening modulus are hardly affected by the addition of silica. This implies that the addition of silica does not induce the embrittlement of the PC matrix. The addition of silica can not hinder the embrittlement of the PC matrix with time.

The addition of silica increases the yield stresses and the modulus of the PC/silica nanocomposites, which are due to the interaction between the PC matrix and the silica nanoparticles, and the reinforcement of the inorganic silica nanoparticles. TEM images of the (PC + 1.7 vol% silica) nanocomposite show that the states of silica dispersion are stable after small deformation. Under larger deformation, the silica nanoparticles in the as-molded sample oriented slightly, while in the annealed sample remain in a similar dispersion state as with small deformation. The results indicate that the annealed samples have more stable state of silica dispersion than as-molded samples.

The results from the tensile tests show that with increasing annealing time, the yield stresses increases and no equilibrium states for the PC/silica nanocomposites are reached after annealing for ~ 30 days. The yield stress of the PC/silica nanocomposites increases slightly by the addition of silica nanoparticles.

The studies over the mechanical properties of the PC/silica nanocomposites confirm that the addition of ~ 0.8 vol% silica nanoparticles to the studied PC matrix remains or slightly increases the mechanical properties of PC, but decreases the viscosity of the PC. Results on the strain hardening of PC/silica nanocomposites do not indicate the changes in the entanglement density induced by the addition of silica nanoparticles. In our study, the highest silica content of PC/silica nanocomposites is ~ 1.7 vol%. The effect of ~ 1.7 vol% silica nanoparticles on the strain hardening of PC/silica nanocomposites is small. Therefore, no entanglement density variations could be demonstrated via the slight changes in the strain hardening. However, the entanglement density variations induced by
the addition of silica nanoparticles, especially ~ 0.8 vol%, can affect the viscosity reduction to a certain extent.

8.5. References

The area of synthetic polymers is seemingly mature in view of the fact that no novel polymers are expected with substantial market potential. As a consequence, the current industrial focus is on exploring and improving the performance of existing polymers, often referred to as ‘salt and pepper technology’.

The performance of polymeric products does not solely depend on the chemical structure but equally well on the processing step, and the use of specific additives. In fact, the difference between a polymer and a plastic (compound) is the use of additives which improve processability and product performance.

Since the start of the 21st century, the focus has been on nano-technology, also in the polymer area. Expectations are running high concerning the use of nanometer-sized additives which can enhance the properties at low loadings. Well-known examples are the (exfoliated) nano-clays, graphene, carbon nanotubes (CNT) and silica nanoparticles.

To date, the general problem with nanoparticles is how to disperse the nanoparticles homogeneously in a highly viscous polymer melt. In our group, the Laboratory of Polymer Technology (SKT), a technique has been proposed to grow in-situ nanoparticles by Goossens et al. via a sol-gel method (hydrolysis of tetraethoxy orthosilicate (TEOS)) in polymer (reactor) powders such as isotactic poly(propylene) (iPP) and poly(ethylene) (PE). It was shown that only a minute fraction of these in-situ synthesized nanoparticles, < 1 wt%, could lower the melt viscosity by ~ 90% without sacrificing the properties. The observation that nano-particles can lower the melt viscosity has also been confirmed by other groups.

In this thesis, the focus was on decreasing the melt viscosity of two industrially important plastics, viz. a semi-crystalline polymer, iPP, and an amorphous polymer poly(carbonate) (PC) by using various methods to incorporate silica nanoparticles.

Indeed, a reduction in melt viscosity of approx. 65% in iPP/silica nanocomposites and approx. 26% in PC/silica nanocomposites could be obtained, albeit in the lower frequency range. A negligible decrease in viscosity in the studied polymer/silica nanocomposites was observed at high frequencies, namely > 100 rad/s. This indicates that the observations reported in the thesis are not beneficial for injection molding processes. The stated approaches in the thesis can be utilized for the applications which need low shear processing conditions.

The conclusion of the work reported in this thesis is that nanoparticles possessing weak interactions with the polymer matrix can induce a lower melt viscosity. A theoretical basis for this phenomenon is not in place yet as discussed in the thesis and a more fundamental understanding is needed to optimize the effects of the beneficial influence of adding only a minute amount of nano-sized fillers on the melt viscosity.

Since the majority of synthetic polymers are processed via the melt and in view of the strong increase of the melt viscosity with increasing molar mass, the use of nano-sized fillers could provide a breakthrough in the world of polymer (plastic) processing.

2 Lemstra, P.J. Polymer R & D, Quo Vadis?

3 Goossens, J.G.; Peters, G.; Jain, S. EP 05101388.6


Samenvatting

De eigenschappen van polymeren worden niet alleen bepaald door de chemische structuur, maar ook door de verwerkingsstap die de orientatie van de moleculen in het eindproduct bepaald. Een groot gedeelte van de polymeren wordt verwerkt via de smelttoestand. In het algemeen nemen de eigenschappen, zoals taaiheid en sterkte, toe met toenemende molecularmassa, maar ook de viscositeit van de polymeer- en smelt met sterk toe met toenemende molecularmassa. De (nul)-viscositeit van polymere smelten schaalt boven een kritische waarde met het (gewichtsgemiddelde) molecuul massa tot de macht 3.4. Dit betekent dat een verdubbeling van de molecularmassa leidt tot een verhoging van de smeltviscositeit met meer dan een decade. In de praktijk betekent dit dat men een compromis moet zoeken tussen een goede verwerkbaarheid (lage viscositeit) en goede eigenschappen.

Naast de chemische structuur en verwerkingsomstandigheden kan men de eigenschappen ook sturen via additieven en/of (nano)deeltjes. Er zijn recent verschillende studies verschenen die laten zien dat de smeltviscositeit van de polymeren kan worden verlaagd door het toevoegen van nanodeeltjes. De technologische consequenties van de verlaging van de viscositeit kunnen enorm zijn, maar op dit moment worden de onderliggende mechanisms nog niet begrepen en kan men de viscositeitsverlaging nog niet voorspellen. De doelstelling van dit proefschrift is om het mechanisme van de verlaging van de viscositeit voor semi-kristalline en amorf polymeren te begrijpen.

Vervolgens kan men de balans tussen de verwerkbaarheid en eigenschappen controleren. In deze context zijn isotact polypropaan (iPP)/silica en polycarbonaat (PC)/silica nanocomposieten bestudeerd.

In het deel van iPP/silica nanocomposieten, zijn er verschillende manieren bestudeerd om de nanocomposieten te bereiden, d.w.z. in-situ silica (nano)deeltjes synthese en compundeerde route in de smelt of via oplossing. De reologie en het kristallisatiedrag van de geprepareerde iPP/silica nanocomposieten zijn vervolgens bestudeerd.

Aangezien compunderen via de smelt de meest gebruikte manier is om polymeren mengsels te prepareren, wordt deze methode gebruikt om de iPP/silica nanocomposieten te bereiden. De toevoeging van de silica nanodeeltjes met diameter ~ 20 nm verlaagt de smeltviscositeit. De verlaging van de viscositeit hangt af van de afmeting van de nanodeeltjes en verdeling. Door de afmeting van de nanodeeltjes te verlagen van ~ 20 naar ~ 10 nm wordt een kleinere viscositeit verlaging waargenomen.

In vergelijking met de in-situ silica (nano)deeltjes synthese en compunderen via de smelt, wordt een betere dispersiegraad van de silica deeltjes verkregen door verwerking via oplossing. Drie verschillende droogprocedures werden gebruikt, zijnde langzame verdamping, precipitatie en rotatie verdamping. Op deze manier geprepareerde iPP/silica nanocomposieten hebben een vergelijkbare dispersiegraad en verlaging van de viscositeit. Kortom, de verlaging van de viscositeit kan waargenomen via de verschillende manieren door gebruik van de juiste afmeting en verdeling van de silica nanodeeltjes. De hoge oppervlakte-energie leidt tot een voorkeursadsorptie van polymeer- en ketens met de hoogste molecularmassa. Dit resulteert in een segregatie van de ketens met een lage molecularmassa.
die de matrix vormen, en ketens met een hoge molecuulmassa die een aparte laag vormen om de silica deeltjes. Deze selectieve fysisorptie van de lange iPP ketens op de silica deeltjes leidt tot een daling van de viscositeit in het lage silica concentratie gebied, waarin de afstand tussen de deeltjes groter is dan de gyratiesstraal van de polymeerketens.

Naast de reologie verandert het kristallisatieproces van de iPP/silica nanocomposieten ook met de toevoegingen van de silica nanodeeltjes. De isotherme kristallisatiekinetiek van de iPP/silica nanocomposieten werd bestudeerd met behulp van de Avrami benadering en liet een kristallisatieproces zien dat bestaat uit twee stadia: het primaire stadium gekarakteriseerd door kiemvorming en groei en een secundair stadium gekarakteriseerd door kristal perfectionering. De toevoegingen van de silica nanodeeltjes verhoogt in eerste instantie de kristallisatiesnelheid met de hoogste kristallisatiesnelheid voor het systeem met de laagste smelt-viscositeit, waarna de kristallisatiesnelheid afneemt met het verder toevoegen van silica nanodeeltjes. De toevoeging van de silica nanodeeltjes verhoogt ook de kristallisatiesnelheid, maar de smelttemperatuur blijft gelijk.

Het stromingsgeïnduceerde kristallisatiegedrag werd bestudeerd met behulp van in-situ kleine hoek Röntgenverstroeiing (SAXS). Het is algemeen bekend dat stromingsgeïnduceerde kristallisatie wordt bepaald door het gedeelte met de hoogste molecuulmassa, maar de verlaging van de viscositeit suggerereert een matrix bestaande uit ketens met een lage molecuulmassa. De afwezigheid van de hoge molecuulmassa ketens in de matrix in combinatie met de lagere afschuifsnelheden als gevolg van de lagere viscositeit resulteert in minder oriëntatie onder stroming. Daardoor hebben deze nanocomposieten een meer uniforme en isotope structuur en morfologie in het uiteindelijke product. De Röntgenverstroeiing studie liet zien dat de oriëntatie minimaal is bij een silica concentratie waarneer de verlaging van de viscositeit maximaal is.

In het deel van de PC/silica nanocomposieten verlaagt het toevoegen van ~ 0.8 vol% silica nanodeeltjes (13 nm) smelt-viscositeit met ~ 26%. Het effect van de afmeting en de geometrie van de silica nanodeeltjes is ook bestudeerd.

Drie verschillende mechanismes zijn in de literatuur beschreven om de verlaging in de viscositeit in de nanocomposieten te verklaren, zijnde het ‘ball-bearing’ effect, extra vrij volume en de selectieve fysisorptie, maar geen van deze mechanismes kan de resultaten van de PC/silica nanocomposieten verklaren. Wij schrijven de verlaging van de viscositeit in de PC/silica nanocomposieten toe aan variaties in het entanglement netwerk. Dit wordt bevestigd door de resultaten van berekeningen en modellering. De toevoegingen van de silica nanodeeltjes verhoogt de molmassa tussen entanglements.

Verder is het effect van de affiniteit tussen PC en het silica oppervlak bestudeerd door het toevoegen van gebromineerde PC (PC_Br) naar PC/silica nanocomposieten. De verlaging van de viscositeit hangt af van de gewichtsverhouding tussen PC en PC_Br. De maximale verlaging van de viscositeit was te zien bij ~ 49%.

De mechanische eigenschappen van de PC/silica nanocomposieten en het effect van anneal was bestudeerd als functie van de silica concentratie. De resultaten van de uniaxial drukproeven lieten zien dat het toevoegen van de silica nanodeeltjes slechts een geringe verhoging geeft van de modulus en de vloeispanning van de PC/silica nanocomposieten, hetgeen te verklaren is door zowel versterkende effect van de silica
nanodeeltjes alsmede de interactie tussen PC and de silica nanodeeltjes. Het verhogen van de annealen tijd en de silica concentratie leidt ook tot een verhoging van de vloeispanning. Er wordt bijna geen verandering van de softening en hardening modulus waargenomen.

In samenvatting, de verlaging van de viscositeit van het semi-kristallijne (iPP) en amorphe (PC) polymeer wordt gerealiseerd via de toevoeging van de silica nanodeeltjes. De verlaging van de viscositeit hangt van de afmeting (distributie) en de geometrie van de nanodeeltjes, maar de mechanische eigenschappen van de nanocomposieten worden niet beïnvloed. Verschillende dispersiemethodes kunnen toegepast worden om de balans tussen de verwerkbaarheid en eigenschappen te controleren.
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Curriculum vitae

The author, Chunxia Sun, was born on May 26\textsuperscript{th} 1980 in Fanxian, Henan Province, China. After finishing her bachelor study in 2003 at the Qingdao University of Science and Technology, Qingdao, China, she participated in the Asia-Link program between the Department of Macromolecular Science in Fudan University, China and the Department of Chemical Engineering and Chemistry of the Eindhoven University of Technology, Eindhoven, the Netherlands. In 2006, she obtained her Master degree in Material Science within the Department of Macromolecular Science of the Fudan University, Shanghai, China, on ‘Thermoreversible Crosslinking of Maleic Anhydride-Grafted Ethylene/Propylene Copolymer (MAAn-g-EPM) Using Hydrogen Bonding and Ionic Interactions’. In June 2006, she started a PhD project at the Eindhoven University of Technology, Eindhoven, the Netherlands of which the results are presented in this dissertation. During her PhD study, the author completed five modules of the course ‘Registered Polymer Scientist’ (RPK) organized by the ‘National Dutch Graduate School of Polymer Science and Technology’ (PTN), which include Polymer Chemistry, Polymer Physics, Polymer Properties, Rheology and Polymer Processing, and Polymer Innovations.