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Processing of thermoplastic polymers using reactive solvents

Han E H Meijer, Rob W Venderbosch, Johannes G P Goossens and
Piet J Lemstra

Centre for Polymers and Composites, Eindhoven University of Technology, PO Box 513,
5600 MB Eindhoven, The Netherlands

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Abstract. The use of reactive solvents offers an interesting and flexible route to extend the processing characteristics of thermoplastic polymers beyond their existing limits. This holds for both intractable and tractable polymers. The first mainly applies for amorphous high- T_g polymers where processing may be limited due to the high temperatures required which can cause problems related to degradation and where the solvent helps to decrease the processing temperature considerably. A prime example here can be found in the system poly(phenylene-ether) PPE/epoxy. The second mainly holds for semicrystalline polymers and the attention here is focused on obtaining low viscosities in order to be able to apply alternative processing routes, like pouring or casting, for those polymers which are generally easy to process by more conventional techniques like injection moulding or extrusion. In this paper the model system poly(ethylene) PE/styrene is investigated. In both cases, based on intractable and tractable polymers, the solvent is polymerized after moulding, thus converting into a non-solvent, and becomes, after the concurrent phase separation and phase inversion, an integral and often structural part of the final product. Interestingly, specific morphologies, in terms of the size of the dispersed (previous solvent) phase formed or the position and thickness of *in situ* formed interlayers when polymerization occurs in the presence of a polar surface, can be obtained which can otherwise extremely difficult, or not at all, be realized. Moreover, flexibility of the choice of the reactive solvent creates tuneable mechanical (and, if requested, other) properties of those phases, varying from glassy, with a T_g of typically 200 °C, to complete rubbery, with a T_g far below room temperature. Of course a disadvantage of the technique is that a polymerization step must occur after the shaping process. Compared to more standard reactive processing techniques, however, clear advantages can exist with respect to the occurrence of early vitrification—yielding a fast demoulding possibility—induced by the reaction induced phase separation, and the fact that the continuous thermoplast phase ultimately determines the main product properties, including the possibility of second-stage deformability and reprocessability.

Introduction

In order to meet the ever-increasing demands put on polymeric materials in new applications, polymer chemists continue to synthesize new polymers that often can be regarded as intractable from a processing point of view. This is the case for either high-temperature polymers, developed for structural applications where a high glass transition temperature is required, or for polymers designed for those applications where a high molecular weight is necessary for mechanical reasons. Often the main advantage of polymers over the more traditional materials, which is their easy processability, is lost. In order to gain processability in practice compromises have to be accepted. Basically, one could state that most recent

polymer development, as occurs in most of the large research laboratories of the main polymer producers all over the world and sometimes in the laboratories of important and big enough end-users, can be summarized as finding a continuous compromise to the stated controversy between introducing a low enough viscosity as required for easy processing while maintaining the most important part of the product's mechanical properties in terms of stiffness, strength and, especially, work-to-break (impact strength).

Traditionally, solutions are sought by tuning the molecular weight distribution, by introducing flexibility to the polymer backbone, thus lowering the T_g , or by blending the intractable polymers with more flexible polymers, for example in poly(phenylene-ether)-poly(styrene) blends (Noryl from General Electric Plastics: PPE-PS). Alternatively, simple processing techniques with hardly any flow can be used combined with expensive post-machining, for example in products made from pressed and fused plates of ultra high molecular weight poly(ethylene) (UHMWPE), or processing aids like volatile solvents are applied, for example in spin coating processes or solution spinning operations for example of the same UHMWPE to produce high-performance fibres. The last compromises are restricted to products with a high surface to volume ratio, typically fibres and films, and violate the more modern environmental requirements and thus necessitate the need of complete solvent recovery. Moreover, the final product is only a (often relatively small) part of the main stream in the production process that almost exclusively consists of closed loop evaporation and condensation operations for the solvent. All those causes make the products of such a process necessarily expensive, but, more important, limit the use of those attractive polymers in many possible new applications. Also reactive processing techniques are used, as in prepreg fabrication, followed by hand lay-up or press operations, and filament winding techniques, as applied in composite manufacturing. Bulk moulding compounds (BMC) were developed that can be injection moulded, with or without the application of in-mould coatings. There are processes like casting and pouring of monomers or more elegant, automated processes like resin transfer moulding (RTM), and reinforced or structural reaction injection moulding (RRIM, SRIM). These techniques seemingly solve the stated contradiction, since monomers are generally present during processing which are converted into polymers only after their final shaping operation. Disadvantages and limitations exist, however. Apart from the introduction of chemistry to the end-user, which does not automatically guarantee the best control during polymerization, there is a need for almost complete conversion, since the product properties are directly and exclusively determined by the chemistry and only at the end of the polymerization are the mechanical properties obtained.

A possible solution to some of the problems mentioned is to process polymers with the use of reactive solvents. Basically the idea is to sell the solvent with and within the product after having it made harmless by applying a polymerization step. During processing, the solvent either allows a large reduction in the processing temperature (which is important for the intractable high-temperature polymers) or decreases the viscosity of the polymer such that standard (for intractable high molecular weight polymers), or (for tractable polymers) alternate, processing techniques, where a low viscosity is prerequisite, come within reach. After shaping, the solvent is converted into a non-solvent induced by the first polymerization step. Phase separation results, generally accompanied by phase inversion which happens to occur already when the volume fraction of the polymer exceeds about 10%. A dispersed phase results, locking the original solvent inside the thermoplastic matrix material that forms the continuous phase. A schematic impression is depicted in figure 1.

In this paper we will review several systems that can be regarded as some primary examples of how this processing technique could function. The first, and by far most

Figure 1. Schematic representation of the concept of processing of intractable polymers using reactive solvents.

extended part (Part I: intractable polymers), deals with the system PPE-epoxy [1–6]. After investigating the miscibility, the focus will be on the rheology, important during processing, and the morphology, which determines the final product properties. Different epoxies, aromatic versus aliphatic, are used to tune the properties of the dispersed phase. Accordingly, we will turn to composite applications where unique morphologies are obtained since the epoxy solvent during and/or after phase separation preferentially accumulates at the polar fibre surfaces. Possibly the optimal composite could be designed using this technique. In the second part (Part II: tractable polymers), the system poly(ethylene)-styrene (PE-St) [7], or alternatively poly(ethylene)-butylmethacrylate (PE-BMA) [8] will be presented. In this case, crystallization can interfere with the chemically induced phase separation and the focus will be on the morphology development during polymerization. The paper ends with some outlooks on possible applications in other fields, making use of the flexibility of this technique.

PART I: INTRACTABLE POLYMERS

1. Miscibility, rheology and morphology

1.1. Materials choice: PPE-epoxy

The materials used in this study were poly(2,6-dimethyl-1,4-phenylene ether) (PPE) as the thermoplast, an aromatic (stiff) epoxy, diglycidyl ether of bisphenol-A (DGEBA),

an aliphatic (flexible) epoxy, diglycidyl ether of polypropylene oxide (DGEPPPO) and the crosslinkers polypropylene oxide diamine (D-400) or the sterically hindered, and thus slow, 4,4'-methylene-bis(3-chloro-2,6-diethyl aniline) (M-CDEA) and 4,4'-methylene-bis(2,6-diethyl aniline) (M-DEA) (see figure 2).

a)

b)

c)

d)

e)

f)

Figure 2. Structural formula of (a) PPE, (b) DGEBA, (c) DGEPPPO, (d) Jeffamine D-400, (e) M-CDEA, (f) M-DEA.

Although epoxy resin proves to be a surprisingly effective solvent for many polymers, as can be concluded from a literature survey [9-53] (see table 1), PPE is chosen as a model polymer for its interesting mechanical properties in terms of a high glass transition

temperature, T_g , a relatively high intrinsic impact strength and more or less standard values for modulus, yield stress and breaking strength. Given its high- T_g of 220 °C, the processing temperature should be around 350 °C. This, in combination with the limited thermal and oxidative stability, results in severe degradation and, consequently, PPE can be considered as a classical example of an intriguing but intractable polymer.

Table 1. Overview of the epoxy/thermoplastic systems reported in literature [9–53].

Polymer	Epoxy resin/curing agent	Molecular weight (kg mol ⁻¹)	Concentration (wt%)
Poly(ethylene oxide)	DGEBA [10]	20 (n)	0–100
	DGEBA/TEPA [10]	20 (n)	0–90
Poly(methyl methacrylate)	DGEBA [11]	28.3 (n)/60 (w)	0–100
	DGEBA/3DCM [11]	28.3 (n)	2–10
	DGEPO/D230 [9]	200 (w)	90–100
Poly(styrene)	DGEPO/D230 [9]	200–400 (w)	50–100
Poly(butylene terephthalate)	DGEBA [12]	37.8 (v)	0–10
	DGEBA/DDM [13]	nr	5–20
Poly(phenylene ether)	DGEBA/PIP [14–16]	34–42.5 (w)	< 15
	DGEBA/M-CDEA [17]	32 (w)	15–100
	DGEPO/M-CDEA [18]	32 (w)	50–100
Poly(ether imide)	TGDDM/DDS [19–25]	12–18 (n)	0–30
	TGAP/DDS [26]	18 (n)	0–40
Poly(imide)	TGDDM/DDS [27]	10 (n), 26 (w)	0–10
Poly(carbonate)	DGEBA/CTBN/DDM [28]	16 (v)	0–20
Phenolphthalein poly(ether ether sulphone)	DGEBA [29]	nr	0–100
	DGEBA/DDM/DDS/MA/PA [29]	nr	0–20
Poly(ϵ -caprolactone)	DGEBA/DGEBF/PGEPPF [30, 31]	20 (v)	0–25
	DDM/NMA/TETA		
Poly(<i>p</i> -phenylene terephthalamide)	DGEBA/DDM [32]	nr	0–10
Poly(ether sulphone)s	TGDDM/DGEBA/TGAP [33–45]	85 (w)–145 (w)	0–60
	DDS/DDM/PA/Dicy	85 (w)–145 (w)	0–60
Poly(aryl ether sulphone)s	DGEBA/DDS/PIP [46–51]	3 (n)–15 (n)	0–25
Poly(aryl ether ketone)s	DGEBA/DGR/DDS/DDM [52, 53]	3 (n)–7 (n)	0–40

nr: no value reported, n, w, v: number, weight or viscosity average molecular weight.

DGEBA: diglycidyl ether of bisphenol-A; DGEBF: diglycidyl ether of bisphenol-F; TGDDM: *N, N, N', N'*-tetraglycidyl 4,4'-diaminodiphenylmethane; TGAP: triglycidyl *p*-aminophenol; DGR: diglycidyl ether of resorcinol; PGEPPF: polyglycidyl ether of phenol formaldehyde novolac; DGEPO: diglycidyl ether of poly(propylene oxide); DDM: 4,4'-diaminodiphenylmethane; DDS: 4,4'-diaminodiphenylsulphone; M-CDEA: 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); PIP: piperidine; Dicy: dicyandiamide; 3DCM: 4,4'-diamino-3,3'-dimethyldicyclohexylmethane; TEPA: tetraethylenepentamine; MA: maleic anhydride; PA: phthalic anhydride; Jeffamine D230: polypropylene oxide diamine; NMA: 'Nadic' methyl anhydride; TETA: triethylenetetramine.

1.2. Thermally induced phase separation (TIPS)

The miscibility of PPE–DGEBA was measured by light scattering (632 nm). The cloud point curve, which indicates the onset of phase separation, was recorded upon slowly cooling ($1\text{ }^{\circ}\text{C min}^{-1}$) solutions of different compositions, contained between two glass covers. Below 30 wt% epoxy the glass transition temperature was measured by using dynamic mechanical thermal analysis (DMTA) at 1 Hz in tensile mode during heating at $3\text{ }^{\circ}\text{C min}^{-1}$. The resulting phase diagram is given in figure 3, from which it can be concluded that rather high temperatures are required to obtain homogeneous solutions. This figure combines the data of light scattering with those obtained via rheological measurements (see section 1.4).

Figure 3. Phase diagram of PPE/epoxy solutions as derived from light scattering experiments ($\bullet$, $\blacktriangle$, $\blacktriangledown$), DMTA ($\circ$, $\triangle$) and rheology ($\blacklozenge$): (—) onset phase separation; (---) T_g -composition line of heterogeneous solutions; (- · - ·) T_g -composition line of homogeneous solutions.

The cloud point curves exhibit a typical upper critical solution temperature (UCST) behaviour, commonly observed for polymer–solvent systems. As expected, a decrease in the PPE molecular weight enhances the miscibility of the system and results in a considerable shift of the cloud point curve to lower temperatures. Since PPE as well as the epoxy resin are polydisperse, the cloud point curves may not be regarded as binodal curves and do not give any information about the composition of the coexisting phases. The inflection in the curves clearly reveals the influence of the molecular weight distribution, i.e. the critical point is not situated at the top of the curves. The T_g -composition lines, as determined by DMTA and as calculated with the Fox equation [54] (using a T_g of 222 and $213\text{ }^{\circ}\text{C}$ for

Figure 4. Scanning electron micrographs of PPE/epoxy solutions with a PPE molecular weight of 10 and 30 kg mol⁻¹ and a PPE content of 30–80 wt%, after cooling from 200 °C to room temperature at a rate of 1 °C min⁻¹.

PPE with a molecular weight of 30 and 18 kg mol⁻¹ respectively and a T_g of -18 °C for the epoxy monomer), are also plotted in the same figure and they intersect the cloud point curves at a PPE content of ~ 70 wt%. Thus, solutions with less than 70 wt% PPE phase separate upon cooling; however, phase separation is not complete, but arrested as soon as the PPE-rich phase vitrifies at this intersection point (the so-called Berghmans point [55,56]).

Figure 5. Glass transition temperature versus curing agent concentration of the epoxy (Δ) and PPE phase ($\blacktriangle$), as determined using DMTA (frequency 1 Hz) for cured blends containing 35 wt% epoxy (30 kg mol^{-1}) (the broken line indicates the stoichiometric concentration).

As a result of this phenomenon, which physically can be regarded as a thermoreversible gelation, all the phase separated solutions exhibit a T_g of $\sim 100^\circ\text{C}$, as indicated by the broken horizontal line in figure 3. This typically TIPS (thermally induced phase separation) behaviour is in essential contrast to the CIPS (chemically induced phase separation) process, which is the genuine topic of this paper. In the latter case complete phase separation can be accomplished as will be shown below. The morphologies resulting from the TIPS process are shown in figure 4 and reveal a phase-inverted morphology, with a dispersed epoxy phase in a continuous PPE phase, for all PPE fractions investigated (i.e. $\geq 30 \text{ wt}\%$). In accordance with the phase diagram of figure 3, a homogeneously vitrified material is found above 70 wt% PPE. The size of the dispersed phase is relatively uniform and depends on the PPE fraction, apparently due to retardation of the coarsening process by the presence of a more viscous matrix.

1.3. Chemically induced phase separation (CIPS)

In solutions with reactive solvents, the main driving force for phase separation is the increase in the molecular weight of the solvent via a step polymerization mechanism. As shown by Verchère and co-workers [57–61] and De Graaf [62], for epoxy systems toughened with (in order to prevent phase inversion) relatively small volume fractions of carboxyl-terminated butadiene–acrylonitrile copolymer (CTBN rubber) and poly(ether sulphone) (PES), respectively, a minor increase in the molecular weight of the solvent significantly reduces the miscibility of the system and phase separation is initiated at relatively low conversions. CIPS can be regarded as inducing a shift, and concurrent change in shape, of the cloud point curves in the phase diagram (see figure 3) towards higher temperatures

Figure 6. Scanning electron micrographs of the dispersed epoxy phase isolated from PPE/epoxy cured at 225 °C with an initial composition of (a) 60, (b) 50, (c) 40 and (d) 20 wt% epoxy.

Figure 7. Number-average particle size of PPE/epoxy systems: as a function of composition after isothermal curing with M-CDEA ($\blacktriangle$) and diethyltoluenedi-amine: DETDA ($\triangle$) at 225 °C or after cooling from the homogeneous region to room temperature at a rate of 1, 2, 5 and 10 °C.

and, comparing the process to the more familiar TIPS, it is sometimes referred to as a 'chemical quench', which is confusing. Of course the tendency of coarsening [63–67], eventually resulting in two fully separated layers as in TIPS, exists, but now it is counteracted by a number of processes. The coarseness of the final morphology is controlled by the competition of the rates of phase separation and coalescence (i.e. diffusion—Ostwald ripening—and hydrodynamically driven break-up and coalescence processes) on one hand and the rates of vitrification and gelation on the other hand.

The required compatibility of the curing agents with the PPE/epoxy solutions makes it difficult to estimate their appropriate concentration. For aromatic diamines, the concentration should be equal to the stoichiometric ratio, but an excess is likely to be required in order to compensate for any loss of curing agent due to dissolution in the PPE phase after phase separation. For this reason the optimal concentration, defined as the concentration which results in the highest T_g of the epoxy phase, was determined using DMTA. Figure 5 shows the results. First, it is recognized, as already anticipated above, that with CIPS higher T_g values of the PPE are obtained compared with the maximum value ($T_g \sim 100^\circ\text{C}$, see figure 3) resulting from TIPS, indicating that now complete phase separation is indeed obtained, at least for polymerization temperatures $\geq T_{g,max}$. This is of utmost importance, not only for the expected mechanical properties, but also for the non-toxicity of the final product. The latter is clearly illustrated by the optimal concentration of (generally toxic)

Figure 8. Dynamic viscosity *versus* reduced frequency of PPE/epoxy solutions with epoxy contents of 30, 50 and 70 wt% and for PPE molecular weights of (a) 30 kg mol^{-1} , (b) 18 kg mol^{-1} , (c) 10 kg mol^{-1} (reference temperature is 170°C).

curing agent that proves to be very close to, or even at, the stoichiometric ratio, as revealed by the pronounced maximum in the epoxy T_g . This can be explained by the fact that both

Figure 9. Zero-shear viscosities of PPE/epoxy solutions as a function of PPE molecular weight and epoxy content (reference temperature is 200 °C).

a deficiency (resulting in incomplete curing) as well as an excess (yielding a more linear polymerization) result in a lower T_g .

The morphology of the cured samples is given in figure 6, for four weight fractions in the relevant mid-region, prepared by extraction of part of the (thermoplastic PPE) matrix. Relatively monodispersed epoxy spheres with a particle size distribution of $D_w/D_n \sim 1.2$ are found.

Comparison of the resulting average particle sizes from the TIPS and CIPS processes reveals a remarkable resemblance in their dependence of the viscosity of the matrix during phase separation, as reflected in the strong dependence on the epoxy content (see figure 7). A clear difference exists, however, in their limits towards high fractions of PPE: 0% for CIPS, showing complete phase separation in this case, versus 30% for TIPS, which is again the Berghmans point where the PPE-rich phase vitrifies. No distinct influence of the cooling rate nor the curing temperature was observed for this system. This is not a general rule, however, since for some other polymer-reactive solvent systems [68], recently under investigation in our laboratory, a distinct dependence on curing temperature and curing rate is sometimes found. This effect becomes even more important for semicrystalline polymers, where locking-in by crystallization, that can interfere with phase separation, is possible (see Part II).

1.4. Rheology and chemorheology

The dynamical rheological behaviour of the homogeneous solutions was studied by using a Rheometrics RDS-II spectrometer with a parallel plate set-up and a frequency range of 0.05–200 rad s⁻¹, at different temperatures. Depending on the viscosity of the solution, a plate diameter of 8, 25 or 50 mm, a gap distance of 0.5 to 2 mm, and a maximum

Figure 10. Rheology of PPE/epoxy solutions upon cooling from the homogeneous region to room temperature at a rate of $5^{\circ}\text{C min}^{-1}$ (parameter is the epoxy concentration in the solutions): (a) dynamic viscosity, (b) loss angle (strain $< 3\%$, frequency = 10 rad s^{-1} , plate diameters of 50 mm (+) and 25 mm ($\square$)). (The arrows indicate the onset of phase separation.)

strain of 3%, was applied. Finally, the complete curves were constructed by shifting the measured curves to a reference temperature of 170°C , according to the time-temperature superposition principle. The results in figure 8 show typical shear thinning behaviour which

Figure 11. Rheology upon isothermal curing of epoxy/M-CDEA (52 phr): top, dynamic viscosity; bottom, loss angle (strain < 2%, frequency = 10 rad s^{-1} , plate diameter of 8 mm).

is commonly observed for semidilute solutions. The expected strong dependence on both the volume fraction and molecular weight of the PPE is confirmed. Moderately high zero shear viscosities are found (see figure 9) which are comparable to those of standard thermoplastic polymers. They demonstrate the success of the original objective for intractable polymers,

Figure 12. The time-temperature-transformation diagram of epoxy/M-CDEA presenting the times to gelation (Δ) and the times to vitrification ($\blacktriangle$) upon isothermal curing.

which was lowering the processing temperature (to 170 and 200 °C in figures 8 and 9 respectively) rather than decreasing the viscosity.

In order to study the morphology development in more detail, three different rheological experiments were performed: (i) solutions without curing agent (PPE-epoxy) were analysed upon cooling at 5 °C min⁻¹; (ii) using M-CDEA as a curing agent, the isothermal curing of epoxy was studied (epoxy-M-CDEA) in a temperature range of 100–225 °C; and (iii) the chemorheology of the complete system (PPE-epoxy-M-CDEA) was investigated.

(i) PPE-epoxy. The dynamic viscosity and loss angle of different PPE-epoxy solutions as a function of temperature, obtained via slow cooling at 5 °C min⁻¹, are plotted in figure 10. Structure development upon cooling is recognized via the onset of phase separation (arrows) followed by the evolution (increase in viscosity due to the formation of a continuous PPE-rich phase) and, finally, vitrification. At high PPE concentrations, it is increasingly difficult to detect the onset of phase separation, due to reduction in its rate and its effect on viscosity. Only in the very dilute regions (≥ 90 wt% epoxy), is a decrease in viscosity found, indicative of a continuous epoxy phase accompanied by a dispersed PPE phase. The vitrification of PPE can still be recognized in the distinct peak in the loss angle, which may be caused by the formation of an interconnected structure. Interestingly, the phase diagram can be derived from these experiments as well, as was already depicted in figure 3. The difference with the light scattering technique is that now also the T_g of the phase-separated systems can be measured directly as well as the vitrification using only a single technique.

(ii) Epoxy-M-CDEA. Due to the large viscosity differences that occur upon the isothermal curing of epoxy, it is difficult to monitor its value using only one parallel plate set-up and other techniques, like torsional braid analysis (TBA) [69], are usually applied. However, since we are mainly interested in measuring the time to gelation and vitrification, and not so much in the exact value of the viscosity in the low range, we decided to install

Figure 13. (a), (b): Rheology upon isothermal curing of PPE/epoxy (50 wt% epoxy) versus temperature: (a) dynamic viscosity, (b) loss angle (strain < 2%, frequency = 10 rad s^{-1} , plate diameter of 8 mm) (the arrows indicate the onset phase separation). (For clarity the curves are shifted upwards by the values indicated in parentheses.) (c), (d): Rheology upon isothermal curing of PPE/epoxy at 200 °C versus composition: (c) dynamic viscosity, (b) loss angle (strain < 2%, frequency = 10 rad s^{-1} , plots are a combination of measurements with a plate diameter of 50 (●) and 8 mm (+), except for the system with 39 wt% epoxy) (the drawn curve in (c) is obtained on a Brookfield rheometer). (For clarity the curves are shifted by the values in parentheses.) t_{gel} and t_{vit} of epoxy/M-CDEA are given as references.

Figure 13. (Continued)

the smallest available plate, 8 mm, accepting some scatter in the initial experimental data. The results of the curing at different temperatures are plotted in figure 11, showing a distinct jump in viscosity at the gel point and a maximum in the loss angle at vitrification.

All these data can be combined in a so-called TTT diagram (time, temperature, transformation) as extensively treated by Gillham and co-workers [69]. This diagram is valid for isothermal curing only and, consequently, may be read in the horizontal direction

only (figure 12).

Gelation occurs, independently of the curing temperature, at a constant conversion (for this system at about 58%). Consequently, an exponential reduction in time-to-gelation is found with increasing temperature. In contrast, the time to vitrification reveals a distinct minimum at about 180 °C, due to the competing effects with increasing curing temperature of the reaction rate on the one hand and the conversion required for vitrification on the other hand. The deflection to shorter times at temperatures higher than 200 °C, could be due to homopolymerization or degradation of the epoxy.

(iii) PPE-epoxy-M-CDEA. Now the total system can be analysed. All experimental results are summarized in figure 13, showing the dynamic viscosity and loss angle versus time with the polymerization temperature (figures 13(a) and (b)) and the composition (figures 13(c) and (d)) as a parameter. Again, first the onset of phase separation (arrows) and the gradual increase in viscosity due to the formation of a PPE-rich continuous phase is recognized (I). Accordingly, vitrification of this phase (II) and gelation of the dispersed epoxy phase (III) is found, although mostly I and II are difficult to distinguish since they happen almost simultaneously, followed by the vitrification of the epoxy phase (IV). At low temperatures, vitrification of PPE occurs before gelation of the epoxy phase and no interference of the gelation on the final morphology can be expected, while at high temperatures this could be the case—although only in the case of reaction rates much faster than the phase separation rate can a pronounced influence be anticipated. In the slow curing system with M-CDEA, as used in this study, this is not the case and the morphology basically depends uniquely on the phase-volume ratio at the moment of phase separation.

The composition data in figures 13(c) and (d) clearly reveal a minimum time for phase separation to occur at 78 wt% epoxy, in accordance with UCST behaviour and the phase inversion is detected to occur between 90 and 78 wt% epoxy, accompanied by a large rise in viscosity yielding early matrix vitrification (most pronounced at intermediate polymer concentrations between 78 and 60 wt% epoxy), yielding possibilities for early demoulding.

In conclusion, rheological measurements prove to be a useful tool in monitoring the morphology development upon isothermal curing of PPE-epoxy-M-CDEA. In this system, the morphology is mainly controlled by the formation of a highly viscous PPE-rich continuous phase at the early stages of the reaction-induced phase separation process. Only at polymerization rates considerably higher than the rate of phase separation is a pronounced influence on the final morphology anticipated.

2. Mechanical properties

2.1. The epoxy phase

In order to systematically vary the mechanical properties of the dispersed phase, two basic routes are available: varying (i) the crosslink density [70–75] or (ii) the flexibility [76] of the epoxy network. The first can be realized by using resins with a higher starting molecular weight; however, this will strongly reduce the solubility of the PPE. Alternatively, an excess in curing agent or the use of bifunctional curing agents could be considered, since both methods yield a more linear polymerization, but these techniques show a high sensitivity towards the stoichiometry and problems with the reproducibility are to be expected. Moreover, by only changing the crosslink density, a limited range in properties is to be expected. Therefore, only the second route is explored here and flexibility was introduced by applying different combinations of aromatic and aliphatic epoxies (see figure 2) DGEBA/DGEPPPO: 110/0, 80/20, 60/40, 40/60, 20/80 and 0/100 with M-CDEA

or D-400 (see [3] for more details). Figure 14 shows that the glass transition temperature of the resulting epoxy material gradually decreases from 200 °C to -30 °C, as a unique function of the total polypropylene oxide content.

Figure 14. Glass transition temperatures, as determined using DMTA ($2^{\circ}\text{C min}^{-1}$, 1 Hz), of mixtures of DGEBA and DGEPO resin cured using M-CDEA ($\blacktriangle$) or Jeffamine D-400 ($\triangle$) versus (a) DGEBA/DGEPO ratio (drawn curves are according to the equation of Fox), (b) total polypropylene oxide (PPO) content.

The Young's modulus, strength and strain-to-break are given in figure 15 and reveal the great flexibility in tuning the properties of the epoxy phase, from a brittle glass to a ductile, but relatively brittle, rubber, depending on the position of T_g relative to room temperature.

2.2. The total PPE/epoxy system

Of course it is intriguing to investigate what will be the influence of the above demonstrated drastic change in mechanical properties of the dispersed phase when we use the different epoxy systems as reactive solvents for PPE. The miscibility of PPE-DGEPO proved to be slightly decreased relatively to PPE-DGEBA; only a very small shift of the cloud point curve towards higher temperatures resulted. The morphology of the cured systems proved to be very similar to what we already found: micrometre sized droplets of epoxy in a continuous PPE phase. The main mechanical properties of the total system are summarized in figure 16, showing the modulus, yield stress and (high-speed) fracture toughness values as a function of the amount of epoxy added with the ratio DGEBA/DGEPO as a parameter.

Indeed properties can be tuned but, more interestingly, the reactive solvent, after being used as a processing aid, is locked-up as an integral part of the resulting product inside the thermoplastic matrix and can form a useful and structural element, as is clearly illustrated by the considerable toughness enhancement obtained when rubbery epoxies are used (see figure 16(c)).

Figure 15. Tensile properties of the epoxy resin system, cured with M-CDEA ($\blacktriangle$) or Jeffamine D-400 (Δ), versus the total PPO content; (a) Young's modulus and elongation at break (values given in parentheses are estimated from neck geometry), (b) stress at break (if observed, additionally the yield stress is presented by the markers in parentheses).

Figure 16. Tensile properties of PPE/epoxy versus the epoxy content, for a DGEBA/DGEPO ratio of 100/0 (∇), 60/40 (∇), 20/80 ($\blacksquare$) and 0/100 ($\square$): (a) Young's modulus, (b) yield stress, (c) fracture toughness (G_{Ic}) (testing speed of 1 m s^{-1}).

3. Composite applications

Making use of these newly developed polymer systems, high- T_g thermoplastic composites were prepared using film stacking technology. By introducing epoxy resin as a reactive solvent, the flow was apparently sufficiently increased to fully wet and impregnate the fibres yielding composite materials of high quality (see figure 17).

Microscopic analysis of the matrix material revealed an interesting structure, i.e. the epoxy phase tends to accumulate at polar surfaces such as those of glass and carbon fibres

Figure 17. Optical micrograph of a polished cross section of PPE/epoxy-based (40 wt% epoxy, 55 phr M-CDEA) carbon-fabric-reinforced composite (50 vol.% fibres).

(see figure 18). Remarkably, this phase segregation is nearly complete in the case of high fibre loadings and, for a fibre volume fraction of 50%, a morphology of epoxy-coated fibres in a pure PPE matrix is found (see figure 19).

This (unique) morphology is not only of great importance with respect to the possibility of drastically improving the strength of the interface or the level of adhesion between fibres and matrix, but also offers the potential to individually coat fibres with a thick and tunable (e.g. glassy or completely rubbery) interphase. The prerequisite for complete phase separation to occur is that, apart from the apparent influence of the fibre volume fraction or fibre spacing, sufficient mobility and time is available to complete this diffusion controlled process. For the fixed reaction rate of the system employed in this study, the viscosity of the matrix plays a dominant role, as is clearly illustrated in figure 20.

This figure reveals that only when more than 30 wt% epoxy is present is complete phase separation to the surface achieved and a nearly neat PPE matrix, without inclusions of remaining epoxy spheres, results. This is confirmed by transverse flexural strength tests on unidirectional composites that show that the maximum properties are obtained as soon as a continuous epoxy interphase is formed (see figure 21).

From all properties measured (with typical values for flexural moduli of 40 GPa and strength values of 0.7 GPa, for this high- T_g (220°C), thermoplastic, 50% carbon fabric reinforced, composite) the impact properties proved to be most interesting, as shown in the mode I and II critical strain energy release rate [77], given in figure 22, and in the C-scan results after impact (see figure 23).

The synergy found in the mode-II results can be explained by an apparent optimal combination of brittle and ductile matrix components. The brittle epoxy phase enclosing all fibres not only yields a strong and good adhering interface, but also induces an increase of the deformation area ahead of the crack, and consequently the level of toughness, assuming that cracks in the epoxy coating can initiate yielding in the adjacent PPE matrix. Since mode-II results of interlaminar fracture toughness tests relate linearly [78–81] to the values of the practical (Boeing) compressive strength after impact (CSAI), these results are of great practical importance. Possibly by introducing these brittle interphases, a method may be

Figure 18. SEM micrographs of fracture surfaces of short-fibre-reinforced composites (17 vol.% fibres) based on PPE/epoxy (56 wt% epoxy, 25 phr Ethacure 100): (a) Grafil X-AS carbon fibre, (b) E-glass fibre.

found to toughen fibre-reinforced composites with a ductile thermoplastic matrix, beyond the usual limits imposed by the presence of the rigid fibres.

The macroscopic properties of the composites are strongly influenced by changing the properties of the interphases from glassy to rubbery, by replacing DGEBA by DGEPPPO. Glassy interphases were shown to be in favour of structural applications, while rubbery interphases are preferred in structures requiring a high energy absorption potential. A detailed discussion of these experiments is, however, beyond the scope of this paper.

By changing the viscosity and the chemistry of the systems employed, for example by using end-modified, low molecular weight PPEs that can co-react with the reactive solvent, the currently existing limits with respect to the diffusion-controlled complete phase

Figure 19. SEM micrograph of fracture surface in fibre-rich area of PPE/epoxy-based (40 wt% epoxy, 55 phr M-CDEA) carbon-fabric-reinforced composite (50 vol.% fibre): (a) fibre (imprint), (b) epoxy layer, (c) PPE matrix.

separation could be surpassed and thinner interphases could be realized. Other possibilities for further optimization, that should be based on micromechanical analyses as demonstrated by de Kok *et al* [82], can subsequently be explored.

PART II: TRACTABLE POLYMERS

4. Miscibility and morphology development

4.1. Materials choice

In the processing of tractable polymers with the aid of reactive solvents, we do not aim so much at decreasing the processing temperature. Nevertheless, to be able to process tractable polymers like polyamines, polyesters or polyolefines, like poly(ethylene) (PE), poly(propylene) (PP) and their copolymer rubbers (EPR) including ethylene-propylene-diene terpolymers (EPDM), at low temperatures could find interesting applications. In contrast, here we focus on decreasing the viscosity during processing (e.g. injection moulding of extremely easy flowing PP-grades, easy impregnatable thermoplastic grades of PP, PET or PBT for composite applications) or we aim at both effects combined (e.g. the development of EPDMs pourable at room temperature). Moreover, tractable polymers could possibly surpass one of the severe limits put on this new development so far (apart from the area of thermoplastic composites that can be easily thermoformed in a second step), i.e. the need for reactive processing routes at the end-user. In that case we should focus the research on obtaining unique, but stable, morphologies via the use of reactive diluents, made via reactive compounding or bulk polymerization of an intermediate product that can be ground or granulated and reprocessed in a subsequent shaping step. Basically, we seek alternative routes for realizing special morphologies like in high-impact poly(styrene) (PS), acrylonitrile-butadiene-styrene terpolymers (ABS) or other heterogeneous polymer systems developed for improved toughness. Given the relative newness of these developments, we will limit ourselves here to some preliminary results on morphology development in some

Figure 20. SEM micrographs of transverse fracture surfaces of unidirectional PPE/epoxy composites versus the epoxy (epikote828EL) content: (a) 0 wt%, (b) 20 wt%, (c) 30 wt%, (d) 40 wt%.

Figure 21. Transverse flexural strength of unidirectional PPE/epoxy composites with a fibre volume fraction of 50 (Δ) and 60% (∇) versus the epoxy (DGEBA) content of the matrix.

Figure 22. Critical strain energy release rate G_c of carbon-fabric-reinforced composites (50 vol.% fibres) versus matrix composition.

of these systems, where crystallization can often interfere with phase separation. Linear poly(ethylene)-styrene (PE/St) is chosen as a model system, while as an alternative for the

Figure 23. Tensile face damage and schematic representation of C-scan images of carbon fabric laminates (50 vol.% fibres) impacted at an energy level of 9 J: (a) epoxy matrix, (b) PPE/epoxy matrix (40 wt% epoxy).

reactive solvent styrene, that ultimately gives a brittle dispersion in the form of PS spheres, butyl-methacrylate (BMA) is investigated, since this yields a rubbery dispersion.

4.2. Miscibility

The miscibility of PE–St was measured by differential scanning calorimetry (DSC). Samples with different PE concentrations were transferred into high-pressure DSC sample pans. Different cooling rates were used to determine the onset of crystallization. For constructing the ‘crystallization line’ in the phase diagram, the onset of the crystallization was linearly extrapolated to a cooling rate of $0^{\circ}\text{C min}^{-1}$. For construction of the ‘melting line’, the temperature of the end of the melting endotherm was used as the melting temperature T_m . The melting temperature depression of a semicrystalline polymer/solvent system can be approximated by [83]

$$\frac{1}{T_m} = \frac{1}{T_m^0} - \frac{RV_2}{\Delta H_m V_1} (\chi \phi_1^2 - \phi_1) \quad (1)$$

with T_m and T_m^0 representing respectively the equilibrium melting temperature of the polymer in the solvent and the equilibrium melting temperature of the pure polymer, ΔH_m the melting enthalpy per monomer unit, and ϕ_1 representing the volume fraction of the solvent. V_1 and V_2 represent the molar volume of the solvent and the polymer respectively and χ is the interaction parameter. The resulting phase diagram is depicted in figure 24. There is no interference [84–88] with liquid–liquid demixing, indicating that styrene is a good solvent for poly(ethylene).

Figure 24. Phase diagram of PE/styrene solutions.

Figure 25. Schematic ternary phase diagram for PE/PS/styrene.

4.3. Chemically induced phase separation (CIPS)

Upon isothermal polymerization of the reactive solvent styrene, a third component (PS) is introduced in the initial homogeneous solution. Since PE and PS are immiscible over the whole composition range, it is clear that phase separation will occur. Unlike the PPE-epoxy system, for which the chemically induced phase separation can be considered as an upward shift and a concurrent change of the shape of the cloud point curve, the chemically induced phase separation for the PE-St system has to be considered as following a reaction line in a ternary phase diagram, as depicted in figure 25 for the PE-St-PS system. The overall composition will follow such a reaction line. However, upon entering the two-phase

Figure 26. Schematic representation of the L-S transition in the PE-rich phase.

region, i.e. crossing the binodal, phase separation will set in, resulting in PE-rich and PS-rich regions. Depending on the polymerization temperature, interference of phase separation with crystallization can take place, making the precise choice of the polymerization temperature of utmost importance (see figure 26).

Interestingly, even at extremely low polymer fractions, it is expected that the polymer will form the continuous phase, given the complete immiscibility of the resulting polymer systems PE-PS.

4.4. Morphology development

With the aid of simultaneous time-resolved small- and wide-angle x-ray scattering (SAXS and WAXS), performed at station 8.2 of the Synchrotron Radiation Source (SRS) in Daresbury, UK, morphology development could be investigated. SAXS and WAXS data were collected during *in situ* polymerization at two temperatures. The SAXS results for 20 and 60 wt% PE, polymerized at 121 °C, are presented in figures 27(a) and 28(a) respectively, as three-dimensional plots of Lorentz corrected intensity, Iq^2 , versus the scattering vector $q = (4\pi/\lambda) \sin(\theta/2)$, where θ is the scattering angle, versus time. For extracting information about the periodicity of the structure, a one-dimensional spacing of the structure can be derived from the maximum in the Lorentz corrected plot. The spacing can then be calculated using Bragg's law

$$d = \lambda/2 \sin q_{max} = 2\pi/q_{max}. \quad (2)$$

Clearly the onset of phase separation is recognized as well as the later start of crystallization when the polymerization temperature is below the crystallization temperature (see figures 27(b) and 28(b)).

Figure 27. X-ray scattering data for the 20 wt% PE in styrene solution polymerized at 121 °C: (a) Lorentz corrected SAXS data as three-dimensional plots of intensity, $I(q)q^2$, versus scattering vector, q , versus time t and (b) WAXS data as three-dimensional plots of intensity, I , versus scattering angle, 2θ , versus time t .

Figure 28. X-ray scattering data for the 60 wt% PE in styrene solution polymerized at 121 °C: (a) Lorentz corrected SAXS data as three-dimensional plots of intensity, $I(q)q^2$, versus scattering vector, q , versus time t and (b) WAXS data as three-dimensional plots of intensity, I , versus scattering angle, 2θ , versus time t .

Figure 29. TEM micrographs of PE/PS blends with a PE content of 20 wt% (top) and 60 wt% (bottom), polymerized at 121 °C.

5. Morphology

Transmission electron microscopy (TEM) pictures of the resulting morphologies confirm the x-ray scattering results. Some illustrative examples are given in figure 29.

Typically 200 nm sized structures are found with many details. The individual lamellae of the folded chain PE crystals form the continuous phase, already at about 6% PE present. By replacing the reactive solvent St by BMA similar structures are found, and a wide range of mechanical properties result from stiff and brittle for PE-PS to rubbery and tough for EPDM-BMA [8].

6. Concluding remarks

It has been shown that the use of reactive solvents in the processing of both intractable and tractable thermoplastic polymers offers a flexible route to extend the processing characteristics of existing polymers to far beyond their existing limits. The method was only demonstrated by using two model systems, PPE-epoxy and PE-St, but it was also implicitly shown that many more challenges still exist. In our laboratory, we are now developing a number of high-performance and low-priced composite systems, based on different thermoplastic matrices. Moreover, we aim at the intrinsic flexibility of this new processing method in order to develop heterogeneous polymer systems with unique, and often extremely fine, morphologies, that otherwise cannot be obtained for instance with the more standard compounding and blending techniques. This can be of utmost importance for obtaining the ultimate properties of polymeric materials in terms of toughness [74]. Although the method is basically limited to end-use applications, thus introducing chemistry to the end-user, some ways out of this obvious disadvantage have been pointed out. Of course, further developments in this direction should be restricted to tractable polymer systems, at least if real flow, and thus a relatively low viscosity, is prerequisite, for example in injection moulding. For thermoforming, fewer restrictions are present and the necessity of chemistry can be restricted to the prepreg manufacturer. Finally, with respect to the more classical reactive processing routes, clear advantages exist, mainly because the main properties of the resulting product are determined by the, originally dissolved, thermoplastic polymer and only in the second instance by the converted solvents that end up as a dispersed phase, or interphase when polar surfaces are present, in this continuous thermoplastic matrix.

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