Investigations of Miscibility in Interpenetrated Systems of Polyurethane and Polystyrene Obtained at Room Temperature

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Summary: Interpenetrating polymer systems based on crosslinked polyurethane (PU) and polystyrene (PS) were prepared at room temperature by a one-shot (*in situ*) method, starting from an initial homogeneous mixture of reagents via non interfering mechanisms. Both polymerizations were performed either simultaneously or one after the other. Crosslinks and/or covalent bonds between components were deliberately introduced by the addition of appropriate monomers, in order to tailor the degree of microphase separation. Depending on the formation process, transluscent or transparent films were obtained, despite the difference in refractive index of the components. The maximum of miscibility, taken as from the glass transition criterion, was obtained for sequential tightly graft interpenetrating networks.

Keywords: dynamic mechanical analysis; *in situ* synthesis; interpenetrating polymer networks; phase separation

Introduction

Nowadays, most high performance materials are phase-separated materials resulting from the combination of existing polymers rather than issued from new monomers. The simplest type of combination is a mechanical blend of two polymers, polymer A and polymer B, which exhibits different properties, classically an elastomer associated with a rigid polymer. If possible from a synthetical point of view, formation of A-B block or graft copolymers is preferred in terms of their physical properties and phase-separated microstructure. But the newest multicomponent materials are interpenetrating polymer networks[1, 2], IPNs, which offer some synergy of properties due to their particular entangled morphology resulting from the control of the preparation conditions and composition. The so-called *in situ* IPNs are obtained by a one-shot process starting from an appropriate homogeneous mixture of monomers and prepolymers which

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is polymerized and crosslinked via non interfering reaction mechanisms, typically a step growth reaction and a chain polymerization. The onset of these two reactions may be concomitant or delayed in time, thus forming *in situ sim* (simultaneous) IPNs or *in situ seq* (sequential) IPNs, respectively. It is worth precising that for in situ *seq* IPNs, the onset of the second polymerization takes place well after gelation of the first component. Many kinds of interpenetrated systems can be formed, depending on the addition (or not) of multi- and/or hetero-functional molecules to the initial reactive mixture. They are denoted f-IPN (full) when both components are crosslinked, and s-IPN (semi) when only one component is crosslinked. IPN-G and IPN-g denote interpenetrated systems having short or long covalent bonds between the components, respectively.

The system under investigation is based on the combination of 35% polyurethane (PU) and 65% polystyrene (PS) by weight, which are two polymers thermodynamically incompatible. It is well known that microphase separation takes place in the course of the chemical reactions, according to a spinodal mechanism [3]. Incompatibility develops from a given conversion degree up to the formation of a sufficient number of entanglements which suppresses molecular mobility. Therefore, the conditions of formation reflect on the state of mixing. Various materials have thus been prepared, just differing by the presence or the absence of crosslinks and/or grafts. Information on the degree of phase separation was mainly gained from the glass transition behavior, determined by means of dynamic mechanical thermal analysis. Additional morphological informations were expected from small-angle X-ray scattering experiments.

Experimental

Interpenetrated PU/PS systems were prepared at room temperature by a one-shot process (*in situ* synthesis). Under vigorous stirring, a proper amount of poly(propylene oxide), MW~2000 g/mol, tris(6-isocyanato hexyl) isocyanurate, styrene and benzoin (0.5% by weight) were mixed for 5 min to form a homogeneous mixture. In some cases, 5 wt-% of divinylbenzene (DVB), and/or 1.5 wt-% of 2-hydroxyethyl methacrylate (HEMA) or 2-isocyanatoethyl methacrylate (IEM) was added to that mixture. The ratio between total isocyanate groups and total hydroxyl groups was 1.07. [4] Then, 1.5% by weight based on the PU components of dibutyltin dilaurate was added under stirring, and the mixture poured into a mold formed by two glass plates separated by an appropriate spacer and clamped together. Entrapped air bubbles were removed under vacuum.

The mold was exposed to the ultraviolet (UV) radiations (predominantly 365 nm) of a 100 W mercury lamp, either immediately after filling or after a 24 h preliminary stay in the dark. Light intensity at the surface was 7 mW·cm^{-2}. Reaction temperature was maintained at 25°C. After 10 h of irradiation which correspond to a plateau in the conversion versus time curves, light was switched off, and the sample was removed from the mold. Unreacted chemicals were eliminated under vacuum overnight. Films of 700 μm thickness were thus obtained.

A Fourier transform infra red spectrophotometer (Bomem Michelson MB 155) was used for kinetic measurements. The apparatus was equipped with an external UV light source (UVP SpotCure) and a flexible UV light guide, allowing simultaneous UV exposure and IR analysis. Scanning resolution was 2 cm^{-1} and 10 consecutive scans were averaged for each specimen. Reaction conversion was calculated from the decay of the normalized absorbance of characteristic peaks: the isocyanate peak at 2275 cm^{-1} and the vinyl double bond peak at 1639 cm^{-1}. Dynamic mechanical analysis (Metravib RAC 815 viscoanalyser) was performed to determine the glass transition temperature (Tg) of the films. Tg was taken at the maximum of the loss tangent (tan δ). Experiments in the tensile mode were done from –70 to 150°C at a fixed frequency of 5 Hz and a heating rate of 2°C/min, under dry nitrogen. The refractive index, *n*, of some samples was measured with an Abbe digital refractometer equipped with a thermostated (25°C) water circulation. Small-angle X-ray scattering (SAXS) experiments were carried out on a Nano Star apparatus using CuKα radiation. The signal was detected by a two-dimensional position-sensitive detector on dry films under vacuum. X-ray patterns were recorded every 10 min.

Results and Discussion

Two series of 35/65 PU/PS s-IPN, s-IPN-g (addition of IEM), s-IPN-G (addition of HEMA), f-IPN, f-IPN-g and f-IPN-G have been prepared, according to the above description. The first series concerns *in situ seq* materials whereas the second series refers to *in situ sim* materials. The reaction kinetics of both processes are illustrated in Figures 1 and 2 by their conversion versus time curves. Figure 1 shows that although both reactions start at the same time, the formation of PU and PS is not simultaneous. The PU formation appears to be faster than the polymerization of styrene, but gelation, which takes place around 70% conversion, occurs too late to prevent polymerization-induced phase separation to extend. On the other hand, concerning the *in situ seq*

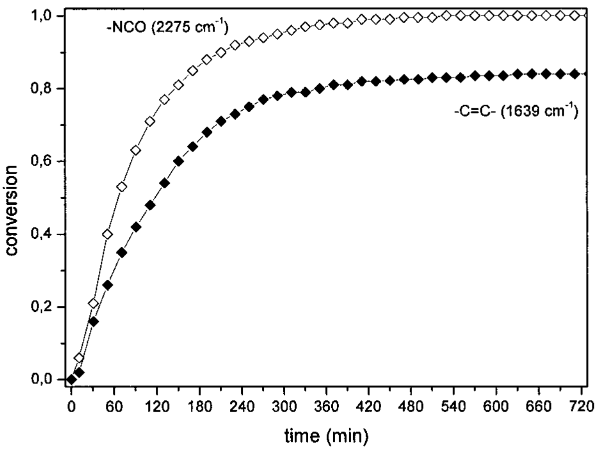

Figure 1. Kinetics of *in situ sim* f-IPN formation. PU (◇) ; PS (◆).

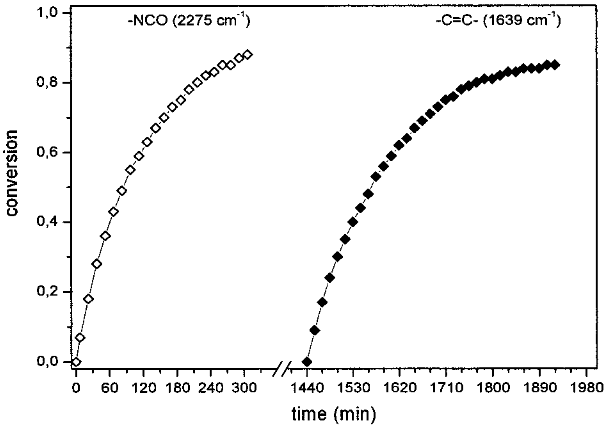

Figure 2. Kinetics of *in situ seq* f-IPN formation. PU (◇) ; PS (◆).

process (Figure 2), the formation of the PU network is complete, and polymerization of styrene can only proceed in the immediate vicinity of the preformed PU network, due to topological hindrances. Therefore, higher miscibility between PU and PS is expected by using this sequential method.

Contrary to previous *in situ seq* full- and graft- IPNs based on the same precursor components and prepared similarly[5] (except for the use of a thermal initiator, which decomposes at 60°C, instead of a photoinitiator) which were opaque, the present *in situ sim* and *in situ seq* PU/PS films are slightly turbid and perfectly transparent, respectively (Figure 3).

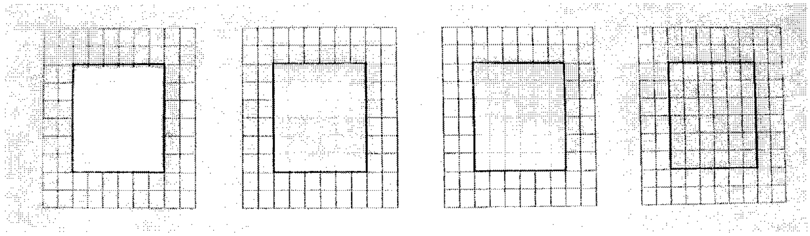

Figure 3. Aspect of 35/65 PU/PS f-IPN films obtained under various experimental conditions: from left to right: *in situ sim* (thermal decomposition of initiator), *in situ seq* (polymerization of styrene at 60°C), *in situ sim* (photopolymerization at room temperature), *in situ seq* (idem).

Since there is a significant difference in the refractive index of PU (n = 1.46) and PS (n = 1.59), the change in optical properties is related to the domain size, and transmission over 90% means that particle sizes under the wavelength of light are obtained when the process develops at room temperature due to higher viscosity which restrains complete phase separation. The refractive index of the films was measured (Table 1): except for the *sim* s-IPN, the refractive index of all samples is higher than the calculated value ($n \sim 1.548$) obtained by rule of mixture from the refractive index of the individual constituants. Systematically, the *in situ seq* film has a higher refractive index than the *in situ sim* film. Also, deviation from the calculated value increases when going from semi- to full-IPNs, and from loosely graft to tightly graft materials. Taking into account the Lorentz-Lorenz equation[6] which relates density and refractive index, the interpenetrated materials are more dense than the corresponding blends. This makes evident the presence of entanglements leading to forced miscibility which increases according to the previously mentioned order.

Table 1. Refractive index, *n*, of interpenetrated materials and deviation from simple additivity.

35/65 PU/PS	simple additivity	*in situ sim*	*in situ seq*	Deviation
s-IPN	1.5472	1.5478	1.5511	0.0039
f-IPN	1.5485	1.5517	1.5525	0.0040
s-IPN-g	1.5469	1.5527	1.5530	0.0061
f-IPN-g	1.5482	1.5538	1.5542	0.0060
s-IPN-G	1.5479	1.5544	1.5552	0.0073
f-IPN-G	1.5492	1.5560	1.5559	0.0069

n_{PU} = 1.4647 ; n_{PU+IEM} = 1.4638 ; $n_{PU+HEMA}$ = 1.4668 ; n_{PS} = 1.5916 ; $n_{PS\text{-}co\text{-}DVB}$ = 1.5936. Accuracy ± 0.0001.

The morphology of the various samples was investigated by using small-angle X-ray scattering. When plotting the scattering intensity versus the scattering vector, *q*, the SAXS curves of the

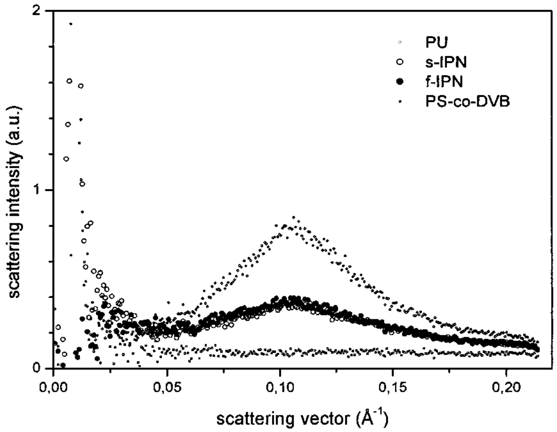

Figure 4. Small-angle X-ray scattering (SAXS) curves obtained for 35/65 PU/PS semi- and full-IPNs, compared to those of the individual components. *In situ seq* process.

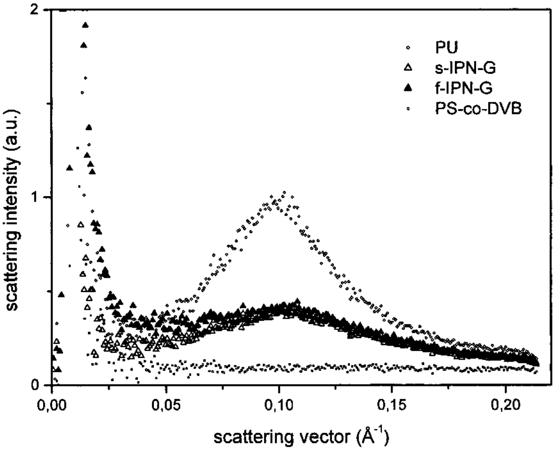

Figure 5. SAXS curves obtained for 35/65 PU/PS tightly graft semi- and full-IPNs. *In situ seq* process.

interpenetrated materials exhibit a broad maximum around 1.1 nm^{-1} , very similar in shape to the curve of the individual PU, but less intense, due to a compositional effect. The *in situ sim* and *in situ seq* curves are superimposable, but the curves of semi- and full-IPNs (Figure 4), and graft materials (Figure 5) are different, with significant broadening of the peak and increase of intensity towards smaller *q*.

This indicates less regular morphologies, i.e. enhanced miscibility. The peaks are too broad to determine the shift of the maximum with enough precision, however, a vague increase (from 5.98 nm to 6.16 nm) suggests that the PU phase is no longer a pure phase, but is enriched by some PS chains. Otherwise, the average distance between urethane groups would remain constant. Hence, these SAXS experiments are qualitative, only.

It is well-known that when a polymer mixture is phase-separated, two or more glass transitions, located at the temperature, Tg, of the individual components, are observed. Any shift in Tg accounts for the degree of miscibility. In general, the Tg of crosslinked polymers is difficult to detect using the classical DSC technique. Therefore, the more sensitive dynamic mechanical thermal analysis was used to determine the Tg of each component, which was taken as the temperature of the maximum of the loss factor, tan δ. Additionally, the half-peak width of tan δ is a good indication of the miscibility.

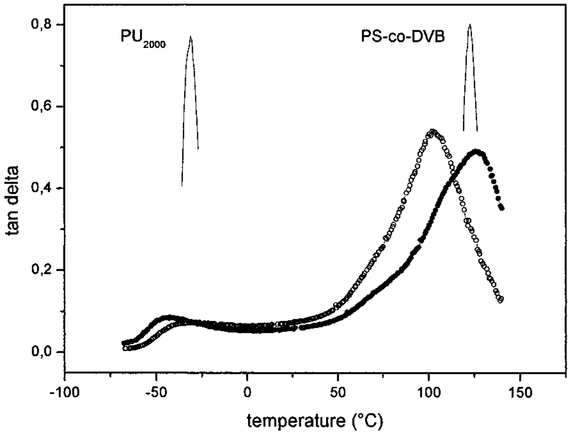

Figure 6. Temperature dependence of the loss tangent of 35/65 PU/PS full-IPNs formed by the *in situ sim* (●) or the *in situ seq* (○) process. The position of Tg of the individual PU and PS is indicated for comparison.

The two series of interpenetrated materials show two broad transitions, typical of phase-separated systems (Figure 6). Compared to the Tg of the individual PU and PS, there is no displacement of the transitions of the *in situ sim* films, but a significant inward shift is observed for the *in situ seq* films. For the latter, at low temperature, the transition of the PU-rich phase is shifted 8 to 23°C to higher temperatures, the maximum shift corresponding to the f-IPN-G sample. At the same time, the lower relaxation becomes less and less distinguishable (Figure 7). Similarly, the Tg of the PS-rich phase is shifted to lower temperatures: the lowest (11°C) and highest (37°C) shifts were for the s-IPN and f-IPN-G samples, respectively. Also, the magnitude of the tan δ peak, especially that of the PS-rich phase, increases together with some broadening of that transition for the *in situ seq* graft samples, compared to s-IPNs and f-IPNs. Consequently, the value of the loss factor in the intermediary region, i.e. between the lower and upper transitions, increases, thus rendering the *in situ seq* graft IPNs interesting as damping materials.

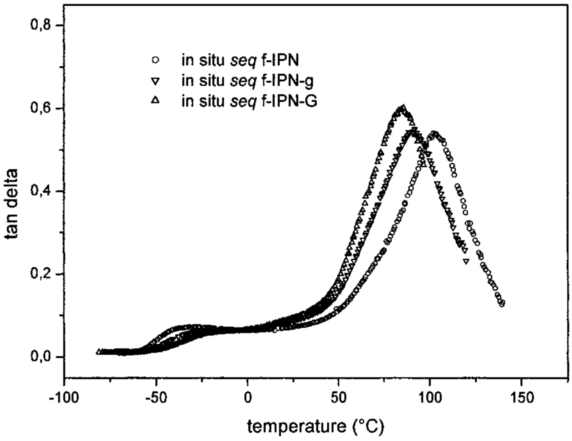

Figure 7. Temperature dependence of loss tangent of 35/65 PU/PS *in situ seq* materials: full-IPN (○), loosely graft IPN (▽) and tightly graft IPN (△).

Conclusion

Polyurethane and polystyrene are two very incompatible polymers. The introduction of steric hindrances like entanglements, crosslinks, covalent bonds increases the miscibility between polyurethane and polystyrene. Also, the *in situ* sequential synthesis of interpenetrated polymers, performed at room temperature and involving photopolymerization of styrene is more likely than the thermal *in situ* simultaneous process, from a miscibility point of view.

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