

# Effect of Crosslink Density and Internetwork Grafting on the Transparency of Polyurethane/Polystyrene Interpenetrating Polymer Networks

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## Synopsis

Because of their incompatibility and the different refractive indices of the homopolymer components, polyurethane/polystyrene interpenetrating polymer networks are turbid by nature. Different parameters likely to enhance their transparency are examined: the crosslink density of each network and the level of internetwork grafting. The results prove that the latter factor is the most effective, as in some cases, very clear and transparent samples are obtained. Correspondingly, preliminary investigations of the dynamic mechanical properties show an inward shift of the glass transition temperatures for such systems. It is concluded that parameters able to cause a higher degree of phase dispersion can yield transparent materials.

## INTRODUCTION

The combination of two polymers as interpenetrating polymer networks (IPNs) usually induces a higher degree of mutual dispersion of the two incompatible phases than mechanical blends or block and graft copolymers.<sup>1</sup> However, except when the refractive indices are not significantly different, such a morphology does not give transparent materials, as the domain size of the dispersed phase still remains too large. According to several authors,<sup>2,3</sup> the introduction of chemical links between the two components of a polymer mixture causes a further decrease in the phase size, and it may then be possible to achieve transparency. Because IPNs can combine the physical entanglements resulting from mutual chain interpenetration with a more or less chemical grafting between the networks, it is quite possible that they can impart transparency to an otherwise opaque polymer blend.

IPNs and semi-IPNs (where one phase remains linear) are currently being investigated in our laboratory.<sup>4,5</sup> One research project is based on IPNs and semi-IPNs containing an elastomeric polyurethane network (PUR) combined with linear polystyrene (PS) or crosslinked polystyrene (PSX), respectively. PUR is formed by a condensation reaction of a triisocyanate with a polyoxypropylene glycol. PSX is formed by styrene co-polymerized with divinylbenzene (DVB). The refractive indices are 1.49 for PUR and 1.59 for PS or PSX, respectively, so that transparency cannot be expected for these incompatible polymers.

In this article, we report two approaches to enhance transparency in PUR/PSX IPNs, namely the variation of the crosslink density of both

networks and the chemical grafting between the two networks. The crosslink density of PUR was changed by using polyoxypropylene glycols of various molecular weights; for PSX, the amount of divinylbenzene was varied. The grafting reaction between both networks was realized by addition of a hydroxy-vinyl difunctional monomer, namely 2-hydroxyethyl methacrylate. The effect of all these parameters on the transparency was studied through turbidity measurements, and the results corroborated by some preliminary investigations on glass transition temperatures.

### EXPERIMENTAL

PUR/PSX IPNs were prepared in a one-shot, two-stage process following the basic procedure developed in our laboratory.<sup>6</sup> Stoichiometric amounts of an aliphatic triisocyanate, Desmodur N (Bayer AG), and a polyoxypropylene glycol (ARCO Chemical) were dissolved in desired amounts of dry styrene (Merck) containing 0.35% by weight of 2,2'-azobisisobutyronitrile (AIBN), and 0–10% by weight of divinylbenzene (DVB) (Merck). The resulting mixture was thoroughly stirred and transferred into a glass mold after addition of stannous octoate (Goldschmidt) as catalyst. The polyurethane network was formed first at room temperature in about 30 min. Styrene was then polymerized by raising the temperature to 60°C. After 15 h at 60°C, the samples were removed from the mold and annealed under vacuum at 120°C for at least 2 h. Graft IPNs were prepared in the same manner except that 2-hydroxyethyl methacrylate (HEMA) (Fluka AG), was added to the initial mixture; in this case, more triisocyanate was used to take into account the hydroxyl groups of the HEMA.

Four polyoxypropylene glycols (POPG) of different chain lengths were used. Their commercial designation and approximate molecular weight,  $M_n$ , appear in Table I. More accurate values were obtained using a Knauer vapor pressure osmometer calibrated with purified 1,12-dodecanediol. All measurements were carried out at 45°C with ethyl acetate as solvent. Molecular weight distributions were evaluated by gel permeation chromatography (GPC) (Beckman model 344, tetrahydrofuran (THF), Styragel columns of 1000, 500, 100, and 50 Å): except for POPG 1004, the polyols were virtually monodisperse. Analysis for hydroxyl groups shows that the POPG have a functionality of approxi-

TABLE I  
POPG Characterization Data

Sample code	DS25	1020	1010	1004
Average molecular weight (g/mol)	4000 <sup>a</sup> 3505 <sup>b</sup>	2000 1910	1050 974	430 461
Hydroxyl value (mg KOH/g)	34.6	60.6	115	251
Refractive index	1.4545	1.4505	1.4495	1.4470

<sup>a</sup>Approximate value given by ARCO Chemical.

<sup>b</sup>Determined by means of vapor pressure osmometer.

mately 2. The molecular weight between crosslinks,  $M_c$ , of the polyurethane networks was assumed to be the molecular weight of the polyol plus two-thirds of the molecular weight of the triisocyanate (478 g/mol for Desmodur N).

The turbidities were determined from measurements of absorbance made with a Varian DMS 80 spectrophotometer from 400 to 800 nm. The samples of about 3.5 mm thickness were polished on both sides. However, the fraction of light reflected on each surface was not taken into account so that there is a systematic error on the turbidity results. The refractive indices of the various materials were determined at the 589 nm doublet of sodium using a thermostatted OPL refractometer.

Dynamic mechanical measurements were performed with a Rheometrics model RMS 7200 mechanical spectrometer at a fixed frequency of 1 rad/s through a temperature range from  $-100^\circ\text{C}$  to  $150^\circ\text{C}$  under dry nitrogen. The test specimens were prepared in rectangular shape about 60 mm in length, 11 mm in width, and 4 mm in thickness. The applied strain was 1%.

## RESULTS AND DISCUSSION

The optical behavior of PUR/PSX IPNs containing 34% by weight of polyurethane has been investigated using a ultraviolet (UV)-visible spectrophotometer. The fraction of light transmitted by the sample,  $T$ , was determined and the turbidity,  $\tau$ , was calculated through the Beer-Lambert extinction law:

$$\tau = -(1/x) \cdot \ln T$$

where  $x$  is the sample thickness.

Turbidity is related to the relative attenuation caused by the scattering of light by the material. The amount of light scattered by a microheterogeneous structure, which can be described by the theory introduced by Debye et al.,<sup>7</sup> depends on the difference in the refractive indices of the scattering particles and the surrounding matrix, and on the size and volume fraction of the dispersed phase. In principle, it is possible to estimate the average domain size of a two-phase system, but in practice the calculations that are involved are quite complex and require assumptions regarding the shape of the heterogeneities. Blundell et al.<sup>8</sup> presented a semiempirical approach for determining the domain size from absorbance measurements. Its applicability to IPNs was verified by small-angle x-ray scattering and electron microscopy.<sup>8</sup> At a given wavelength  $\lambda$ , the mean chord intercept length,  $L_1$ , of the heterogeneities is deduced from the relationship:

$$L_1 = \frac{\lambda \cdot y}{4\pi(1 - \phi)}$$

From the following set of equations,  $y$  may be determined through the experimental value of turbidity:

$$\tau = \frac{2\pi\phi(1 - \phi)}{\lambda} \cdot \frac{(\Delta n)^2}{n} \cdot B(y)$$

TABLE II  
Light Transmission (%) of 34/66 Polyurethane/Polystyrene IPNs at 700 nm:  
Influence of Crosslink Densities

$M_c$ (PUR) \ %DVB	0	1	3	5	10
3824	0	15	34	44	—
2229	5	26	47	49	—
1293	41	69	73	79	79
780	60	—	80	—	—

where

$$B(y) = \frac{y^2 + 2}{y} \cdot \left[ \frac{y^2 + 2}{y^2 + 1} - \frac{2}{y^2} \cdot \ln(y^2 + 1) \right]$$

$\phi$ ,  $n$  and  $\Delta n$  are the volume fraction, the refractive index of the dispersed component, and the difference in refractive indices between the two phases, respectively. An attempt to apply that approach to the present IPNs is presented.

The influence of the addition of divinylbenzene on light transmission is reported in Table II. It appears that the introduction of crosslinks into the rigid phase has a positive effect on the transparency of IPNs. The main increase is already obtained with about 1–3% DVB, and higher amounts of crosslinker do not enhance the transparency significantly: even by adding 10% DVB (an amount that is never used in practice because it makes materials too brittle) no further improvement is observed with regard to the sample containing 5% crosslinker. One possible explanation is that not all the available double bonds of DVB can react due to the high viscosity of the reaction medium, so actual crosslink density is lower than expected from the amount of DVB introduced. Another explanation based on structural considerations is given further on.

The crosslink density of the polyurethane network has been varied by using polyoxypropylene glycols of various chain lengths. As can be seen from Table II, light transmission increases as  $M_c$  decreases. However, only 80% of light is transmitted in the best cases and these PUR/PSX IPNs cannot be considered as transparent materials.

Instead of varying the crosslink densities of either network, the introduction of a molecule that would covalently bond both phases may also enhance transparency. The results obtained by adding various amounts of HEMA to the reaction medium are shown in Table III. For a given POPG, increased HEMA content causes increased transparency. Again, as for the amount of DVB, it seems that for HEMA contents of 3% and more, the evolution is less important. When the amount of HEMA is kept constant, transparency is improved with POPG of lower molecular weight, though the contribution of both parameters cannot be evaluated separately.

Of the three parameters (crosslink density of network 1, crosslink density of network 2, and internetwork grafting), the latter is the only one that allows a polyurethane–polystyrene combination, turbid by nature, to attain a trans-

TABLE III  
Light Transmission (%) of Graft IPNs<sup>a</sup> at 700 nm:  
Influence of Internetwork Grafting Level

<i>M<sub>c</sub></i> (PUR) \ %HEMA	0	1	3	5	7
3824	34	70	77	85	—
2229	47	—	79	—	—
1293	73	82	87	88	89
780	80	—	89	—	—

<sup>a</sup>Polystyrene crosslinked with 3% DVB.

parency of nearly 90%, close to that of polyurethane/poly(methyl methacrylate) IPNs.<sup>9</sup>

IPNs are built of two networks thought to be continuous;<sup>10</sup> it is therefore difficult to describe their morphology in terms of matrix/dispersed phase, as for classical polymer blends. On the other hand, it is generally admitted that the network formed first governs, to some extent, the formation of the second network.<sup>11</sup> In this view, the polyurethane network in the present IPNs may be regarded as the matrix, and the polystyrene as the dispersed phase consisting of interconnected microgels of various sizes and representing the heterogeneities of the material. Thus, when the crosslink density of the polyurethane network increases, the rigid phase becomes more dispersed, and light transmission is improved. The addition of DVB also reduces the mobility of the polystyrene chains, and avoids the formation of large domains due to chain migration, as observed in semi-IPNs.<sup>1</sup> Note that the ineffectiveness of higher DVB contents can also result from the presence of the polyurethane network, already formed, rather than from (or together with) the chemical reason discussed earlier. Finally, the introduction of chemical links between the networks places limits on the degree to which phase separation can occur, and leads to smaller domains, as observed in block copolymers.<sup>12</sup>

One can also explain the increased transparency for IPNs from miscibility considerations: the interlocked chain structure suggests greater molecular mixing at the interphase than in mere mechanical blends. Hence, when the crosslink densities increase, the interphase expands and the PUR phase becomes enriched in polystyrene, and vice versa. Consequently, the difference in refractive indices between the two phases is reduced, resulting in clearer samples. It is obvious that if chemical links are further introduced between the phases, the decrease in  $\Delta n$  will be more pronounced.

By assuming that the polyurethane phase, whatever its content may be in the IPN, constitutes the matrix in which polystyrene forms the heterogeneities, the random two-phase model of Debye et al.<sup>7</sup> can be applied to our system, and the mean chord intercept length,  $L_1$ , has been evaluated. It can be seen in Table IV that in the absence of internetwork grafting, heterogeneities in the range from  $L_1 = 70$  nm to  $L_1 = 30$  nm exist. As expected, the domain size decreases with increasing crosslink densities of both networks. Additional decrease of  $L_1$  is observed when HEMA is used for deliberate internetwork grafting (see Table V). Roughly, there is a decrease by a factor of 3 between the less crosslinked IPN and the most densely crosslinked graft IPN. Our data are consistent with those of Blundell et al.,<sup>8</sup> who examined

TABLE IV  
Average Size of Heterogeneities ( $L_1$  in nm) of 34/66 Polyurethane/Polystyrene IPNs:  
Influence of Crosslink Densities

$M_c$ (PUR) \ %DVB	0	1	3	5	10
3824		56.1	46.0	41.5	—
2229	68.2	50.6	41.9	41.0	—
1293	46.2	34.4	32.4	29.2	29.2
780	41.3	—	30.9	—	—

TABLE V  
Average Size of Heterogeneities ( $L_1$  in nm) of Graft IPNs<sup>a</sup>:  
Influence of Internetwork Grafting Level

$M_c$ (PUR) \ %HEMA	0	1	3	5	7
3824	46.0	31.7	28.4	24.4	—
2229	41.9	—	27.4	—	—
1293	32.4	27.7	24.7	24.3	23.3
780	30.9	—	24.8	—	—

<sup>a</sup> Polystyrene crosslinked with 3% DVB.

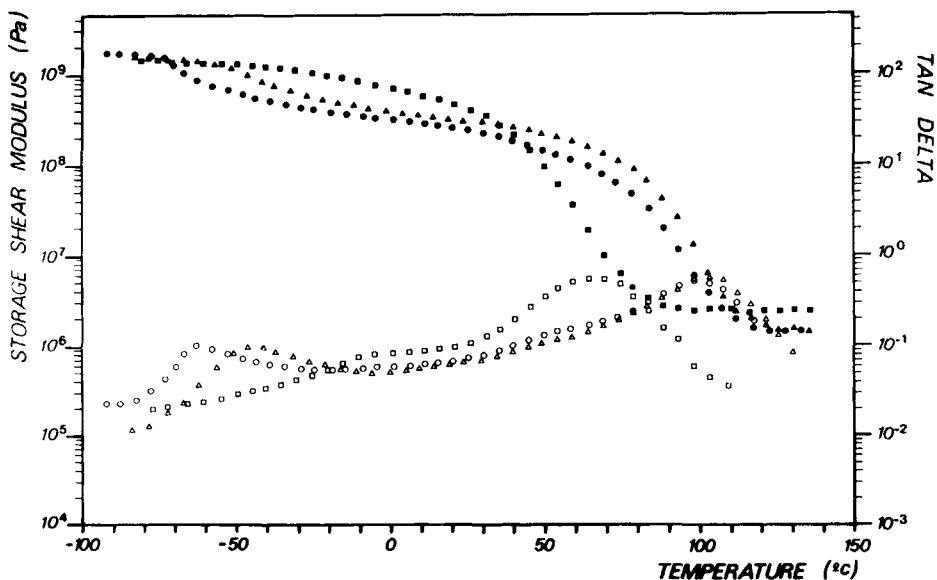


Fig. 1. Tan  $\delta$  (open symbols) and storage modulus  $G'$  (full symbols) curves for 34/66 PUR/PSX IPNs and graft IPNs. PSX with 3% DVB.  $M_c$  (PUR): ( $\bullet$ ,  $\circ$ ): 3824 g/mol, ( $\blacktriangle$ ,  $\triangle$ ,  $\blacksquare$ ,  $\square$ ): 1293 g/mol; % HEMA: ( $\bullet$ ,  $\circ$ ,  $\blacktriangle$ ,  $\triangle$ ): 0, ( $\blacksquare$ ,  $\square$ ): 5.

poly(methyl methacrylate)/polyurethane semi-IPNs: they found  $L_1$  values of the same order of magnitude for a different system in which phase separation is not that restricted since one polymer is linear.

The conclusions drawn from optical density measurements on the various IPNs agree with the results obtained by dynamic mechanical analysis. The latter will be reported in detail in a subsequent article. However, Figure 1 shows an example of how crosslink density and internetwork grafting may influence the damping behavior of IPNs. As already mentioned for other IPNs,<sup>13</sup> the lower (PUR) and the upper (PSX) glass transition temperatures are broadened and shifted inward with regard to the corresponding homopolymer networks, indicating some forced miscibility of the phases. When the crosslink density of the polyurethane network is increased, the low temperature peak is notably shifted, but the inward shift is much more pronounced when grafting between the networks takes place.

From the above results, it follows that if high transparency is required for a combination of polyurethane and polystyrene, only a graft IPN can fulfill this condition. If the material must exhibit other properties such as better impact strength, the crosslink density of the component networks will also play a role, and a compromise between the various properties may be necessary.

## CONCLUSION

From the three parameters examined to enhance transparency of polyurethane/polystyrene interpenetrating polymer networks, namely the crosslink densities of both networks and internetwork grafting, the latter proves to be the most effective. The variation of the crosslink density of PUR plays a more important role than that of PSX, showing again the preponderance of the tridimensional structure formed first in an IPN. It remains that all three parameters have, at various levels, a marked influence on the degree of phase dispersion, and therefore on the final properties of IPNs.

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Received October 23, 1987

Accepted February 12, 1988