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Processing of intractable polymers using reactive solvents.
6. A new reactive solvent concept based on reversible depolymerisation

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Abstract

The use of reactive solvents which reversibly (de)polymerise to facilitate the processing of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was explored. PPE can be dissolved at elevated temperatures in very low molecular weight thermoplastic poly(urethane) (TPU) fragments obtained via depolymerisation and these solutions can then be processed at the relatively low temperature of 250 °C. After processing and upon cooling, the TPU fragments repolymerise which induces a L–L phase separation between PPE and TPU followed by vitrification of the PPE matrix phase and at lower temperatures vitrification of the TPU dispersed phase. Since phase separation occurs during cooling, the phase separation is induced thermally as well as chemically, since the molecular weight of the 'solvent' increases upon lowering the temperature. The properties of the final materials, such as heat resistance, are dominated by the continuous PPE matrix. The starting molecular weight of TPU and the composition of the blend had pronounced effects on the phase separation, morphology and viscosity of the blends. Increasing the amount of TPU resulted in larger TPU particles but no effect on the T_g of the PPE-rich matrix was observed. Increasing the starting molecular weight of TPU resulted in higher phase separation temperatures and higher T_gs for the PPE-rich matrix. Possibilities for diminishing the residual TPU fractions were explored. The interference of vitrification with phase separation could be postponed and, consequently, the residual fraction of TPU in the PPE phase could be reduced either via an increase in the starting molecular weight of TPU or a decrease in cooling rate or T_g of the matrix.

Keywords: Phase separation; Reactive solvent; Depolymerisation

1. Introduction

The use of solvents in the processing of intractable polymers, i.e. polymers possessing a high T_g combined with a relatively low degradation temperature or polymers possessing a high molecular weight, has been studied extensively. Both volatile solvents [1,2] and 'solid' solvents [3] (low molecular weight crystalline materials) can be adequately used to lower the processing viscosity or processing temperature and in this way processing of the intractable polymer is possible. However, in the case of conventional solvents, the solvent has to be removed in order to regain the polymer properties, while for the solid solvents residual solubility of the solvent in the polymer is encountered, which inherently affects the original polymer properties. It is evident that the solution processing of intractable polymers is a compromise between regaining the intrinsic material properties and ease of processing.

A solution to circumvent this compromise can be found in the use of *reactive* solvents, i.e. monomers. At the processing temperature, the reactive solvent should act as a solvent to obtain a homogeneous solution, thus lowering the viscosity and/or the processing temperature. However, instead of removing the solvent after the shaping step, the reactive solvent is polymerised in situ. As a consequence of the in situ polymerisation of the reactive solvent, liquid–liquid (L–L) phase separation is induced resulting in a morphology of polymerised 'solvent' particles dispersed in the matrix of the 'intractable' polymer. Consequently, the resulting material properties are dominated by the intractable polymer without the necessity to remove the solvent. In contrast with the solid solvent concept, virtually no residual solvent is present in the matrix phase provided that the solvent is polymerised at temperatures above the T_g of the intractable polymer.

A distinction in the reactive solvent systems can be made according to the polymerisation mechanism by which the monomer (reactive solvent) is converted into polymer, i.e.

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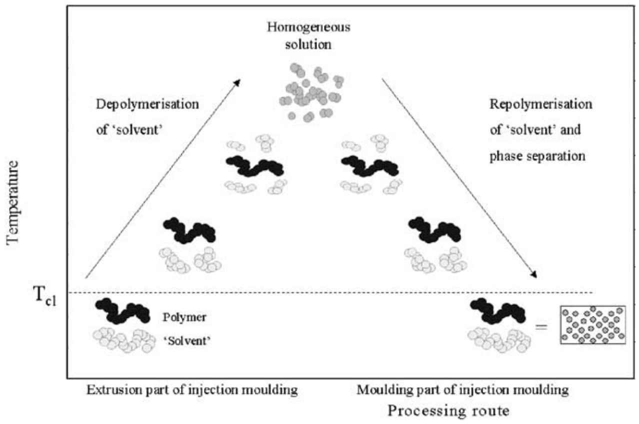

Fig. 1. Schematic representation of the use of reactive solvents based on reversible depolymerisation in the processing of polymers.

step-growth or chain-growth polymerisation. An example of the former is epoxy resin which can be used in the processing of for instance poly(2,6-dimethyl-1,4-phenylene ether) (PPE) [4], poly(ether sulphone) (PES) [5,6], poly(sulphone) (PSF) [7] or poly(ether imide) (PEI) [8]. The use of styrene in the processing of poly(ethylene) (PE) [9] is, on the other hand, an example of a reactive solvent which polymerises via a chain-growth mechanism. On comparing both polymerisation mechanisms, a substantial difference in the effect of the conversion of monomer to polymer on the miscibility can be observed. Step-growth polymerising reactive solvent systems can remain in a homogeneous state to relatively high conversions depending on the system, the concentration and the temperature. For instance, Park and Kim found a conversion of 10% for the system PEI/epoxy [8]. For chain-growth polymerising systems, the conversion at which phase separation starts is typically only a few percent when the two polymers are immiscible, which can be ascribed to the almost instantaneous formation of full-grown polymers in the system upon polymerisation and the relative insensitivity of the phase behaviour to temperature. Consequently, the miscibility window, and thus the processing window, for this kind of systems is much smaller compared to step-growth polymerising reactive solvent systems.

Although both types of reactive solvent systems have proven to be adequate solutions to overcome processing problems for a number of polymers, there are some disadvantages. The major drawback is that in all cases additional chemicals and the related chemistry are introduced in the processing step, which severely complicates the implementation of these processing techniques on standard processing equipment such as injection moulding. Furthermore, for successful implementation, short cycle times are necessary and, as a consequence, fast polymerisation of the reactive solvent is required. To prevent premature polymerisation in the extruding/homogenising step for these systems, the initiator/curing agent should either be added to the mixture just before moulding or be carefully developed to be active in a small temperature window. The former requires adaptation of the conventional injection moulding equipment, which is a major drawback for end-users. Examples of the latter are already known, but the disadvantage for these systems is that post curing steps are necessary to obtain sufficiently phase separated systems with high conversion [10–12].

In view of these drawbacks, a new reactive solvent concept that could circumvent the above-mentioned problems has been developed in our laboratories and the first results are reported in this paper. The concept is based on reversible depolymerisation of a reactive solvent at the processing temperature. In general, a polymerisation reaction can be considered as an equilibrium reaction between monomer and polymer that can be described by the Gibbs free energy ($\Delta G_{\text{pol}} = G_{\text{polymer}} - G_{\text{monomer}}$) [13]. As the entropy and enthalpy for addition polymerisations are usually both negative, the Gibbs free energy becomes positive above a certain temperature, which is referred to as the ceiling temperature (T_{cl}) [13,14]. This implies that high molecular weight polymers cannot be formed above this temperature or, in other words, a polymer with an already high molecular weight will depolymerise to a lower molecular weight until equilibrium conditions are established again. At the processing temperature, the reactive solvent possessing this behaviour should depolymerise to low molecular weight fragments which are able to dissolve the polymer.

The major advantage of this new reactive solvent concept is that the (re)polymerisation of the reactive solvent is thermodynamically controlled and not kinetically; it only occurs upon lowering the temperature which shifts the polymerisation equilibrium towards high molecular weights. In this way, polymerisation of the reactive solvent is achieved without the risk of premature polymerisation and without the introduction of additional chemicals or chemistry. The concept is schematically depicted in Fig. 1.

For successful application, the reactive solvent should possess a ceiling temperature which is situated below its degradation temperature or the temperature at which irreversible reactions can take place in order to assure reversibility of the polymerisation. In this respect, it is unfavourable to select a solvent which (de)polymerises via a chain-growth mechanism. As explained earlier, systems consisting of chain-growth polymerising reactive solvents already show phase separation at only a few percent conversion. This implies that, in order to obtain homogeneous solutions, depolymerisation of this solvent has to proceed up to almost 100% conversion to monomer. This in contrast with step-growth 'solvents' which have to depolymerise to substantially lower conversions to be able to form homogeneous solutions. Considering these requirements, thermoplastic polyurethane (TPU) is a potential solvent in the reactive solvent concept based on reversible depolymerisation [15].

In this study, the possibilities and limitations for the processing of PPE using TPU are explored. After determination of the constituents and the initial molecular weight of the TPU and the processing conditions required for successful application, the processability, phase separation, morphology and properties of a model PPE/TPU system are investigated. Next, the effects of the starting molecular weight of TPU and the composition on the characteristics of the system are discussed, including the comparison between batch and continuous preparation. Finally, some methods to reduce the residual fraction of TPU in the PPE matrix are presented and discussed.

2. Experimental

2.1. Materials and blend preparation

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) with a viscosity average molecular weight of 30 kg/mol and a polydispersity of 2.5 was supplied by General Electric Plastics. Thermoplastic poly(urethane) (TPU) with a M_n of 30.5 kg/mol, consisting of alternating 4,4′-methylene-diphenyldiisocyanate (MDI) and 1,6-hexanediol (HD) building blocks was supplied by DOW Chemical (ISOPLAST™ 2530 resin) [16]. This compound will be referred to as TPU-0%. Three low molecular weight TPUs consisting of MDI and HD were synthesised at DOW Chemical using 2, 4 and 8 wt% of 1-hexanol (HEX) as chain terminator based on the total weight [17]. The three reactants were simultaneously fed to a Berstorff model ZE40X47D 40-mm twin-screw extruder, operated at a screw speed of 450 rpm and a temperature of 100 °C. The output of the extruder was set to 135 kg/h and the extrudates were chopped under water into small granules. The compounds will be referred to as TPU-2%, TPU-4% and TPU-8% depending on the amount of 1-hexanol added. The absolute molecular weights of the TPUs were determined via triple detection size exclusion chromatography (Triple-SEC) using hexafluorisopropanol (HFIP) as the mobile phase and were, respectively, 9.3, 4.5 and 2.2 kg/mol.

Batch-wise preparation of blends of PPE and TPU was performed in a circulating co-rotating twin screw mini-extruder (volume 5 cm^3) at 250 °C and 100 rpm. A mixing time of 5 min proved to be sufficient to obtain transparent homogeneous solutions. Blends containing PPE and 20 wt% of low M_n TPU were also extruded in a continuous operation using a Werner & Pfleiderer ZSK-25 extruder with a screw diameter of 25 mm, a screw length of 106 cm and a volume of approximately 400 cm^3. The screw configuration can be described as:

$$5 \times t, 3 \times k_t, t_{neg}, 4 \times t, k_t, t, 2 \times k_t, t, 2 \times k_t, t, 2 \times k_t, t_{neg}, t, 2 \times k_t, t_{neg}, 3 \times t, \text{die}$$

where t represents a positive transport element, k_t is a positive mixing element and t_{neg} is a negative transport element, all with their own characteristic standard lengths. TPU has been added to the extruder as the main stream, while PPE was added via a side stream extruder. The addition of the components controlled using two gravimetric K'tron Soder feeders (K-CL-KQX2 single screw for the TPU granules, K-CL-KT20 double screw for the PPE powder). The output of the extruder was set to 2 kg/h and the screw speed was 300 rpm. Upon exiting the extruder, the extrudate was cooled with air and chopped into small granules.

2.2. Characterisation

The glass transition temperatures and the moduli of the PPE blends were determined using dynamic mechanical thermal analysis (DMTA) (Polymer Laboratories MkII). The samples were analysed in the dual cantilever bending mode using a frequency of 1 Hz and a heating rate of 2 °C min^{-1}.

Differential scanning calorimetry (DSC) was used to determine the phase separation temperature on a Perkin–Elmer Pyris-1 DSC-apparatus. Indium was used for temperature and enthalpy calibration ($T_m = 156.6$ °C and $\Delta H_m = 28.45$ J/g) and the applied scanning rate was 10 °C min^{-1}. For the determination of the phase separation temperature, the onset of the exothermic signal upon cooling was taken [18,19].

The dynamic rheological behaviour was characterised using a Rheometrics RDSII spectrometer. A parallel-plate test set-up was used to determine the dynamic viscosity at a frequency of 10 rad s^{-1} and a strain of 1%. The applied scanning rate was 5 °C min^{-1}.

The morphology of the samples was visualised by Scanning electron microscopy (SEM, Philips ESEM-FEG XL30). Samples for SEM were fractured at room temperature and some samples were subsequently etched for 15 min in N,N'-dimethylformamide (DMF) to remove the TPU phase.

3. Results and discussion

3.1. Choice of TPU and processing conditions

As mentioned in the introduction, the (de)polymerisation characteristics of TPU and the processing conditions (processing temperature and composition) required for successful application have to be determined. The depolymerisation curves for both the high molecular weight TPU and the low M_n TPUs containing 1-hexanol have been reported elsewhere [15] and will be shortly summarized here. The critical molecular weight for phase separation for TPU is found in the range from approximately 300 g/mol for TPU-0% to 500 g/mol if 1-hexanol is present (1-hexanol is a

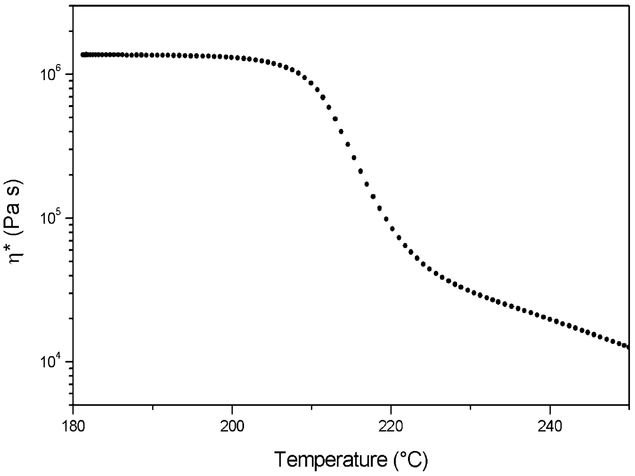

Fig. 2. Complex viscosity versus temperature at 10 rad s^{-1} for the PPE/TPU-8% 80/20 wt% model system.

better solvent for PPE than 1,6-hexanediol) [20]. For TPU-0%, a processing temperature of 280 °C should be applied in order to obtain small enough fragments to dissolve PPE. However, this temperature is above 260 °C, the temperature at which irreversible reactions for TPU, such as carbodiimide formation, begin to occur [21]. Therefore, it can be anticipated that TPU-0% is not suitable as reactive solvent for PPE, which was experimentally validated at temperatures ranging from 250 to 280 °C. For the low M_n TPUs, however, the temperature at which the critical molecular weight is reached is situated below the degradation temperature of TPU. Consequently, these low M_n TPUs are suitable reactive solvents. The three main characteristics of the reactive solvent concept based on reversible depolymerisation, i.e. processability, phase separation and morphology, are studied using the PPE/TPU-8% 80/20 wt% model system produced on the ZSK-extruder.

3.2. The PPE/TPU-8% 80/20 wt% model system

PPE can generally not be processed at 250 °C due to the very high intrinsic viscosity at this temperature, but it can easily be processed at this temperature using the ZSK-extruder upon addition of only 20 wt% of TPU. The obtained solution is optically transparent and shows no sign of so-called 'black spots', pieces of degraded PPE, which indicates that PPE remains completely intact. Obviously, the first of the three criteria for a successful reactive solvent can be met by the PPE/TPU system.

The processability of the system was investigated in more depth using rheometry. Unfortunately, the standard approach of determining the viscosity over a large shear rate range via the time-temperature superposition principle cannot be used for this system. Since the molecular weight of the TPU changes with temperature, the curves cannot be shifted. To get some indication of the viscosity at the processing temperatures, the dynamic temperature ramp approach was used in which the viscosity is determined at

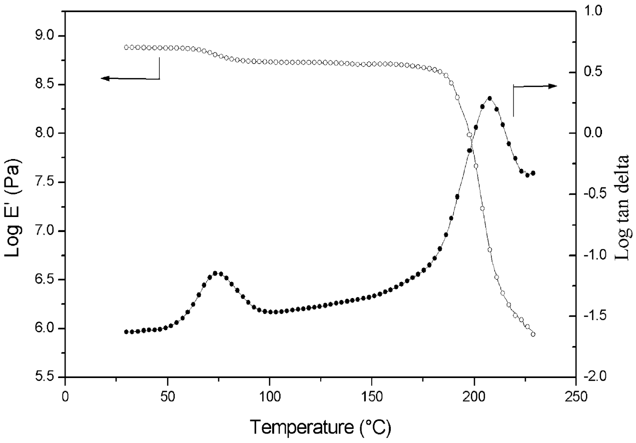

Fig. 3. DMTA measurement of the PPE/TPU-8% 80/20 wt% model system: (○) Storage modulus E', and (●) tan delta.

different temperatures at a fixed frequency. The resulting plot for the model system is depicted in Fig. 2. Upon cooling, the viscosity increases until at a certain temperature an additional increase can be observed which is probably caused by the vitrification of the matrix after phase separation. At low temperatures, the viscosity reaches a plateau value, which is not a material value, but it is determined by the machine stiffness. Although the shear thinning effect cannot be explored in this way, it is anticipated that it will be much less than the pronounced shear thinning behaviour of neat PPE. As already observed by Venderbosch et al. [4], the addition of a reactive solvent to PPE results in a more Newtonian-like behaviour of the solution.

After processing and cooling to room temperature, the blend was characterised using DMTA. The DMTA data of the PPE/TPU-8% 80/20 wt% model system are shown in Fig. 3. It is evident that phase separation has occurred as two well-separated T_gs in the plot of tan delta are distinguishable. The lower T_g at 74 °C can be assigned to the TPU-8% dispersed phase while the higher T_g at 207 °C is related to the PPE-rich matrix. The fact that the PPE-rich phase is the matrix phase is evident from the temperature dependence of the E-modulus, which remains almost constant until the T_g of the matrix phase is reached at which a large decrease in E-modulus occurs. Furthermore, the scanning electron micrograph of the blend, shown in Fig. 4a, clearly shows dispersed particles in a matrix material. Etching the fracture surface of the blend with DMF, which is a good solvent for TPU, gives further evidence that TPU is indeed the dispersed phase (Fig. 4b).

From Fig. 4, another interesting characteristic can be seen; the dispersed TPU particles show a rather large size distribution with particles ranging from 100 nm to 5 μm. Due to the fast cooling and the subsequent fast shifting of the demixing curve as a result of the increase of the molecular weight of the reactive solvent, the quench depth for phase separation is large and spinodal decomposition is anticipated, which in general results in more regular

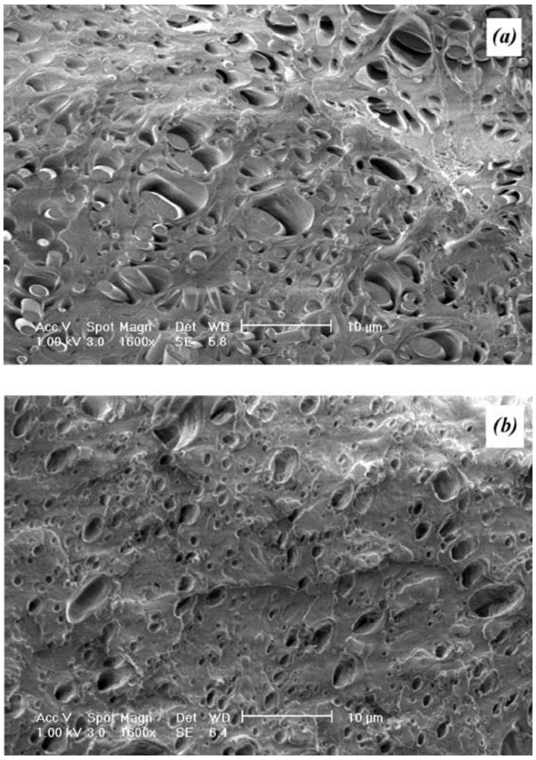

Fig. 4. Scanning electron micrographs of the PPE/TPU-8% 80/20 wt% model system. (a) Not-etched and (b) etched with DMF.

structures [22]. On the other hand, the observed large distribution in particle size could indicate the occurrence of binodal decomposition, although a large distribution may also be explained by the continuously increasing quench depth during cooling which could result in spinodal decomposition with continuously increasing correlation lengths of concentration fluctuations [23,24]. To determine the onset and the type of phase separation, i.e. spinodal versus bimodal, small angle light scattering was used. However, despite the fact that a very sensitive CCD-detector was used, no appearance of a regular structure could be observed upon controlled cooling. Investigating the blend with light microscopy revealed the appearance of dark regions at 150 °C which could be indicative for phase separation. However, the constructed depolymerisation curves described elsewhere [15] give a strong indication that the onset temperature of phase separation should be much higher. From literature, it is known that the refractive index of PPE is 1.59 [25,26] and that the refractive index of TPU varies between 1.5 and 1.6 depending on the constituents [25]. Since the refractive index of a material is dependent on the molecular weight, as shown for the reacting system of PES and epoxy [6], and temperature, it may be possible that the refractive indices of PPE and TPU are very similar in the temperature region where phase separation occurs. Therefore, light scattering techniques cannot be used to determine the onset and the type of phase separation.

As an alternative technique, DSC is used to determine the onset temperature of phase separation. The onset of thermally induced L–L phase separation can be accurately detected using DSC for polymer–solvent systems [18,19]. But also the chemically induced L–L phase separation for the PPE/TPU-8% 80/20 wt% model system is detectable with DSC as can be seen in Fig. 5. In this figure, the exothermic signal at 210 °C during cooling from 250 °C can be assigned to the heat release resulting from L–L phase separation. Apparently, the phase separation starts at this temperature. The phase separation continues until the temperature is lowered to below the T_g of the matrix phase and, consequently, the system vitrifies, which can be seen in the DSC-curve by the return of the heat flow signal to the baseline. From Fig. 5, it is clear that vitrification sets in almost immediately after the phase separation has started, since the temperature of the onset of phase separation is very close to the T_g of the matrix material.

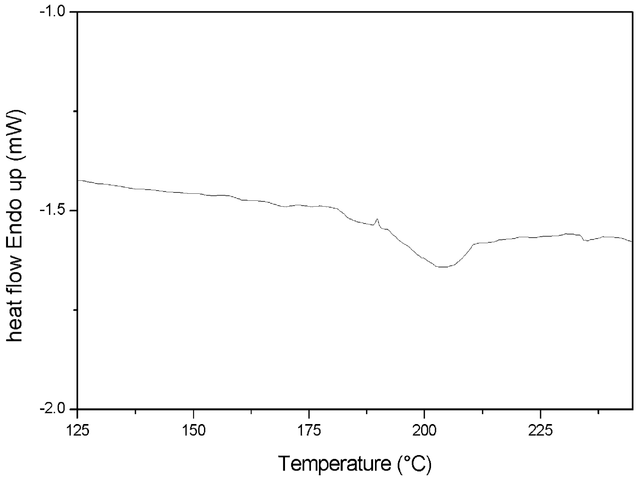

Fig. 5. Cooling curve for the PPE/TPU-8% 80/20 wt% model system measured with DSC with cooling rate of 10 °C min^{-1}.

3.3. Effect of composition

For the model system containing 20 wt% of TPU, both the batch operation using a circulating mini-extruder and the continuous operation of the ZSK-extruder result in homogeneous solutions with PPE. However, for TPU contents of 30 wt% and higher, the continuous operation led to inhomogeneous systems. The concentration of TPU for which the system is homogeneous could be extended to 40 wt% for the batch operation. These results are summarized in Table 1.

An important practical parameter of the system is the time required for dissolution. The most important difference between both processing devices is that the residence time can be easily adapted in the batch operation via the circulation time in the mini-extruder, while for the continuous operation using the ZSK-extruder a completely different screw configuration and throughput is necessary. In most cases, the screw configuration is optimised for mixing and the throughput is set as high as possible.

Table 1
Processing data for PPE and low M_n TPU solutions at 250 °C: (+) homogeneous solutions, (0) not available due to practical limitations during feeding, (−) inhomogeneous solutions

PPE solutions containing varying amounts of TPU (wt%)	Mini-extruder	ZSK-extruder
10	+	0
20	+	+
30	+	−
40	−	−

However, in the case of PPE/TPU blends, dissolution is much more important. This means that the residence time of the blend in the extruder should be long enough to obtain the required homogeneous solution. Therefore, the screw configuration described in Section 2 was used containing a large number of alternating positive mixing and transportation elements to make sure the screw is highly filled. Combining this screw configuration with a very low extruder output (2 kg/h) results in the required residence time, which is in the order of minutes for the blends containing 20 wt% of TPU. However, for the blends containing 30 wt% of TPU, the extruded material from the ZSK-extruder was not completely homogeneous, while in the mini-extruder homogeneous solutions were obtained using a residence time of 5 min. This stresses the importance of the residence time, which is strongly related to the kinetics of dissolution. This was apparently too short in the case of the ZSK-extruder to completely dissolve PPE in TPU. Unfortunately, a further extension of the residence time was not possible due to practical limitations.

From the experimental observations of the blends containing 40 wt% of TPU, it is evident that the thermodynamics of mixing are also important. These blends are immiscible independent of mixing time due to the fact that this composition may already be situated within the binodal curve at 250 °C, as is schematically shown in Fig. 6. Only increasing the temperature may result in a miscible blend again, but also irreversible isocyanate reactions are then likely to occur.

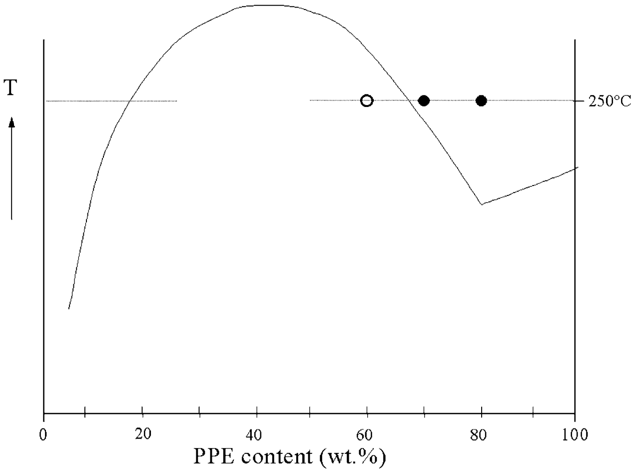

Fig. 6. Schematic phase diagram for a PPE/low M_n TPU blend at 250 °C. The dots represent different compositions indicating: (•) homogeneous solutions, and (○) phase separated solutions.

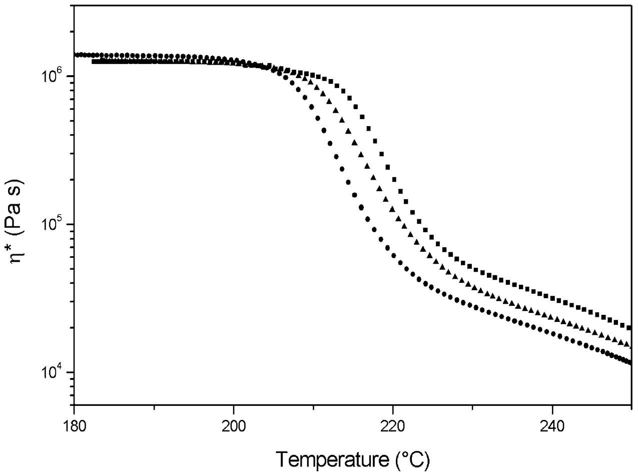

Fig. 7. Complex viscosity versus temperature at 10 rad s^{-1} for blends of PPE and (■) 10 wt%, (▲) 20 wt%, and (•) 30 wt% of TPU-8%.

As expected, increasing the amount of TPU in the blend results in a lower complex viscosity at high temperatures, as shown in Fig. 7. Furthermore, the onset temperature of vitrification of the system is higher for lower amounts of TPU. On the contrary, the DMTA-experiments depicted in Fig. 8 show a constant T_g of the PPE-rich phase for different amounts of TPU. This indicates that the composition of the matrix phase is virtually independent of the amount of TPU. The difference between the two results could be caused by the fact that rheometry probes the structure during its development, while DMTA probes the structure after it has been developed. It is obvious that more systematic experiments are required to draw more solid conclusions, for instance the influence of the cooling rate and cooling jumps to different isothermal phase separation temperatures,

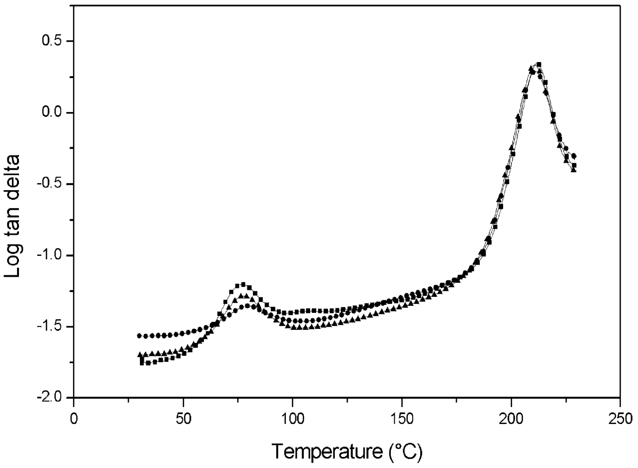

Fig. 8. DMTA measurements of PPE/TPU-8% blends containing (•) 10 wt% TPU, (▲) 20 wt% TPU, and (■) 30 wt% TPU.

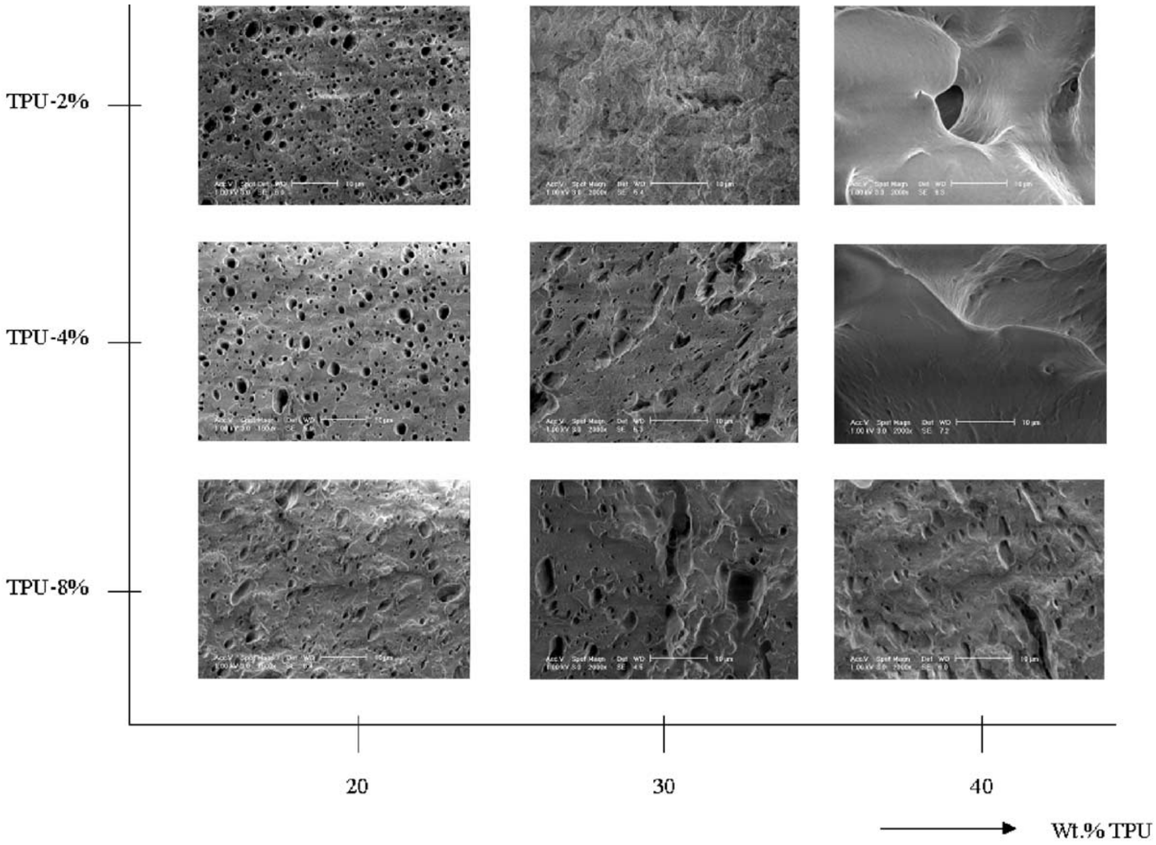

Fig. 9. Scanning electron micrographs of PPE/TPU blends etched with DMF with different compositions and types of TPU. The depicted scale bars all represent 10 μm.

to distinguish between thermally and chemically induced phase separation.

As can be expected from the observed trends in other phase separating polymer-reactive solvent systems [4], the particle size of the TPU dispersed phase is larger when the amount of TPU is increased (Fig. 9). However, this is only the case for compositions from 20 to 30 wt% of TPU and blends containing TPU-8% or TPU-4%. In the case of blends with TPU-2%, the morphology seems to have changed from a matrix-dispersion morphology to a more or less co-continuous morphology. This may be related to a change in the type of phase separation (binodal or spinodal), but as explained before, experimental evidence is inaccessible yet. Increasing the compositions from 30 to 40 wt% TPU results in (partially) immiscible blends due to thermodynamic restrictions. For the blends containing 40 wt% of TPU-2% or TPU-4%, very large domains can be observed, suggesting that the TPU phase has not been obtained via phase separation from a homogeneous solution, but via dispersive mixing of immiscible polymers. For the blends containing 40 wt% of TPU-8%, small particles can be distinguished, additional to the large domains. The presence of these particles may be found in the fact that the system was partially miscible during processing and the small particles are thus formed as a result of L–L phase separation.

3.4. Effect of starting molecular weight of TPU

The effect of the starting M_n of TPU on the processability of the PPE/TPU system can be seen in Fig. 10. As expected, for a given temperature, the melt viscosity increases on increasing starting molecular weight of TPU. This can be explained by the higher molecular weights of the depolymerised fragments of TPU at this temperature [20] and the

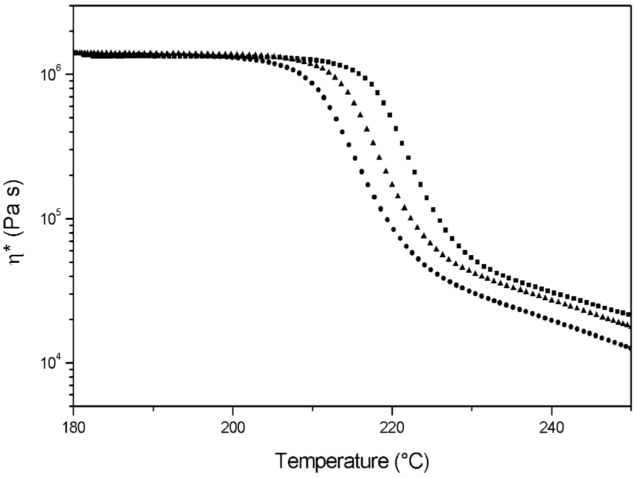

Fig. 10. Complex viscosity versus temperature at 10 rad s^{-1} for blends of PPE and 20 wt% of (■) TPU-2%, (▲) TPU-4%, and (•) TPU-8%.

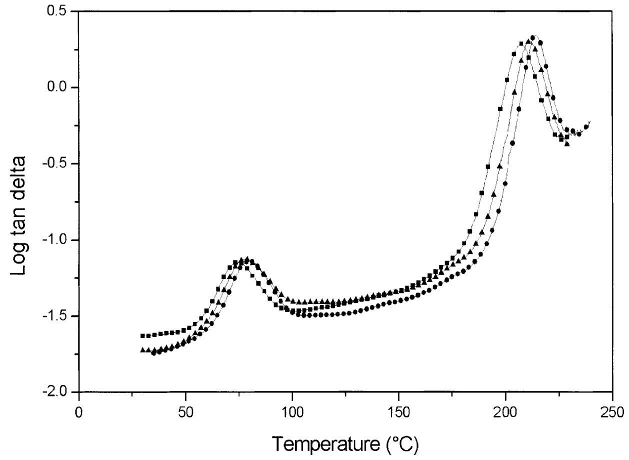

Fig. 11. DMTA measurements of PPE/TPU 80/20 wt% blends containing (■) TPU-8%, (▲) TPU-4%, and (•) TPU-2%.

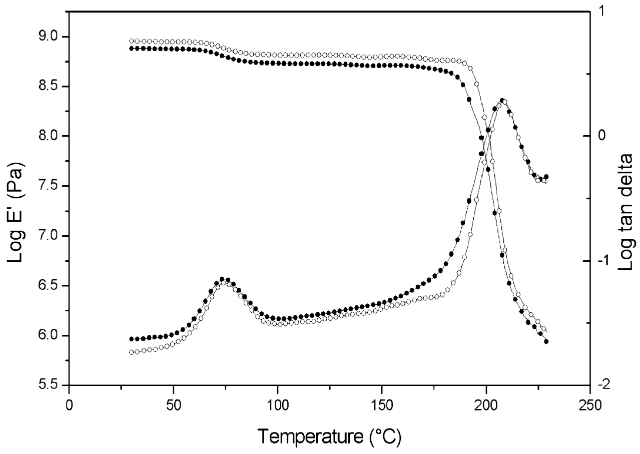

Fig. 12. DMTA measurements of PPE/TPU-8% 80/20 wt% blends (•) cooled fast, and (○) cooled slowly.

higher T_g of the system. Furthermore, the onset temperature of vitrification is shifted to higher temperatures with increasing molecular weight of TPU. From DMTA-experiments (Fig. 11), an increase in T_g of the PPE-rich phase upon increasing the starting M_n of TPU is observed. These results are summarized in Table 2, in which also the phase separation temperatures as derived from the DSC-experiments are given.

From the results in Table 2, it can be seen that a higher starting molecular weight of TPU results in a higher T_g of the PPE-rich phase and in a higher phase separation temperature. Due to the higher molecular weights of the depolymerised fragments of TPU, the critical molecular weight for phase separation is reached earlier upon cooling and thus phase separation and subsequent vitrification occurs at higher temperatures. The T_g of the PPE matrix phase is higher for these blends, because the fraction of TPU fragments possessing a M_n below M_{crit} is less, reducing the residual solubility. The observed increase in T_g of the TPU phase in the blend is as expected, because the T_g of the pure low M_n TPUs is higher for higher molecular weights.

3.5. Residual fraction of TPU in the PPE-rich phase

One of the most important reasons to use reactive solvents is that complete phase separation can be obtained. However, the DMTA-results, as discussed in Section 3.4, showed that there is a residual fraction of TPU present in the PPE phase which results in a slightly lower T_g of the PPE-rich phase compared to pure PPE. This is unfavourable in view of regaining the intrinsically high heat resistance of PPE. Therefore, this residual fraction of TPU in the PPE phase has to be reduced.

This residual solubility originates either from fragments of TPU which posses a molecular weight (M_n) lower than the critical molecular weight (M_{crit}) or from the fast vitrification of the not completely phase separated PPE-phase. The residual solubility of TPU in PPE can be lowered by increasing the starting molecular weight of TPU, as can be seen in Table 2 and Fig. 11. In this way, the fraction of fragments possessing a M_n below M_{crit} is reduced and consequently, the T_g of the PPE-rich phase will be higher. The residual fraction of TPU in PPE originating from vitrification can be lowered by either decreasing the cooling rate or the T_g of the matrix phase. Both approaches are based on postponing the vitrification process after phase separation. The effect of decreasing the cooling rate can be seen in Fig. 12 where the drop of the E-modulus is shifted to higher temperatures when compared to the fast cooled blend. By cooling slowly, the system has more time between the onset of phase separation and vitrification, resulting in a more complete phase separation.

An unsuccessful attempt was made to investigate the effect of cooling rate on the morphology (development)

Table 2
Phase separation temperatures derived from DSC experiments and T_g of the dispersed and matrix phase derived from DMTA experiments for different blends with different TPUs. All blends contain 20 wt% of TPU

Compound	Phase separation temperature T_{ps} (°C)	T_g of the dispersed phase (°C)	T_g of the matrix phase (°C)
PPE	–	–	218.2
PPE/TPU-2%	222	79.5	214.5
PPE/TPU-4%	217	78.3	211.3
PPE/TPU-8%	210	74.3	207.0
PPE/PS 50/50	–	–	159.5
PPE/PS/TPU-8%	224	75.0	153.8

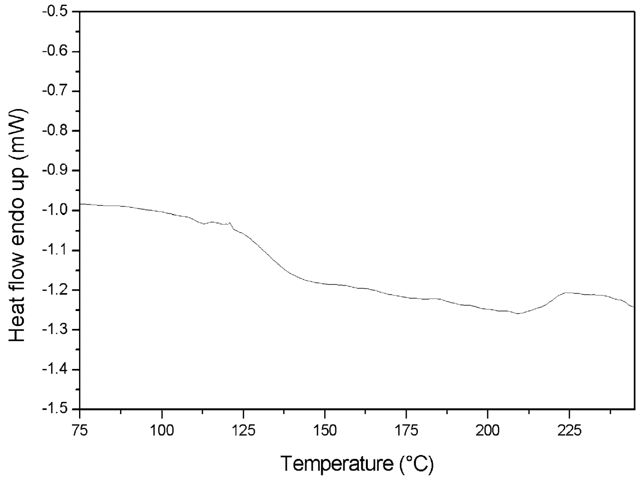

Fig. 13. Cooling curve for PPE/PS/TPU-8% 40/40/20 wt% measured with DSC with cooling rate of 10 °C min^{-1}.

using DSC. As anticipated, due to the fact that the heat flow rate signal is directly proportional to the scanning rate [27], it turned out that for low cooling rates phase separation is not detectable anymore. However, for high cooling rates, poorly resolved signals that are difficult to interpret were obtained, similar to the observations of Van Mele and co-workers [28]. Therefore, DSC was not suitable to study the effect of cooling rate.

The effect of decreasing the T_g of the matrix phase via the addition of a miscible fraction of poly(styrene) (PS) to postpone the vitrification is illustrated in Fig. 13. The exothermic signal upon cooling in DSC returns to the baseline at much lower temperatures, indicating that phase separation continues over a longer period of time. Nevertheless, it can be observed from Table 2 that the T_g of the matrix phase is still lower than the virgin material. This residual solubility originates again from the fragments of TPU-8% which posses a M_n smaller than M_{crit}, although M_{crit} for TPU in PPE/PS is probably lower due to the high molecular weight of the added PS (130 kg/mol). This is confirmed by the higher onset temperature of phase separation for this system compared to the PPE/TPU-8% system, as shown in Table 2.

4. Conclusions

In this study, it was shown that low molecular weight TPU is a suitable reactive solvent for PPE as it reversibly depolymerises to very small fragments at processing temperatures of 250 °C resulting in homogeneous solutions of PPE and TPU. Upon cooling, L–L phase separation between PPE and TPU occurred followed first by vitrification of the PPE-rich phase and at lower temperatures vitrification of the TPU-rich phase. The final blend consisted of a PPE-rich matrix and dispersed TPU particles. As phase separation occurred during cooling, the phase separation is induced thermally as well as chemically, since the molecular weight of the solvent increases upon lowering the temperature.

The starting molecular weight of TPU and the amount of TPU had pronounced effects on the phase separation, morphology and viscosity of the blends. The maximum amount of TPU which can be added proved to be 30 wt%; higher levels of TPU resulted in (partly) immiscible blends. Furthermore, increasing the amount of TPU resulted in larger TPU particles but no effect on the T_g of the PPE-rich matrix was observed. In contrast, increasing the starting molecular weight of TPU resulted in higher phase separation temperatures and higher T_gs for the PPE-rich matrix. The main drawback of the PPE/TPU systems is that there always remains a fraction of TPU in the PPE-matrix. This is a result of vitrification during phase separation, which arrest the phase separation process, or residual solubility of fragments below the critical molecular weight, which are already present in the pure low molecular weight TPU systems. Possibilities for diminishing the residual TPU fractions were explored. The interference of vitrification with phase separation could be postponed and, consequently, the residual fraction of TPU in the PPE phase could be reduced either via an increase in the starting molecular weight of TPU or a decrease in cooling rate or T_g of the matrix.

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