

Reactive blending by *in situ* polymerization of the dispersed phase

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Abstract

The formation of a polyethylene/polyurethane blend polymer via *in situ* polymerization of diols and diisocyanate monomers dispersed in a molten polyethylene matrix was investigated in an internal mixer. Two urethane systems were used in this study. The evolution of the blend morphology with increasing molecular weight of the polyurethane phase was discussed. The difference in viscosity between the minor and major phases has a controlling influence on the qualitative compounding behaviour exhibited. Furthermore, the viscosity ratio appears to be the physical parameter which governs the blend morphology development. The phase inversion was observed at $\eta_d/\eta_m = 0.05$. Beyond the phase inversion point, Wu's model (*Polym. Eng. Sci.*, 1987, 27, 335) quantitatively predicts the decrease of the size morphology with increasing molecular weight of the polyurethane phase. Nevertheless, high solubility of isocyanate monomers and low solubility of alcohols in molten polyethylene induce an imbalance stoichiometry which limits the degree of polymerization (molecular weight) during the blending process. A pre-polymerizing step of the urethane system limits this solubility phenomenon. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Reactive processing of polymer blends has emerged as one of the most attractive fields in polymer science. The properties of polymers can be modified within a wide range by blending and alloying with other polymer components. However, it is widely known that the final morphology of the blend has a controlling influence on the final properties of the blends. Usually, morphology development studies deal with the evolution of the blend morphology from pellet or powder particles to the submicrometre droplets which exist in the final blend. There have been many studies which have reported on the influence of processing conditions on the resultant morphology of a blend [1,2]. Moreover, new developments in thermoplastic polymer blends and alloys have increased sharply because reactive compounding may provide viable mechanisms for the *in situ* elaboration of the desired blend with controlled structure and morphology. For example, the formation of interpenetrating networks via cross-linking reactions in completely immiscible polymers can lead to systems more homogeneous than those formed by classical methods of polymer mixing [3,4]. Unfortunately, very little work has

been reported on polymer blending via *in situ* polymerization of monomers dispersed in a thermoplastic matrix. Kye and White [5] investigated polymerization of caprolactam/polyether sulfone solutions in a twin-screw extruder to form reactive polyamide-6/polyether sulfone blends.

The complex nature of polymer reactive modification processes in the dispersed phase requires a fundamental understanding of the mechanisms that govern chemical reactions in polymeric melt phases, as well as a critical assessment of the role of key process parameters on the end-usage properties of the polymer. The goal of the current work is to investigate both theoretically and experimentally the effect of macroscale chemi-physical phenomena on the molecular and morphological properties of the new polymeric alloys produced with the developed modification technologies in the dispersed phase. Correlations between process parameters, reaction kinetics, molecular weight and morphology are discussed in order to determine the mechanisms of mixing during the compounding of an *in situ* polymerizing system with a molten polymer throughout all process regimes: dispersion of monomers into high polymer to fluid flow of two high polymers. A polymerization reaction without volatile products was used, such as alcohol/isocyanate addition polymerization reaction for the formation of a polyurethane (PU) phase in a polyethylene (PE)

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matrix. The formation of a PE/PU blend polymer via *in situ* polymerization of diols and diisocyanate monomers in a melt polyethylene as matrix was conducted using a Haake Rheomix 600 batch mixer.

It should be noted that the formulation of PU-based alloys [6] has developed over the past years as a means of improving some properties and/or reducing manufacturing cost. Thermoplastic polyurethanes (TPUs) are also widely used in the form of blends with polyvinyl chloride, polyamide, polycarbonate, ABS plastic, polyolefins, etc. [7].

2. Experimental

2.1. Urethane systems

In the formation of linear PU elastomer, the reactants (diisocyanate and diols) join end-to-end to produce polymer chains linked together through urethane groups. Moreover, due to the extensive diversification of possible constituents, a rather wide variety of mechanical properties can be obtained from these materials. Therefore, two urethane systems were chosen as basic systems of this study. As the urethane bonds are considered unstable above 170°C [8], all experiments were carried out at temperatures lower than 160°C.

The first urethane system (system 1) was made from diphenyl methane-4,4'-diisocyanate (MDI; Desmodur 44M, Bayer) and a polyether diol (PEO; $M_n = 1$ kg, Desmophen 1600U, Bayer) of functionality two. The kinetics and the viscoelastic behaviour of the bulk polymerization of this urethane system were studied in a previous work [9]. Consequently, we only focus hereafter on the main elements necessary for the understanding of the present paper.

The Newtonian viscosity η_0 was found to obey the following power law at 140°C:

$$M_w > M_c = 7 \text{ kg}, \quad \eta_0 = 1.24 \times 10^{-4} M_w^{3.45} \quad (1)$$

$$M_w < M_c, \quad \eta_0 = 1 \times 10^{-2} M_w^{1.2} \quad (2)$$

The second urethane system (system 2) was made from dicyclohexylmethane-4,4'-diisocyanate (or H_{12} MDI; Desmodur W, Bayer) and two diols. The polyether diol used in the first system was used as the soft segment and 1,4-butanediol (BDO; Aldrich) was added as chain extender. Only one molar composition of BDO/PEO was used and fixed at 2:1, which corresponds to three moles of diisocyanate, since the polymerization is run near the stoichiometric ratio. Then, a three-component system comprising 51% by weight of hard segment (H_{12} MDI + BDO) was used throughout the study. The initial concentration of diol or diisocyanate monomers was $[A_0] = 3.12 \text{ mol l}^{-1}$. The kinetic constant k was observed as:

$$k = 5.45 \times 10^9 [\text{Cat}]^1 \exp(-E/RT) \quad (3)$$

where E is the activation energy of the reaction ($E = 48.5 \text{ kJ mol}^{-1}$) and $[\text{Cat}]$ is the catalyst concentration.

The flow activation energy was obtained from the Arrhenius plot of the shift factors a_T of time-temperature master curves for samples of different molecular weights. Surprisingly, contrary to system 1, the flow activation energy was observed to be dependent on the molecular weight, even at high molecular weights ($M_w/M_e > 30$). Generally, the flow activation energy was observed to be constant for entangled linear polymers. This singular behaviour can be explained from the copolymer structure of the PU formed from three components. It was shown [10] that the molecules of an original PU are quite dissimilar in chemical composition and average hard-segment length. Therefore, it can be expected that the microstructure of the chain varies with the degree of polymerization, and consequently with the molecular weight. Experimentally, the flow activation energy was observed as:

$$E_v = 4.25 \times 10^4 M_w^{0.25} \text{ J mol}^{-1} \quad (4)$$

and the Newtonian viscosity as:

$$\eta_0 = 1.7 \times 10^{-3} M_w^{3.2} \exp\left[\frac{E_v}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (5)$$

T_0 is the reference temperature ($= 140^\circ\text{C}$).

2.2. Blending

Experiments were carried out in a Haake Plasticorder discontinuous batch-type reactor equipped with a Rheomix 600 chamber. It contains non-intermeshing counter-rotating rotors with double flighted designs, the resistant torque developed on the rotors being recordable. The rotor speed was fixed at 50 r.p.m. Presuming that the assumption of Goodrich and Porter [11] can be used, that the Haake Rheometer be considered as two adjacent co-axial cylinders, the average shear rate is about 200 s^{-1} . This value is only a first approximation of the average shear rate inside the reactor. Conversely, the variation of the torque can be qualitatively correlated to the apparent viscosity of the molten polymer system inside the reactor.

The PE phase was first melted in the reactor and the thermal regulation was adjusted in order to obtain a melt temperature of 140°C. Then, diisocyanate and diol (plus catalyst) were introduced into the reactor on the molten PE phase thermally stabilized at the melt temperature of 140°C. The blend ratio (in weight) was fixed at 85% PE and 15% PU. At different reaction times, sample products were collected from the reactor (about 1 g) directly into 8-ml vessels containing a solution of *n*-butylamine in tetrahydrofuran (THF; 2% by weight) in order to quench the reaction.

2.3. Analysis

As THF is a non-solvent of the PE matrix, two problems

arise: (1) the polymerization reaction is not instantaneously quenched in the core of the sample and (2) the solvent does not extract sufficient PU dispersed in the PE phase to enable measurement of the molecular weight distribution by size exclusion chromatography (SEC). Note that the SEC analysis requires concentrations of polymers in the solvent of about 5 mg ml^{-1} . The samples in THF were then stored in a freezer at -20°C . At this temperature, close to the T_g (-25°C) of the PU samples, the kinetics of polymerization can be considered as negligible over many weeks. In order to extract the PU phase from the PE matrix, the samples were sliced with a microtome in order to obtain sample PE/PU films of $5 \mu\text{m}$ thickness. As the average diameter of a PU droplet is about $2 \mu\text{m}$ (see Results and Discussion), it is then possible to extract sufficient PU polymer for an SEC characterization.

The samples were fractured in liquid nitrogen and after dissolution of the dispersed PU phase in THF, the morphology of the blend was examined by scanning electron microscopy (Jeol JSM35) and characterized by image analysis of 500 particles in order to obtain the particle size distribution (average radius in number R_n and average number in volume R_v).

3. Results and discussion

Assuming that the kinetic law of bulk polymerization is valid in dispersed media, the catalyst concentration was calculated for the two urethane systems in order to fit the kinetics of polymerization to the sampling procedure. For example, requiring a molecular weight of about 100 kg at the end of a sampling procedure of 60 min, the catalyst concentration was fixed at $[\text{Cat}] = 4.5 \times 10^{-6}$ and $1.0 \times 10^{-4} \text{ mol l}^{-1}$ for urethane systems 1 and 2, respectively.

Although the viscosity ratio of the two incompatible blend constituents at representative process conditions cannot describe the complexity of the melting and melt-flow processes that control the evolution of the blend morphology, it is generally a useful starting point. The viscosity ratio, $\lambda = \eta_d/\eta_m$, expresses the relative viscosities of the matrix phase (η_m) and the dispersed phase (η_d). Therefore, the complex viscosities of the blend components were measured at 140°C and the shear viscosities were calculated from the Cox–Mercx rule [$\eta^*(\omega) = \eta(\dot{\gamma})$]. In the present study, as the molecular weight increases with the blending time, the evolution of the viscosity ratio will be expressed *versus* the molecular weight of the PU phase at a representative process stage ($T = 140^\circ\text{C}$ and $\dot{\gamma} = 200 \text{ s}^{-1}$). At 200 s^{-1} , the PE phase presents non-Newtonian behaviour and the viscosity is observed to be 700 Pa s . Under identical processing conditions, urethane system 1 exhibits Newtonian viscosity at molecular weights lower than 100 kg, whereas urethane system 2 exhibits Newtonian behaviour for molecular weights lower than 40 kg. The viscosity ratio was calculated from Eqs. (1) and (5) with respect

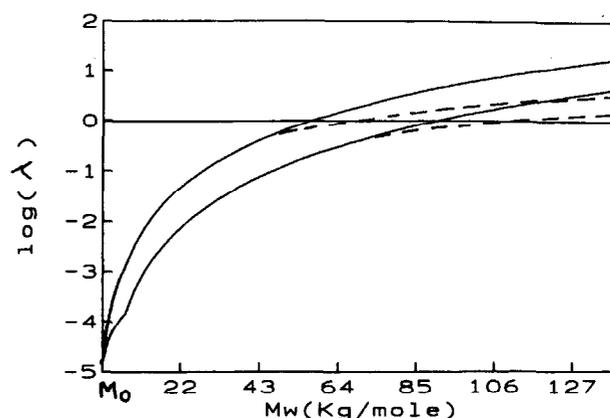


Fig. 1. Variation of the viscosity ratio $\lambda = \eta_d/\eta_m$ versus molecular weight of the PU phase. (—) Newtonian viscosity ratio; (---) viscosity ratio at $\dot{\gamma} = 200 \text{ s}^{-1}$; $T = 140^\circ\text{C}$.

to the Newtonian behaviour region. Outside this region, for higher molecular weights, the viscosity ratio was calculated by interpolation of the viscosity $\eta(\dot{\gamma})_T$ at different molecular weights. Fig. 1 shows the variation of the viscosity ratio *versus* molecular weights (\equiv extent of the urethane polymerization) of the two urethane system phases. The viscosity ratios of the two systems exhibit an identical trend. Considering system 1, the variation of the viscosity ratio ranges from 3×10^{-5} to 1 at $M_w = 100 \text{ kg}$. However, system 2 presents a higher viscosity compared with system 1. Recall that system 2 has a copolymer basic structure due to the presence of hard segments (BDO) as chains extenders. It can therefore be expected that the presence of these hard segments will tend to increase the friction coefficient of the PU chains.

Conversely, the interfacial tension between the PU and the PE phase was estimated from Palierne's model [12], based on the linear viscoelastic behaviour of the blend. From this model, the value of the interfacial tension was estimated to be $\gamma_{12} = 18 \pm 2 \text{ m N m}^{-1}$. This value is close to that given in the literature [13] on polyolefin/PU blends.

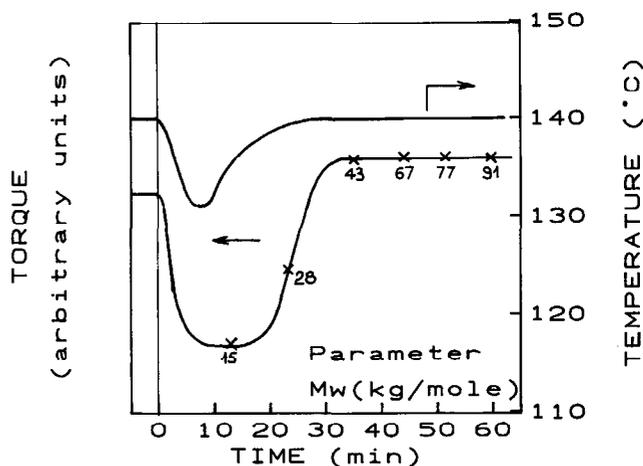


Fig. 2. Reactive compounding of PE/PU system 1: resistant torque and temperature histograms. $T = 140^\circ\text{C}$, $N = 50 \text{ r.p.m.}$

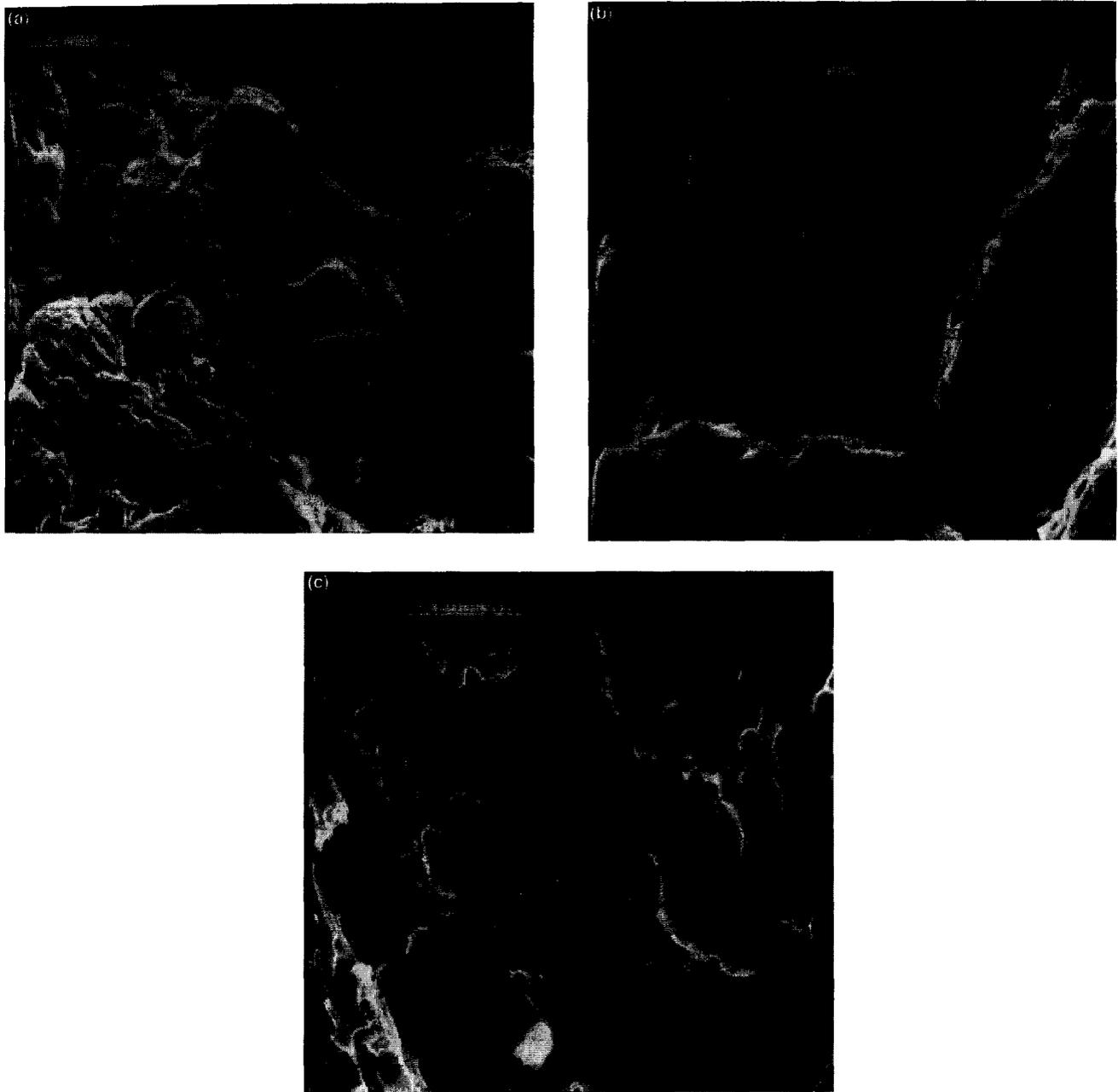


Fig. 3. Scanning electron microscopy of the PE/PU blend. (a) Macroscale co-continuous morphology, magnification $\times 100$. (b) Microscale co-continuous morphology, magnification $\times 600$. (c) Micronodular morphology, magnification $\times 1000$.

3.1. Urethane system 1

Fig. 2 shows the variation of the resistant torque *versus* the reaction time for the polymerization of the MDI/alcohol system 1 in molten PE. Molecular weights of the different samples collected at different reaction times are reported in this figure. As explained in the Experimental section, at time $t = 0$, diisocyanate and diol (plus catalyst) monomers were introduced into the reactor in which the PE had previously been melted. A spectacular decrease in the torque can then be observed. At this stage of blending, the system is composed of a viscoelastic matrix of relatively high

viscosity ($\eta_m = 7 \times 10^2$ Pa s), whereas the minor phase (oligo-urethane) presents a low Newtonian viscosity ($\eta_d = 1 \times 10^{-1}$ Pa s) at $t = 5$ min ($M_w = 8$ kg). At this reaction time, no dispersion occurs in the reactor and the reaction system is divided into two macro-phases. Actually, the apparent rheology of the system is governed by the viscosity of the PU phase, which 'coats' the PE phase. Indeed, a solubility test in THF shows that a macroscopic dispersion (size about 1 mm) of PE in the solvent is obtained. Furthermore, SEM analysis (Fig. 3a) confirms this macroscopic co-continuity between the two phases.

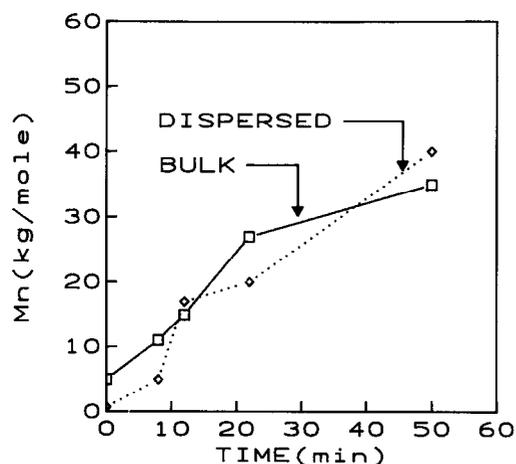


Fig. 4. Polymerization kinetics (M_n versus curing time) in bulk and in dispersed media; urethane system 1, $T = 140^\circ\text{C}$.

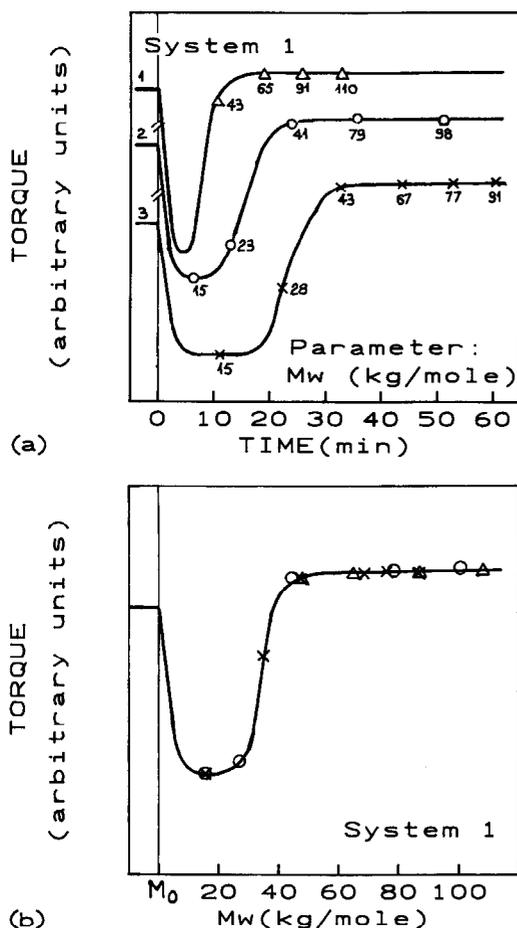


Fig. 5. Urethane (system 1) polymerization in PE phase for different kinetics. (a) Variation of the resistant torque versus reaction time at three catalyst concentrations. Curve 1, $[\text{Cat}] = 2.8 \times 10^{-5}$; curve 2, $[\text{Cat}] = 4.5 \times 10^{-6}$; curve 3, $[\text{Cat}] = 3.1 \times 10^{-6} \text{ mol l}^{-1}$. (b) Master curve: variation of the resistant torque versus molecular weight. Symbols as in (a).

Table 1
Solubility constants of the different diisocyanate and alcohol monomers at $T = 140^\circ\text{C}$

	Monomer			
	BDO	PEO	MDI	H ₁₂ MDI
S/ρ	0.01	0.023	0.40	1.80

With increasing molecular weight of the PU phase ($15 < M_w < 40 \text{ kg}$), the resistant torque (\equiv viscosity) of the system increases because the growing molecular weight of the PU produces a higher viscosity. The system presents a micro-co-continuous morphology, as shown in Fig. 3b. At higher molecular weights of the PU phase ($M_w > 40 \text{ kg}$), the torque reaches a constant value, which means that the viscosity of the system is constant and close to the viscosity of the PE matrix. Actually, the torque generated by the PE/PU system at this stage of blending is slightly higher than the torque generated by the pure PE phase. This difference can be attributed to the degree of fill of the chamber, which increases with the addition of the PU phase. Furthermore, a perfect nodular morphology of the dispersed PU phase is observed, as shown in Fig. 3c. Therefore, the rheology of the blend is governed in a first approximation by the rheology of the PE matrix. One can note that the variation of the melted temperature presents a similar trend with the resistant torque histogram. The temperature decrease at injection of the monomers into the reactor is due to the fact that the monomers are at room temperature. Also, slip phenomena due to the macroscale between molten PE and the monomers, which limits self-heating by viscous dissipation, cannot be excluded in this process.

The torque mixing curve then shows a phenomenon of phase inversion, resulting in a continuous PE phase and a PU dispersed phase occurring near a critical molecular weight ($M_w = 40 \text{ kg}$). Similar increases in torque caused by phase inversion have been observed by Scott and Joung [14] in non-reactive systems. This study concerned the mechanisms of mixing during the compounding of a low-viscosity, immiscible additive (polyethylene of low molecular weight) with a molten polymer (polystyrene). It was shown that the rise in mixing torque that occurs in conjunction with the phase inversion is primarily due to an increase in blend viscosity caused by the morphological transformation. Although it was shown that the time interval to phase inversion decreased with increasing viscosity ratio of the two constituents, it can be assumed in the present study that phase inversion phenomena are time independent and a function of only the degree of polymerization of the PU phase. The effects of *in situ* reactive blending, through the variation of the molecular weight of the minor phase, can be minimized in comparison with the time-dependent effects of pure mechanical blending. The kinetics of urethane polymerization in bulk and in an internal reactor in the presence of PE (polymerization in the dispersed phase) are plotted in Fig. 4, as explained previously. From

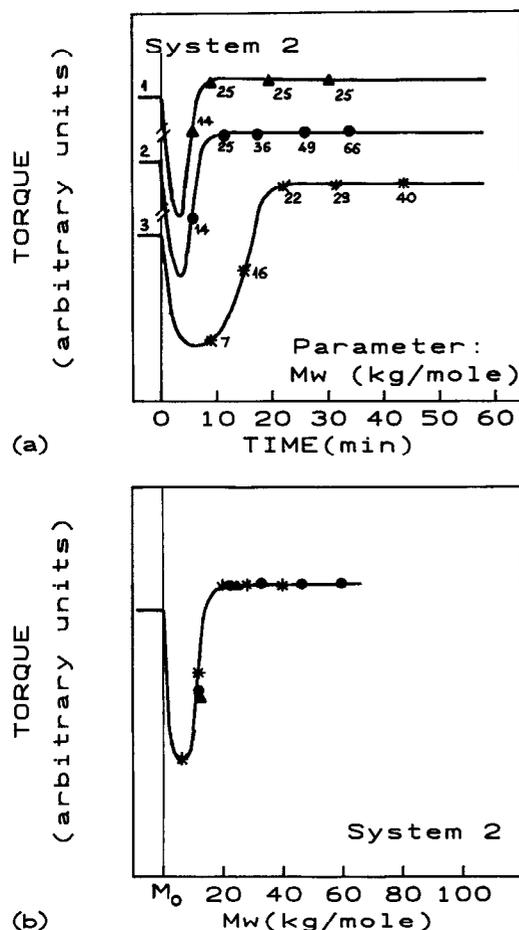


Fig. 6. Urethane (system 2) polymerization in PE phase. (a) Variation of the resistant torque versus reaction time (curve 1, $[Cat] = 2 \times 10^{-4} \text{ mol l}^{-1}$). Effects of addition to the reactor of monomers or oligomers (curve 2, $[Cat] = 2 \times 10^{-4} \text{ mol l}^{-1}$; curve 3, $[Cat] = 1.6 \times 10^{-5} \text{ mol l}^{-1}$). (b) Master curve, variation of the resistant torque versus molecular weight. Symbols as in (a).

the point of view of the mechanisms of polymerization, this figure clearly shows that polymerization in the dispersed phase, in the given processing conditions, is identical to bulk polymerization. That is, the molecular weight increases linearly with the reaction time.

In order to confirm the molecular weight–torque dependence, two additional experiments were performed with slower and faster kinetics of urethane polymerization at the same temperature of 140°C . The catalyst concentrations used were $[Cat] = 3.1 \times 10^{-6}$ and $[Cat] = 2.8 \times 10^{-5} \text{ mol l}^{-1}$, respectively. Fig. 5a displays the time dependence of the torque for three different kinetics of polymerization. Identical behaviour can be observed, which means that the previous general comments on the reactive blending mechanisms, as stated above, remain valid whatever the kinetics of polymerization are. Quantitatively, Fig. 5b shows that a master curve is obtained when plotting the variation of the resistant torque as a function of the molecular weight. These results prove that only the molecular weight of the reactive PU phase has a controlling

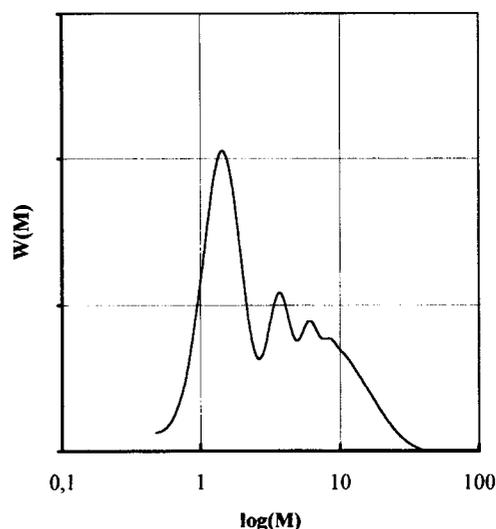


Fig. 7. Molecular weight distribution of urethane oligomers (system 2); $M_w = 5 \text{ kg}$.

influence on the qualitative compounding behaviour exhibited.

3.2. Urethane system 2

Fig. 6a shows the variation of the resistant torque versus compounding time. The torque behaviour of this system has some similarities, but also a major difference with urethane system 1. An identical trend was observed for the variation of the resistant torque with increasing molecular weight of the PU phase, as already pointed out for urethane system 1. During the compounding process, where a molecular weight of about 80 kg was expected, the molecular weight of the PU phase reached a low value ($M_w = 22 \text{ kg}$), which remained constant to the end of the experiment. Remembering that the efficiency of a poly-addition reaction depends mainly on the stoichiometric isocyanate : alcohol ratio, the present results show that a stoichiometric imbalance develops in the PE matrix during the polymerization of urethane system 2. From Carother's equation, this result implies that the stoichiometric ratio is 0.945. One possible explanation of a stoichiometric imbalance is a different partial solubility of alcohols and isocyanate in the molten PE phase. In order to test this assumption, solubility experiments were performed at a temperature of 140°C under static conditions. PE discs (diameter = 25 mm, $h = 0.5 \text{ mm}$) were introduced into vessels containing one of the reactants (MDI, H_{12} MDI, PEO and BDO) used in this study. The solubility constant was measured by a weight method of the monomers' absorption into the PE discs. The values of the solubility (divided by the volumetric mass) S/ρ are reported in Table 1. These data indicate that the H_{12} MDI reactant presents a high solubility in the PE phase, whereas alcohols, as expected, present a very low solubility in melted PE. The MDI used in urethane system 1 also presents a high solubility, but lower than that of H_{12} MDI. The high solubility of H_{12} MDI in

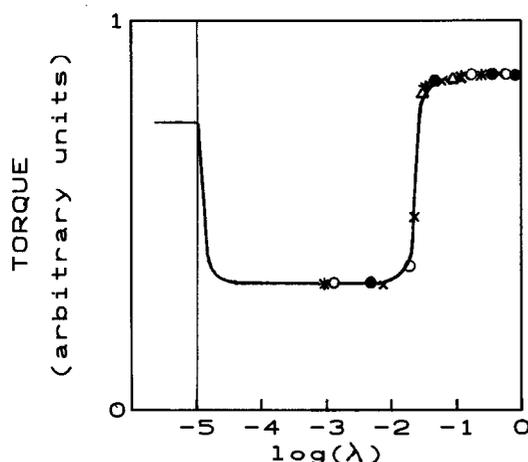


Fig. 8. Master curve. Predominant influence of the viscosity ratio on the blend morphology development. Variation of the resistant torque versus viscosity ratio for the two urethane systems. Symbols as in Fig. 5a and Fig. 6a. $T = 140^{\circ}\text{C}$, $N = 50$ r.p.m.

molten PE is the origin of the stoichiometric imbalance which induces the low molecular weight of the PU sample at the end of the experiment. Two possible ways to achieve a high molecular weight at the end of the blending experiment are (1) to increase the concentration of H_{12}MDI in order to compensate for the amount of diisocyanate which has diffused into the PE or (2) limit the solubility of H_{12}MDI . From the point of view of development of PE/PU blends, method (1) is not appropriate due to the high toxicity of H_{12}MDI ; residual monomers can be trapped in the PE at the end of the elaboration of the blend. The second method, which appears to be more promising, is to limit the solubility of diisocyanate by pre-polymerizing the isocyanate/alcohol system in order to form urethane oligomers with low solubility in PE. So, before introducing the isocyanate/alcohol monomers into the melted PE, the reactant system was pre-polymerized at a temperature of 140°C over 5 min. As a result, PU oligomers of low molecular weight ($M_w = 5$ kg) are generated in the system, as shown in Fig. 7. It can be concluded that the solubility of H_{12}MDI vanishes with the formation of urethane oligomers. Fig. 6a shows that a significant improvement occurs at long reaction times, because the PU phase reaches high molecular weights close to $M_w = 60$ kg whatever the kinetics of polymerization. These results prove that the solubility of the monomers plays an important role in the blending phenomena of *in situ* polymerization of the PU phase.

Plotting the variation of torque versus molecular weight (Fig. 6b) shows, as observed previously for urethane system 1, that a master curve can be obtained whatever the kinetics of polymerization. As already discussed in the case of system 1, PU phase molecular weight has a controlling effect on the blend development.

However, phase inversion was observed at a low molecular weight ($M_w = 20$ kg) compared with urethane system 1, which means that molecular weight is not the

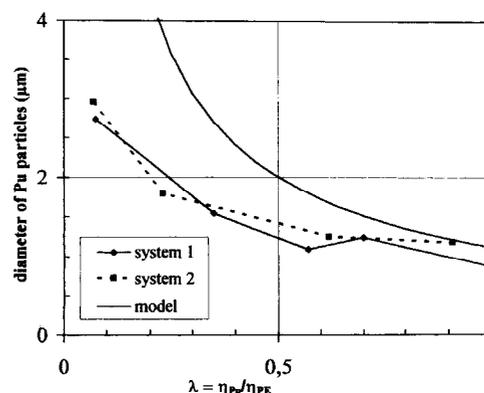


Fig. 9. Variation of the morphology size versus viscosity ratio for the two urethane systems. Prediction of Wu's model.

universal parameter for the development of morphology in different urethane systems.

3.3. Morphology development

It is well known from the literature that the viscosity ratio plays an important role in the blend morphology development. Coupling the variation of the viscosity ratio (Fig. 1) with the variation of the resistant torque versus molecular weight of the two urethane systems, the variation of the resistant torque can be plotted versus the viscosity ratio as a master curve (Fig. 8). The phase inversion point is observed at a viscosity ratio close to 5×10^{-2} . When investigating the phase inversion phenomenon, the component volume fractions and their respective viscosity ratios have been used to predict the point of phase inversion. Experimentally, it was found that the usual semi-empirical relation $\varphi_m/\varphi_d = \eta_d/\eta_m$ is not satisfied when the viscosity ratio differs from 1. For example, applying this criterion to our blend, phase inversion should occur at $\eta_d/\eta_m = 0.17$, which means that phase inversion should occur at $M_w = 120$ and 60 kg for urethane systems 1 and 2, respectively. Alternative criteria for the phase inversion point have also been proposed [15]. However, these criteria are inadequate for prediction of the phase inversion of our blends, because the viscosity ratio is too low ($\eta_d/\eta_m < 0.25$). As already concluded by Scott and Joung [14], the factors controlling phase inversion during compounding are not yet well understood.

At the phase inversion point, the morphology is co-continuous and becomes nodular beyond this point. Beyond the phase inversion point, the quantification of the size morphology is reliable. The evolution of the morphology with the reaction was determined for the two urethane systems. Fig. 9 shows the variation of the number average radius versus the viscosity ratio. This figure shows that the two urethane systems present identical behaviour of the variation of the morphology size versus viscosity ratio. The morphology size decreases with increasing viscosity ratio, as predicted by Wu [16]. Wu reported that droplets

can break up during extrusion at high viscosity ratios. He obtained a correlation between capillary number and viscosity ratio. The following expression for the final particle radius, R , was derived:

$$R = \frac{\gamma_{12}}{\eta_m \dot{\gamma}} 4 \left[\frac{\eta_d}{\eta_m} \right]^{\pm 0.84} \quad (6)$$

where the (+) sign in the exponent applies for $\eta_d/\eta_m > 1$ and the (-) sign applies for $\eta_d/\eta_m < 1$.

This empirical relationship includes the different mechanisms occurring in the system, such as break-up and coalescence. Serpe *et al.* [17] proposed taking into account the influence of the concentration of the dispersed phase by a modification of the capillary number. Thus, the droplet radius can be estimated through the following relationship:

$$R = \frac{\gamma_{12}}{\eta_m \dot{\gamma}} \frac{(\eta_d/\eta_m)^{\pm 0.84}}{[1 - 4(\varphi_d \varphi_m)^{0.8}]} \quad (7)$$

Fig. 9 shows that Wu's model accurately predicts the variation of the size morphology with increasing viscosity ratio.

4. Conclusion

The PE/PU blends produced through the developed modification technologies in dispersed media were investigated. Experiments were performed in a discontinuous reactor in order to elucidate the effect of the chemi-physical phenomena on the morphological evolution of the PE/PU blend. Two urethane systems were used in this study. The following results were obtained.

- High solubility of isocyanate monomers and low solubility of alcohols in molten PE induce an imbalanced stoichiometry which limits the degree of polymerization (molecular weight) during the blending process. A pre-polymerizing step of the urethane system before injection into the molten PE limits diffusion phenomena.
- The difference in viscosity between the minor and major phases has a controlling influence on the qualitative compounding behaviour exhibited. Furthermore, viscosity ratio appears to be the physical parameter which governs blend morphology development. From the

point of view of rheological behaviour, the phase inversion point was observed at $\eta_d/\eta_m = 0.05$.

- Beyond the phase inversion point, Wu's model quantitatively predicts the decrease of the size morphology with increasing viscosity ratio, i.e. with increasing molecular weight of the PU phase.

This study proves that blends based on thermoplastic PU can be developed in dispersed media in discontinuous reactors from modification technologies. A follow-up paper will describe the application of this technology to continuous reactors such as twin screw extruders.

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