Physical aging in polycarbonate nanocomposites containing grafted nano silica particles

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Physical Aging in Polycarbonate Nanocomposites Containing Grafted Nanosilica Particles: A Comparison between Enthalpy and Yield Stress Evolution

Vaidyanath Ramakrishnan,^{1†} Sepehr Harsiny,^{2‡} Johannes G. P. Goossens,^{2‡}
Theodorus L. Hoeks,^{2‡} Gerrit W. M. Peters¹

¹Department of Mechanical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

²Laboratory of Polymer Materials, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Correspondence to: G. W. M. Peters (E-mail: g.w.m.peters@tue.nl)

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ABSTRACT: Understanding and controlling physical aging below the glass transition temperature (T_g) is very important for the long-term performance of plastic parts. In this article, the effect of grafted silica nanoparticles on the physical aging of polycarbonate (PC) below the T_g is studied by using the evolution of the enthalpy relaxation and the yield stress. The nanocomposites were found to reach a thermodynamic equilibrium faster than unfilled PC, implying that physical aging is accelerated in presence of grafted nanosilica particles. The Tool-Narayanaswamy-Moynihan model shows that the aging is accelerated by the grafted silica nanoparticles, but the molecular mechanism responsible for physical aging remains unaltered. Furthermore,

dynamic mechanical analysis shows that the kinetics of physical aging can be related to a free volume distribution or a local attraction-energy distribution as a result of the change in mobility of the polymer chain. Finally, a qualitative equivalence is observed in the physical aging followed by both the enthalpy relaxation and yield stress. © 2016 Wiley Periodicals, Inc. *J. Polym. Sci., Part B: Polym. Phys.* **2016**, *54*, 2069–2081

KEYWORDS: differential scanning calorimetry; enthalpy relaxation; free volume; glass transition; mechanical properties; nanocomposites; physical aging; polycarbonates; structure-property relations; structural relaxation; yield stress

INTRODUCTION To address the constant need for improved properties, such as mechanical, electrical, and thermal conductivity of the resin for various market segments, such as automotive, electronic, electrical, infrastructure, and construction, polymers are often reinforced with micron- and nano-sized fillers. Compared to micron-sized filler, nanoparticles have a larger surface area and consequently require only a few vol % (i.e., <5 vol %) achieve the desired property. This results in the intrinsic properties of the neat polymer be retained. Nanoparticles have shown to improve the stiffness and toughness of the polymers more dramatically than microfillers.^{1–8} Additionally, the mechanical properties of polymer nanocomposites can be tailored by changing the shape and size of the filler particles, the volume fraction and concomitantly the interparticle distance.⁹ Given the wide range of applications, PC and PC-based blends are good candidates for the use of nanofillers to enhance the mechanical, optical and rheological properties. Fillers such as nanoclay, mineral fillers, nanosilica, carbon nanotubes, and graphene have been used to enhance the tensile strength and the

Young's modulus of PC.^{10–12} Besides the use of fillers, processing conditions, and aging also affect final properties. For example, nonuniform fast cooling during injection molding makes the material to go out of equilibrium in the glassy state. For a polymer such as PC, physical aging just below its T_g results in the rapid change of mechanical properties, which can lead to embrittlement.^{13,14} Fillers are known to affect the physical aging behavior of the host polymer. Boucher et al. showed that the addition of surface-functionalized silica and gold particles accelerated physical aging of poly (methyl methacrylate) (PMMA) and poly(styrene) (PS), respectively.^{15–18} They showed that functionalization did not alter the molecular mechanism for physical aging, but increased the surface-to-volume ratio accelerated physical aging. Besides this, other studies showed that nanofillers can also decelerate physical aging of polymers.^{19,20} This was attributed to the presence of a layer with reduced mobility near or at the filler interface, leading to changing time-dependent properties resulting from the heterogeneities in the melt and in the glassy state.

[†]Present Address: SABIC, Plasticslaan 1, Bergen op Zoom 4612 PX, The Netherlands.

The first attempt to study the role of fillers on the chain dynamics was made by Lee and Lichtenhan.²¹ They showed that the addition of POSS to a cured epoxy increased the T_g and the relaxation time, thereby slowing down the molecular dynamics, and in turn the physical aging. Rittigstein and Torkelson showed that the addition of silica or alumina nanoparticles to thin films of PS, PMMA, or PVP decelerated physical aging as a result of confinement of the polymer chain by the nanoparticles.²² They showed that at 4 vol % of alumina particles, the aging can be reduced by a factor of 17. Priestley et al. and Vlasveld also found similar results in their study on PMMA-silica and poly(amide-6,6)-sodium fluorosilicate nanocomposites, respectively.^{23,24} In case of PMMA the physical aging rate of PMMA was reduced by more than a factor 20 with the addition of 0.4 vol % nanosilica, which was attributed to the reduced strength of the β -relaxation process resulting from hydrogen bonding between the PMMA ester side groups and the hydroxyl units on the surface of silica nanoparticles. Cheng et al. showed that impact modifiers can be used to delay the onset of physical aging by improving the toughness when the matrix loses its inherent ductility.²⁵ Dan et al. added poly(acrylate)/TiO₂ composite particles to PC to slow down the aging rate.²⁶ Physical aging is studied by following the recovery of a thermodynamic property below T_g , evolution of yield stress, and the instantaneous relaxation (or retardation) time after applying a perturbation.

The most common techniques used to study physical aging are DSC, Broadband Dielectric Spectroscopy, Mechanical Testing, Positron Annihilation Lifetime Spectroscopy, and Fluorescence Spectroscopy.²⁷

This article explores the effect of grafting on the physical aging and embrittlement of PC nanocomposites using enthalpy recovery and yield stress evolution experiments to capture the aging kinetics. The results are analyzed using the Tool-Narayanaswamy-Moynihan (TNM) model and a diffusion model. Finally, dynamic mechanical spectroscopy is used to understand the molecular features leading to the observed behavior in both PC and PC/silica nanocomposites.

EXPERIMENTAL

The bisphenol A-based polycarbonate (PC) used in this study was provided by SABIC Innovative Plastics, Bergen op Zoom, The Netherlands. The silica nanoparticles with an average particle diameter of 12 nm were purchased from Nissan Chemical Industries, Japan, as a suspension in methyl ethyl ketone (MEK) with ~30 wt % nanoparticles. All materials were used as received. The samples are coded as PC_{30y}, where y stands for the vol % of nanosilica.

The PC powder was first dried for 12 h at 110 °C before mixing with the nanosilica dispersion at concentrations of 0.7 and 3.0 vol %, and 0.1 wt % tris(2,4-di-tert-butylphenyl)-phosphite as processing stabilizer. The material was then dried for 24 h to remove the solvent. The silica nanoparticles were used without any further surface modification. This

material was compounded by using a ZSK-25 twin-screw extruder (Krupp Werner and Pfleiderer, GmbH, Germany) at a screw speed of 300 rpm. The temperature of the extruder was set at ~40 °C for the feeding section and up to 300 °C in the melting zone. Injection-molded ISO-tensile bars were used for the characterization. The samples were molded at a melt temperature of 280 °C with the mold temperature set at 60 °C.

After the extrusion and injection molding steps the molecular weights of the samples were analyzed to exclude degradation during processing. The molecular weight and the polydispersity index was determined by using size exclusion chromatography (SEC) on a Polymer Laboratories PL gel 5 μ m MiniMIX-C 250 $\times$ 4.6 mm column and a UV detector, operated at 254 nm. Measurements were performed at room temperature using dichloromethane as the solvent and toluene as flow marker. SEC calculations were performed against narrow PS standards. For the PC samples, the molecular weight obtained relative to PS data was converted to PC standards using a transfer function obtained by measuring 6 PC standards of known M_w .

The nanosilica is expected to react with PC during the extrusion step resulting in grafting to occur at the surface of the nanosilica particles. The evidence of chain grafting is provided by analyzing the extracted nanosilica particles from the PC nanocomposite by using Fourier Transform Infrared (FTIR) spectroscopy. To perform this, the PC nanocomposite was dissolved in dichloromethane at room temperature and centrifuged at 6000 rpm for 10 min. The supernatant solution was removed and the white precipitate (nanosilica) was collected at the bottom. Before characterizing the extracted nanosilica, the nanosilica was further purified to remove the physically bound polymer on the nanosilica. This was done by thoroughly washing the extracted nanosilica with dichloromethane followed by sonification and centrifugation for 10 cycles. The washing operation was repeated until no dissolved polymer was found in the supernatant solution, which was confirmed by FTIR spectroscopy. The dried nanosilica, neat polymer and the composites were characterized by using FTIR to study if the PC chains were chemically grafted on to the nanoparticle surface. A similar method was used by Wang et al.²⁸

FTIR spectroscopy was performed by using a Perkin Elmer Spectrum One FTIR spectrometer equipped with a Perkin Elmer spotlight 300 infrared microscope with a liquid nitrogen cooled HgCdTe (MCT) 16 $\times$ 1 linear array detector that was used to record micro-ATR spectra by employing a germanium hemispherical internal reflection element (IRE). Spectral acquisitions were performed in the reflection mode. To collect the ATR-FTIR spectrum from a flat surface with the miniature-Ge IRE, the sample was placed on the microscope XY-stage. A sampling spot on the surface was selected through an objective. The miniature-Ge IRE was then slid into the prealigned position and the microscope stage was elevated until the selected sampling area touched the tip of

FIGURE 1 DSC program for physical aging.

the IRE. Particular care was employed in order to achieve the same degree of contact for all measurements. Once good contact was established, the ATR-FTIR spectrum of the selected area on the surface was collected. The micro-ATR germanium crystal allowed a contact sample area with a diameter of 100 μm . The background spectrum was collected through the IRE when it was not in contact with the sample. All spectra were collected by using 16 scans in the range from 4000 to 600 cm^{-1} with a 4 cm^{-1} spectral resolution.

The dispersion of the nanosilica in PC after extrusion was analyzed by using transmission electron microscopy (TEM). The morphological studies were performed by using a Tecnai G2 transmission electron microscope, operated at 120 kV in bright field. Ultra-thin sections of 100 nm were obtained at room temperature by using a Leica Ultracut E microtome. Staining of the sections was not required, since the electron density of silica is much higher than that of PC.

Thermal analysis of the samples was carried out by means of the differential scanning calorimeter (DSC; Q2000 from TA Instruments). The heat capacity and the temperature were calibrated by using sapphire and indium, respectively. All DSC measurements were performed under a nitrogen atmosphere on samples of ~ 10 mg. Hermetic aluminum pans were used for all experiments. The physical aging experiments started with erasing the thermal history by heating the sample up to 200 $^{\circ}\text{C}$. The samples were subsequently cooled down to 30 $^{\circ}\text{C}$ at a rate of 20 $^{\circ}\text{C}/\text{min}$ and allowed to equilibrate before being stabilized at the temperature used for structural recovery (80, 125, and 143 $^{\circ}\text{C}$). All samples were aged at the same temperature as the difference in the glass transition temperature between the unfilled PC and the PC/silica nanocomposites was ~ 2 $^{\circ}\text{C}$. The samples were aged from a few minutes to 30 days before being cooled to 40 $^{\circ}\text{C}$ at a cooling rate of 20 $^{\circ}\text{C}/\text{min}$, prior to reheating at 10 $^{\circ}\text{C}/\text{min}$ to the melt. For aging times > 24 h, an external vacuum oven was used, after erasing the thermal history and quenching the samples in the DSC. After aging, the samples were cooled down to 30 $^{\circ}\text{C}$ and DSC thermograms were recorded. The second heating scans were performed immediately after a new quench (at 20 $^{\circ}\text{C}/\text{min}$), see profile shown in Figure 1.

The enthalpy recovery for an aging time t_a at a given temperature T_a was evaluated by integration of the difference between thermograms of aged and unaged samples, according to the relation:

$$\Delta H(t_a, T_a) = \int_x^y (C_p^{\text{aged}}(T) - C_p^{\text{unaged}}(T)) dT \quad (1)$$

where H is the enthalpy, C_p is the heat capacity.

Tensile tests were conducted on a Zwick/Roell Z5.0 tensile tester with a 5 kN load cell at ambient temperature (23 $^{\circ}\text{C}$). All experiments were conducted at a constant strain rate of 10^{-3} s^{-1} . To study embrittlement, samples were aged at 110, 125, 135, 140, and 145 $^{\circ}\text{C}$ for various times between 0 and 300 h. All tensile yield stresses listed in the results section are engineering yield stresses and each test was done in triplo to obtain reliable results.

The thermomechanical properties were characterized by using an ARES G2 rheometer from TA Instruments using a rectangular torsion fixture. The samples were tested from -130 – 170 $^{\circ}\text{C}$ with a heating rate of 3 $^{\circ}\text{C}/\text{min}$ by varying the frequency from 1 to 10 Hz. The dynamic variables such as the storage and loss modulus and phase angle were recorded.

THEORETICAL CONSIDERATIONS

Any system out-of-equilibrium always wants to go to equilibrium to minimize its internal energy. Amorphous glass formers achieve this by means of structural relaxation (i.e., evolution of thermodynamic variable like volume or enthalpy) when cooled down from an equilibrium melt and held isothermally at temperatures below T_g .²⁹ The change in physical properties of glass-formers as a consequence of structural recovery is known as physical aging, see Figure 2.

The most commonly used models to describe structural relaxation are the TNM model and the KAHR (Kovacs-Aklonis-Hutchinson-Ramos) model.^{30,31} Below the glass transition, the driving force for the relaxation in these models is the distance from the equilibrium. The TNM model uses the fictive temperature T_f to fully define the thermodynamic state of the material, whereas the KAHR model uses the distance of the property under investigation from its equilibrium value as a state parameter.^{32,33} Both are multiparameter models and are found equivalent for all practical applications. Here, we will adopt the TNM model approach to describe the aging and equilibrium kinetics, the model parameters are dependent on the material and are independent of the thermal history used.

The TNM model expresses the dependence on the structure and the temperature of the relaxation time as:

$$\ln \tau_{\text{TNM}} = \ln A_{\text{TNM}} + \frac{x \Delta h}{RT} + \frac{(1-x) \Delta h}{RT_f} \quad (2)$$

where τ_{TNM} is the relaxation time associated with physical aging, A_{TNM} is a constant, $\Delta h/R$ is the apparent activation

energy in the temperature range of the experiment, and x is the nonlinearity parameter, which partitions the dependence of τ_{TNM} on temperature and structure, the latter of which is quantified by the fictive temperature T_f . The fictive temperature is calculated as the intersection of the extrapolated liquid (above T_g) and glass (below T_g) heat capacity (C_p) by the relation¹⁸:

$$\int_{T_f}^{T > T_g} C_{p-\text{liquid}} - C_{p-\text{glass}} dT = \int_{T < T_g}^{T_g} C_p - C_{p-\text{glass}} dT \quad (3)$$

The TNM model parameters were calculated by fitting the model to the heat capacity data obtained from DSC. These model parameters are used to calculate the structural relaxation function, $\phi(t_a)$, as given below:

$$\phi(t_a) = \exp\left(-\frac{t}{\tau_{\text{TNM}}}\right)^\beta \quad (4)$$

where β is the shape or nonlinearity factor and it describes the width of time relaxation time distribution. The structural relaxation can also be determined experimentally as the ratio of the enthalpy at aging time $t_a = 0$ and $t_a \rightarrow \infty$ and is given by:

$$\phi(t_a) = \frac{\Delta H(t_a) - \Delta H_{\text{Plateau}}}{\Delta H(t_a = 0) - \Delta H_{\text{Plateau}}} \quad (5)$$

where $\Delta H_{\text{Plateau}}$ is defined as the value where the enthalpy does not change upon further aging.

Similarly, the structural relaxation function from the yield stress (σ) evolution can be calculated by using the following relation:

$$\phi(t_a) = \frac{\sigma(t_a) - \sigma_{\text{Plateau}}}{\sigma(t_a = 0) - \sigma_{\text{Plateau}}} \quad (6)$$

As mentioned above, the kinetics of physical aging (or structural relaxation) are intimately related to the molecular mobility (or the local dynamics in the glassy state). In case of nanocomposites, the segmental mobility is affected by¹⁸:

1. The interaction between the nanoparticle and the polymer matrix, being active at or close to the nanoparticle surface.
2. The presence of a physical barrier (due to interaction), which might change the length scale (or size) and temperature dependence of molecular mobility in glass-forming systems.

Based on this, the aging kinetics can be affected by the diffusion of free volume holes as shown by Boucher and coworkers. The diffusion of these holes can be described by^{15,17,18,34}:

$$\phi(t_a) = 1 - \frac{2}{\pi^{0.5}} \frac{A}{V} D^{0.5} t^{0.5} \quad (7)$$

$$\frac{d\phi(t_a)}{dt^{0.5}} = -\frac{2}{\pi^{0.5}} \frac{A}{V} D^{0.5} \quad (8)$$

where A is the total surface area where free volume holes disappear, V is the total volume, A/V is area-to-volume ratio

FIGURE 2 Schematic representation of the enthalpy and volume as a function of temperature for an amorphous polymer. Below the glass transition (T_g), an out-of-equilibrium amorphous polymer exhibits excess properties (volume or enthalpy) with respect to its equilibrium state. During the process of physical aging, a time-dependent decrease of these excess properties occurs. T_a , t_a are the aging temperature and aging time, respectively. Reproduced from Ref. 27.

of the nanoparticle, D is the diffusion coefficient at zero aging time, and t is the aging time.

RESULTS AND DISCUSSION

This section is organized in the following manner. First, the results from nanoparticle dispersion and grafting will be discussed. Then the thermal experiments will be presented followed by the mechanical analysis. Finally, the thermo-mechanical properties from DMTA will be shown. All results will be discussed in the framework of the TNM-model.

Nanoparticle Dispersion

Figure 3(a,b) shows the TEM micrographs of the dispersion of nanosilica in the PC matrices as a function of its concentration. At a concentration of 0.7 vol %, the agglomerate sizes are at an average diameter of 25–50 nm.

Increasing the concentration of nanosilica results in slightly larger agglomerates of the order of 70–100 nm with fewer primary particles visible. In both cases the particles are considered to be well dispersed as the interparticle/interagglomerate distance are fairly constant across the sample. This can be attributed to the interaction between the polar silica surface and the polar PC.

Evidence of Grafting

To verify whether grafting of the polymer chain takes place during melt extrusion, FTIR spectroscopy was used. Since the grafting of PC chain segments only occurs at the surface of the silica, using these techniques on the nanocomposite (bulk) samples might not give enough evidence for the grafting reaction. Therefore, extracted silica particles from the PC nanocomposites were used. A similar approach was used by Wang et al.²⁸ It is hypothesized that during the melt compounding of PC and silica nanoparticles, a reaction of the

FIGURE 3 TEM micrographs of the PC/nanosilica composites: (a) PC with 0.7 vol % nanosilica and (b) PC with 1.5 vol % nanosilica.

carbonate group of PC with the surface hydroxyl groups of the nanosilica occurs. Figure 4 shows a comparison of the FTIR spectra of extracted SiO_2 , pure SiO_2 , and PC. The spectra reveal that the SiO_2 extracted from the PC-matrix has additional peaks compared with the pure SiO_2 .

As a result of the grafting reaction, a shift of the $\text{C}=\text{O}$ and the $\text{C}-\text{O}$ peak in the FTIR spectrum can be expected. In case of the extracted SiO_2 the peak seen at 1775 cm^{-1} can be assigned to the stretching vibration of the carbonyl group, while the peaks at 1222 , 1190 , and 1162 cm^{-1} are due to the vibration of the $\text{C}-\text{O}$ bonds and the peak at 1100 cm^{-1} is due to the $\text{O}-\text{Si}$ stretching. The small peaks at 2966 and 1600 cm^{-1} can be attributed to the stretching vibration of CH_2 and the aromatic $\text{C}=\text{C}$ bonds, respectively. These peaks are characteristic peaks of PC, and when compared with the corresponding peak position of unfilled PC, all peaks shift to higher wavenumbers. This can be explained by the reaction between PC and the hydroxyl group on the surface of silica. Furthermore, the peak of hydroxyl group of extracted SiO_2 at 3439 cm^{-1} becomes distinctly weaker. This result reveals that the carbonyl group of the PC chains is bound to the SiO_2 particles, which results in the downshift of the $\text{C}=\text{O}$ stretching.

The lengths of the grafts could not be determined exactly as the reaction between the nanosilica and the polymer matrix (which is polydisperse) was not controlled. Therefore, it is postulated that the lengths of the grafts follow a polydisperse distribution, and the average of the distribution could be of the order of the molecular weight between entanglements or the entanglement molar mass (M_e) of PC. Furthermore, it was difficult to estimate the exact number of terminal hydroxyl groups on the silica surface and thus difficult to estimate the number of PC chains that might have reacted. However, as an estimate the ratio of the intensity of hydroxyl peaks might be used. Using this approach, we can say that $\sim 35\text{--}40\%$ of the OH on the surface have reacted.

Enthalpy Recovery

Physical aging is observed as an enthalpy or heat capacity overshoot around the glass transition temperature in a DSC heating experiment.²⁷ In general, the overshoot increases with aging time. This is shown in Figure 5 for an aging temperature of $125\text{ }^\circ\text{C}$.

Furthermore, the plot also shows an increase in the peak temperature, T_p , with aging time. These results are in agreement with what can be found in literature for PC as well as for nanocomposites in general.^{18,35,36} The PC/silica nanocomposites [Fig. 5(b,c)] also show broader and lower overshoot intensities as compared with the neat PC (5a) at aging time, $t_a > 1680\text{ min}$. The amount of enthalpy recovery, that is, $\Delta H(t_a)$ is calculated using eq 1 at an aging temperature of $125\text{ }^\circ\text{C}$ for various aging times, see Figure 5(d). Figure 5(d) shows that for short aging times, the amount of enthalpy recovery for the nanocomposite is comparable to the bulk (or unfilled PC). For long aging times, the values of $\Delta H(t_a)$ reach a plateau, which happens earlier in the nanocomposite compared with the bulk PC and is proportional to the silica concentration. This implies that the nanocomposites reach a final equilibrium structural state earlier, which is most probably caused by increased mobility of PC chains due to the grafting on the silica.

The difference in the plateau values and the amount of enthalpy recovery between the unfilled PC and PC/nanosilica is not negligible. It can be argued that this could arise from the equilibrium line (as shown in Fig. 2) shifting vertically down (below unfilled PC). However, given that the difference in glass transition temperatures is $\sim 2\text{ }^\circ\text{C}$ (between the unfilled PC and its nanocomposite) this hypothesis is not fully justified. Therefore, it can be concluded that the grafted nanoparticles have a real effect on the aging kinetics and the final structural state of PC.

The structural relaxation isotherms, calculated using eq 6, are shown in Figure 6. This approach is commonly used to quantify the physical aging and takes into account the thermodynamics for aging. Figure 6(a) shows that the addition of nanosilica to PC does not change the slope of the structural relaxation, implying that the aging behavior is similar, that is, compared with the unfilled PC the underlying molecular mechanism does not change for the PC/silica nanocomposites.

FIGURE 4 FTIR spectra of extracted SiO_2 compared with pure SiO_2 and PC. The curves are vertically shifted to make a comparison between extracted and pure nanosilica and PC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 5 DSC scans of the heat capacity versus temperatures for (a) PC₃₀, (b) PC₃₀ + 0.7 vol % nanosilica, (c) PC₃₀ + 1.5 vol % nanosilica, and (d) relaxed enthalpy versus log aging time for PC and its nanocomposites. All results are for an aging temperature of 125 °C. The dashed lines are guide to the eye. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This is also confirmed by a horizontal superposition of the data as shown in Figure 6(b), taking PC + 1.5 vol % silica as the reference. The curves superimpose very well and an activation energy of 1.2 MJ/mol is required for the shift of equilibrium. This value is in the same range as the one obtained by Engels (1.6 MJ/mol) in case of PC using the zero viscosity method.³³

Furthermore, Figure 6(a) demonstrates that PC/nanosilica samples begin to structurally relax faster than the unfilled PC sample. This indicates that the nanocomposites age faster. The rate of physical aging or structural relaxation is quantified by the time it takes for the sample to reach the plateau rather than its slope. Thus, the results shown in Figure 6(a,b) are consistent with the physical aging observed when comparing it with Figure 5(d).

To further strengthen this conclusion, the data are analyzed using the TNM model as described in the previous section. $\Delta H/R$, β , x , and $\ln A$ are the four parameters used to describe the glass transition kinetics in the TNM model, see eqs 2 and 5. An estimate of the apparent activation energy

parameter can be obtained from the cooling rate (φ) dependence of T_g or T_f , see eq 9 and Figure 7.

$$\frac{\Delta H}{R} = - \frac{d \ln \phi}{d \left(\frac{1}{T_f \text{ or } T_g} \right)} \quad (9)$$

Based on the fit, a value of $\Delta H/R = 138$ kK is obtained, see Table 1.

The results presented in Figure 7 are in line with the findings of Tao and Simon, where they report a similar cooling rate dependence on the fictive temperature and no significant change in the polymer dynamics associated with T_g .^{37,38} The value of x in the TNM model lies between 0 and 1, see Table 1. Values closer to 0 imply a strong structural dependence and therefore a more nonlinear relaxation process, and values close to 1 indicate a lesser dependence on structure. The value of β also lies between 0 and 1; $\beta = 1$ indicates a single exponential relaxation process and the degree of nonexponentiality or the broadness of the relaxation process increases with decreasing values of β .^{39,40} The values of

FIGURE 6 (a) Structural relaxation function of PC and PC/silica nanocomposites at 125 °C, solid lines represent the fit to TNM model and (b) superposition of structural relaxation function of PC and PC/silica nanocomposites using 1.5 vol % silica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 7 Variation of T_f with cooling rate (ϕ) for PC and PC/silica nanocomposites. The solid lines represent the best fits to the data. Based on the fit a $\Delta h/R = 138 \text{ kK}$ was found for all samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1 TNM Model Parameters from DSC

Sample	$\ln A$ (s)	x	β	$\Delta H/R$ (kK)	$\Delta H_{\text{plateau}}$ (J/g)
PC ₃₀	-294.1	0.46	0.65	138.0	3.30
PC ₃₀ 0.7S	-294.1	0.43	0.60	138.0	2.90
PC ₃₀ 1.5S	-294.0	0.41	0.57	138.0	2.20

β and x are determined by fitting the TNM model to the heat capacity data of PC and PC/silica nanocomposite (see Fig. 5). The fitting results are shown in Figure 8.

The values obtained from these fits were also used to fit the structural relaxation data shown in Figure 6(a). As can be seen, both from Figures 6(a) and 8, the TNM model can describe the physical aging process for both PC and PC/silica nanocomposites well. The values obtained for the pre-exponential factor $\ln A$ are constant. It is interesting to note the decrease in β and x from the unfilled PC to the PC nanocomposites.

This decrease indicates that the addition of nanosilica broadens the distribution of relaxation times and makes aging more dependent of the structure. Furthermore, Boucher et al. showed that these parameters are sensitive to surface-to-volume ratio of the nanoparticles.

The above observations along with Figure 6(b) and the 2 °C difference in glass transition temperature provide evidence that the grafted nanosilica does not alter the “molecular mechanism” or the underlying mechanism for physical aging of PC. However, their presence accelerates aging. It should be noted that the values obtained for $\Delta H/R$, β , x , and $\ln A$ are in good agreement with the values published in literature for PC.^{29,41,42}

FIGURE 8 TNM model fits of 10 K/min heating rate data for PC and PC/silica nanocomposites using a constant value of $\Delta H/R = 138 \text{ kK}$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 9 Enthalpy relaxation function $\phi(t)$ with the square root of the aging time for the different samples. Solid line are the fits. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As discussed above, the addition of grafted nanoparticles accelerates the aging process while the state of equilibrium is reached faster. It is proposed that the acceleration occurs due to the “diffusion” of free-volume holes or distribution of the potential energy landscape, as described in the theoretical section. The higher the diffusion coefficient faster the aging rate. The diffusion coefficient at the beginning of the aging process can be calculated from the slope of the tangent to the plots of $\phi(t)$ versus $t^{0.5}$. As illustrated in Figure 9 the diffusivity is calculated, by using eqs 7 and 8.

The surface-to-volume ratio and the diffusivities were calculated and the results are shown in Table 2. The surface-to-volume ratio for the unfilled PC was calculated by using the procedure described by Boucher et al. and Curro et al.^{18,43} The diffusion rates shown in Table 2 indicates accelerated physical aging of PC in the presence of nanosilica and supports the observations from the TNM model.

Yield Stress Evolution

In this section, the effect of grafted nanosilica particles on the mechanical properties of PC upon aging is studied. It is known that annealing PC below T_g results in an increase of the yield stress which leads, at some point in time, to embrittlement.^{14,44} The embrittlement occurs as a result of strain localization, which can be accelerated by increasing the annealing temperature (dependent on the geometry and testing conditions).⁴⁵

For instance, annealing PC at 125 °C makes it brittle within 1 h.^{14,33} With the addition of fillers, the strain localization increases at the interface of the nanoparticle thus leading to faster embrittlement. However, this can be controlled by making the interface of the filler compatible with the bulk.^{46,47} Bearing this in mind and recalling that part of the PC chains are grafted onto the silica surface, this section will evaluate the mechanical performance of PC/silica nanocomposites by using the approach used by Engels et al.¹⁴ The

results obtained from the mechanical testing will be compared with the TNM model and other results obtained from thermal analysis.

Figure 10 shows the evolution of the yield stress as a function of time and temperature for PC₃₀. At 140 °C (close to the glass transition, T_g , i.e., 145 °C), a leveling off is observed indicating that PC has reached equilibrium. The data shown in Figure 10(a) can be transformed into a master curve by using Time-Temperature-Superposition (TTS), under the assumption of thermo-rheological simplicity. The master curve is constructed by using an Arrhenius-type temperature dependence, resulting in a shift factor (a_T) given by:

$$a_T = \exp\left(\frac{\Delta U}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \quad (10)$$

where ΔU is the activation energy, R is the universal gas constant, T is the annealing temperature, and T_{ref} is the reference temperature. The same procedure is followed for the PC/silica nanocomposites, see Figure 10(b). For all samples a $\Delta U = 205$ kJ/mol is used.²⁶ The above procedure was used for temperature below T_g . For temperatures close to T_g , an additional vertical shift was required. The vertical shift for both the nanocomposites and the neat polymer were the same.

The yield stress evolution can be described by:

$$\sigma_y(t, T) = \sigma_{y0}(T) + c \log\left(\frac{t_{\text{eff}}(t, T) + t_a}{t_0}\right) \quad (11)$$

where σ_{y0} and c are constants, which give the vertical intersection of the curve with the vertical axis at $t = 1$ s, and the slope of yield stress with time, respectively. t_a is the initial age of the material, which is dependent on the mold temperature, and $t_0 = 1$ s is a scaling constant and the effective time t_{eff} is defined as:

$$t_{\text{eff}} = \int_0^t a_T^{-1}(T(t)) dt \quad (12)$$

a_T is given by eq 10.

The relations mentioned in eqs (10–12) were used to describe the data in Figure 10 and are represented by solid lines. Table 3 gives the parameters used.

The equations given above can describe the yield stress evolution for aging times $< 10^5$ sec quite well, that is, the linear part of the TTS curve (annealed below T_g).

TABLE 2 Diffusion Coefficient Values Obtained from DSC Measurements

Sample	V/A (cm)	D (cm ² s ^{−1})
PC ₃₀	2.7×10^{-7}	9.4×10^{-20}
PC ₃₀ 0.7S	3.3×10^{-7}	2.2×10^{-19}
PC ₃₀ 1.5S	3.3×10^{-7}	4.6×10^{-19}

FIGURE 10 Yield stress versus annealing time: (a) different annealing temperatures for PC₃₀OS and (b) TTS curves constructed from (a) using $T_{\text{ref}} = 125^\circ\text{C}$ and $\Delta U = 205\text{ kJ/mol}$ for all materials. The dashed line is given by eq 12. The error in the yield stress is $\pm 0.2\text{ MPa}$. The lines indicate fit to the model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As expected, at annealing times $< 10^5\text{ s}$, the nanocomposites show a higher yield stress (proportional to the silica nanoparticle concentration - due to reinforcement). After aging time $> 10^5\text{ s}$, the yield stress reaches a plateau value. The plateau value decreases with increasing nanosilica concentration. The plateau indicates that the samples have reached their equilibrium, which occurs earlier in the nanocomposites than unfilled PC. Eq 11 does not capture the yield stress evolution at the equilibrium state. This higher values of yield stress at shorter times and the lower values at longer times suggests that the grafted nanosilica particles are acting as an antiplasticizer and plasticizer, respectively. Furthermore, the decrease in yield stress occurs close to the glass transition temperature, indicating an increase in the mobility of the polymer chains. While the decrease in the yield stress plateau is in line with observed T_g decrease, the magnitude cannot be fully explained by that alone, and the increased mobility due to the presence of the grafts

on the nanosilica particle has to be taken into account. The results obtained on the evolution of the yield stress on annealing are very similar to the enthalpy overshoots observed for PC and PC/silica nanocomposites in the previous section, indicating that the nanocomposites age faster. This demonstrates the qualitative equivalency between the bulk (such as mechanical properties) and calorimetric measurements. This equivalency was previously shown for unfilled PC.^{35,41,48} Furthermore, these master curves are analyzed using the TNM model as shown in Figure 11. Figure 11(a) shows the TTS-shifted curves of the yield stress and their corresponding fit to the TNM model. The model describes the master curve very well.

The parameter set obtained by fitting the model is given in Table 4. The values of $\Delta H/R$ and β are similar to the ones obtained via fitting the TNM model to the DSC experiments, while the nonlinear parameter, x , is different. The lower value of x suggests that physical aging has a strong structural dependence. This supports the argument that the relaxation close to the glassy region is affected due to the grafts.

The parameters in Table 4 are used to plot the structural relaxation parameter using eq 6, see Figure 11(b). The results obtained in Figure 11(b) are similar to the structural relaxation parameter obtained from the enthalpy relaxation experiments, and thus the same conclusions that we reached are valid. However, unlike the structural relaxation obtained in Figure 6(a), the slope of the relaxation curve is not the same for the nanocomposites and the unfilled PC, see Figure 11(b) inset. This indicates that the kinetics of aging has a structural dependence. Furthermore, the relaxation function decays slower in case of the yield stress and the time to full structural relaxation differs by approximately a decade between the enthalpy relaxation and yield stress experiments. This difference could arise from the stress-induced relaxation, which affects the time scales of relaxation processes for different structural units.

Dynamic Mechanical Analysis (DMA)

DMA was performed to observe and understand the changes in cooperative segmental motions in the presence of nanosilica (grafted with PC) and upon aging. Figure 12 shows the various relaxations in PC and PC/silica nanocomposites. The relaxations can be divided into γ_1 , γ_2 , β , and α (or T_g). The γ -transitions are related to molecular motions, in particular to the phenyl ring rotation (γ_1) and carbonyl rocking (γ_2). The β -transition is related to the residual stress in the system due to chain packing in the glassy state, which is affected by

TABLE 3 Master Curve Parameters

Sample	σ_{y0} (MPa)	c (MPa)	t_a (s)
PC ₃₀ 0S ^a	22.0	3.6	7.5×10^{10}
PC ₃₀ 0.7S	23.5	3.6	7.5×10^{10}
PC ₃₀ 1.5S	24.5	3.6	7.5×10^{10}

^a Parameters used by Engels et al.¹⁴

FIGURE 11 (a) Master curves of yield stress versus annealing time and (b) structural relaxation at $T_{\text{ref}} = 125^\circ\text{C}$. The solid lines indicate the fit to the TNM model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aging. Finally, the transition is refers to the glass transition temperature.

In case of PC, the relaxation peaks are observed at -100 , -50 , 80 – 120 , and 148°C , respectively.⁴⁹ On comparing the effect of grafted silica on the relaxation, that is, PC vs. PC/silica nanocomposites, the following points are observed:

1. The γ_2 -relaxation has shifted to a higher temperature, that is, from -50 to 0°C for nanocomposite,
2. A decrease in intensity of the γ_1 -relaxation in case of the nanocomposite. This is proportional to the silica concentration and suggests that the silica nanoparticles affect the free volume.
3. T_g shows a decrease with increasing silica content in line with the DSC results.

TABLE 4 TNM Model Parameters from Mechanical Testing

Sample	$\ln(A)$	x	$\Delta H/R$ (kK)	β	σ_{plateau} (MPa)
PC ₃₀	−251	0.36	117	0.6	81
PC ₃₀ 0.7S	−251	0.3	118	0.57	79
PC ₃₀ 1.5S	−250	0.25	117	0.55	75

FIGURE 12 Various transitions in PC and PC/silica nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The shift in γ_2 -relaxation suggests that the PC could be altered due to reaction with the nanosilica via the carbonyl bond.^{49–51} It could be most likely that the grafts on the nanoparticles resulted in altering the mobility (increase) around the nanoparticle with an influence zone approximately equal to the length of the grafts and around the nanoparticle. Other studies showed that the γ_2 -transition does not shift if there is no chemical interaction. For instance, Pötschke et al. showed that melt blending carbon nanotubes with PC did not alter the any of the above transitions.⁵²

Next, the effect of the strong interaction between PC and silica and its effect on aging was also analyzed by DMA, see Figure 13. The following can be observed upon aging the samples at 125°C :

1. The T_g slightly increases and reaches a constant value.
2. The increase in the storage modulus on the addition of nanosilica indicates that the nanosilica particles might act as an antiplasticizer.^{53,54}
3. The β -relaxation is related to both relaxation of stress and embrittlement and the intensity is proportional to the rate of change. The decrease in intensity for the nanocomposites occurs faster, indicating that the residual stress decreases faster, while the embrittlement occurs faster.
4. The intensities of the γ_2 -relaxation show an increase followed by a decrease, while the γ_1 -relaxation continuously decreases.

Wyzgoski and Yeh showed that there is a direct relation between the peak intensity of the $\tan(\delta)$ and the free volume.⁵⁴ In their study, they showed that adding either a plasticizer or anti-plasticizer decreases the free volume. Similar results were found by Kierkels et al. in PC and PS.^{53,55} Therefore, it can be concluded that all samples showed a decrease in the free volume as a result of a decrease in intensity of γ_1 -peak. Figure 14 shows a plot of the normalized peak intensity of the γ_1 -transition with reference to 0 h annealing versus annealing time. The plot shows that the

FIGURE 13 (a) Storage modulus (G') versus temperature, and $\tan(\delta)$ versus temperature for various aging times at an aging temperature of 125°C and at 1 Hz for (b) PC₃₀, (c) PC₃₀ + $0.7\text{ vol \%}$ silica, and (d) PC₃₀ + $1.5\text{ vol \%}$ nanosilica. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

maximum decrease in free volume is found for $1.5\text{ vol \%}$ silica followed by $0.7\text{ vol \%}$ silica and unfilled PC. This decrease in free volume can also be linked to embrittlement via chain mobility, that is, the decrease in free volume restricts the mobility.^{56,57} Thus, based on Figure 14, it can be expected that PC/silica nanocomposites are more brittle than PC and that the samples embrittle on increasing the silica concentration and aging time. Considering the reduced free volume observed in the DMA experiments as well as the diffusion experiments (Fig. 9), it can be argued that the nanosilica has caused PC to get closer to equilibrium state, that is, the shift in the out-of-equilibrium thermodynamic parameter closer to the equilibrium line as shown in Figure 2. Furthermore, the faster equilibrium reached by nanocomposites could indicate that the initial value of the enthalpy already corresponds to a partially relaxed structure of the polymer. This can be explained by the increased chain mobility close to the glass transition caused by the interaction between the grafts and the bulk.

Therefore, deceleration of physical aging mentioned in the introduction section may be apparent and could be the result of accelerated aging.¹⁸ This conclusion is also in line with the mechanical testing and the TNM model.

CONCLUSIONS

The effect of grafted silica nanoparticles on the physical aging of PC was studied by using calorimetry and mechanical testing (i.e., yield stress evolution and DMA.). By plotting the enthalpy recovery measured in DSC and the yield stress measured in tensile test versus aging time, it was observed that nanocomposites reach the plateau earlier than unfilled PC. Thus, the grafted silica nanoparticles were found to accelerate the physical aging. The time taken to reach the plateau and the value of the plateau in both cases decreased with increasing the concentration of nanosilica. The TNM model was used to model the aging kinetics. According to

FIGURE 14 Normalized intensity (γ -transition) versus annealing time for PC and PC/silica nanocomposites at 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this model, the silica nanoparticles accelerate the structural recovery of PC, while they do not affect the molecular mechanism. According to this model, the silica nanoparticles accelerate the structural recovery of PC, while they do not affect the molecular mechanism. Furthermore, the TNM model parameters indicate a stronger structural dependence on the aging followed via the yield stress evolution than the enthalpy recovery implying that the relaxation time scales in thermal and mechanical experiments are different.

The DMA analysis revealed that the decrease in free volume upon aging was more significant in case of the PC/silica nanocomposites. This further confirms that the aging in nanocomposites occur faster and could indicate that PC/silica nanocomposites embrittle faster.

Finally, all the observations can be rationalized considering that the physical aging process is driven by the distribution of the energy landscape due to the increased chain mobility in the surroundings of the particle.

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