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THE TRANSPARENCY OF POLYURETHANE–POLY(METHYL METHACRYLATE) INTERPENETRATING AND SEMI-INTERPENETRATING POLYMER NETWORKS

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Abstract—Various combinations of polyurethane (PUR) and poly(methyl methacrylate) (PMMA) were prepared as interpenetrating polymer networks (IPN) or semi-IPNs. In the latter, either the PUR or the PMMA component was crosslinked. The optical transmissions of these materials were measured as a function of the crosslink degrees of both phases. The role of the PUR chain extender, poly(oxypropylene) glycol, is discussed. It is concluded that any means which increases the degree of phase dispersion favours the transparency of PUR/PMMA based IPNs and semi-IPNs.

INTRODUCTION

Because of their high transparency, certain polymers have been utilized for many years for optical purposes, although they do not usually meet all the other requirements, e.g. good scratch or impact resistance. In other applications, polymer blends, where each component imparts its special properties to the end material, are generally considered in order to overcome the problem of inadequate properties of a given homopolymer. Thus, the introduction of an elastomeric phase into a rigid polymer yields blends with improved impact resistance [1]. However, this method is not valid when transparency is required, as the mixing of two polymers usually yields opaque materials except when the components have nearly the same refractive indices. The loss of transparency is due to the domain size of the dispersed phase, which is rather large as most polymers are incompatible and tend therefore to phase separate [2]. With polymers of the same refractive indices, the particle size is obviously of no significance.

Interpenetrating and semi-interpenetrating polymer networks (IPN and semi-IPN) are currently being investigated in our laboratory [3, 4]. One research project is based on IPNs and semi-IPNs containing an elastomeric polyurethane network (PUR) combined with poly(methyl methacrylate) (PMMA); the latter is crosslinked in the IPNs [5]. The starting reagents have been selected to give polymers with similar refractive indices ($n = 1.49$). Thus, the resulting materials are expected to be transparent and usually they are, although several specific conditions have to be met during their preparation. In other cases, faint cloudiness is observed, indicating that during the reaction process some synthesis parameter has not worked properly.

In this paper, an investigation of the transparency problem in PUR/PAc IPNs and semi-IPNs is reported. The occurrence of turbidity is examined and its origin explained. The conditions under which PMMA-like transparency may be obtained in such materials are given.

EXPERIMENTAL

Materials and synthesis

All the reagents are listed in Table 1. When necessary, functional and other analyses were carried out to check the information given by the manufacturers. Water traces were eliminated but the methacrylic monomers were not freed from the inhibitors. The PUR catalyst, stannous octoate, (OcSn) was used as received. More details, and the determination of the compositional parameters, were given in a previous paper [5]. A standard synthesis proceeds as follows: the calculated amounts of the various reagents are mixed and stirred thoroughly in a dry N_2 atmosphere for a few minutes. The blend is poured into a glass mould. The PUR network is formed first at room temperature, in 15 to 20 min and without a noticeable exotherm. Thirty minutes after the complete mixing of the reagents (taken as the origin of reaction time), the mould is transferred into an oven at 56° where the radical (co)polymerization of the PAc phase is initiated. A forced air circulation in the oven allows temperature regulation within ±2°. After 1 hr, the temperature is raised to 75° for a further period of 2 hr. Time/temperature curves are recorded when necessary. t_{max} is the temperature corresponding to the maximum of the exotherm peak. Finally, the semi-IPN is annealed at 75° overnight and at 120° for 3 hr. If not otherwise indicated, the standard values for a given PUR content are: K = NCO/OH = 1.07; OcSn = 1.45%; AIBN = 1%. In the full IPNs, the PAc component is crosslinked with 5% TRIM. Sometimes, the abbreviation PAc is used as a more general term, instead of PMMA.

Optical transmission

The optical density (O.D.) was measured on a CARY mod. 1501 spectrometer, from 300 to 700 nm. Sample

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Table 1. Materials

Materials	Description	Source	Code
Polyol	Poly(oxypropylene)glycol; $\overline{M}_n$ 2000; 1.05 OH/kg; density: 1.0 g/ml; viscosity: 370 cps.	P.C.U.K. (P1020)	POPG
Polyisocyanate	Trimethylol-1,1,1 propane/toluene diisocyanate adduct, containing 25 weight % of ethyl acetate, 3.1 NCO/kg; density: 1.17 g/ml.	Bayer (L 75)	L 75
PUR catalyst	Stannous octoate: 28.5% tin; density: 1.25 g/ml.	Goldschmidt (KOSMOS 29)	OcSn
Acrylic monomer	Methyl methacrylate; stab.: hydroquinone 50 ppm.	Fluka	MMA
Acrylic crosslinker	Trimethylol-1,1,1 propane trimethacrylate; stab.: methylhydroquinone 100 ppm; density: 1.06 g/ml.	Degussa	TRIM
Initiator	Azobisisobutyronitrile.	MERCK	AIBN
Model compound for PUR	α, ω-Phenylurethane derivative of POPG; zero % NCO; viscosity: 2800 cps.	Our laboratory	POPUR

thickness: 3–3.5 mm. From the O.D., the transmission (T) was calculated through the relationship:

$$T(\%) = \frac{100}{10^{\text{O.D.}}}.$$

Accuracy: 0.5%

Refractive index

The refractive indices of the various materials were determined on a O.P.L. refractometer (D line of sodium). Accuracy: ± 0.002.

RESULTS AND DISCUSSION

The transparency and the occurrence of turbidity have been investigated on three comparable series of materials *viz.*: (a) full IPNs; (b) semi-1 IPNs, where only the PUR phase is crosslinked; and (c) PAc networks containing a poly(oxypropylene) glycol (POPG) or its α, ω-diphenylurethane derivative (POPUR) as a filler. The latter materials are in fact semi-2 IPNs, where the linear species might be regarded as a precursor of the PUR network.

The transparency of full PUR/PAc IPNs does not depend on their composition, at least in the 5–50% PUR range investigated in the present work. In all cases, the optical transmission is found to be around 90%. On the contrary, the crosslink degrees of both networks play an important role. The crosslink degree of PUR is given by its stoichiometry factor, K = NCO/OH = 1; depending whether K is inferior or superior to unity, either incomplete or over-crosslinked networks are formed [6]. In the latter case, other reactions besides the NCO/OH polyaddition take place. In the acrylic phase, the amount of TRIM governs the crosslink density of the second component.

The variation of the optical transmission of PUR/PAc IPNs, containing 34% by weight of PUR, has been studied as a function of K. The results appear in Table 2. For K values at least equal to unity, the percent of light transmission (% T) at 600 nm is around 90, comparable to that of homo-PMMA. This value decreases markedly when K falls below one, and the corresponding plates show a regular white cloudiness, which is most pronounced for K = 0.77. The last value reported in Table 2 concerns an IPN with only 81% transmission, although it had a K value of 1.07. The difference from other IPNs having the same K lies in its synthesis. It has been polymerized in the presence of light, so that the onset of the polymerization of the acrylic system has been induced too early with respect to the formation of PUR. In an earlier work, it was shown that such experimental conditons yield an incompletely formed PUR network also [7]. Both examples clearly indicate that some precursor species has not been integrated into the PUR and segregates, due to its incompatibility with the reaction medium. Now, only the POPG chains, which remain either free or are fixed by one extremity to the network, have a solubility parameter which differs significantly from those of PMMA and PUR (Table 3), *viz.* more than one Hildebrand unit. As POPG and PMMA have different refractive indices, their incompatibility is seen on a macroscopic level. Thus, if the appearance of any turbidity has to be avoided, the first condition is that the

Table 2. The optical transmission of PUR/PAc IPNs with various K = NCO/OH values

K = NCO/OH	1.28	1.13	1.07	0.89	0.77	1.07*
% T (at 600 nm)	90.2	90.2	90	85.1	81.3	81.3

All IPNs contain 34% PUR. *Sample polymerized in the presence of light.

Table 3. Refractive index n_D^{20}, and solubility parameter (δ) of various species

	L 75	POPG	PUR	PMMA crosslinked	IPN
δ $(cal^{1/2} \cdot cm^{-3/2})$	—	7.7*	9.4†	9.2*	—
n_D^{20}	1.533	1.451	1.491	1.492	1.493

* Calculated according to Small [14]. † Determined by the swelling method [15].

PUR network in an IPN must be formed almost completely before the polymerization of the second phase begins.

However, recent investigations on PUR/PAc semi-IPNs of the first type, i.e. where only the PUR is crosslinked, have shown the effect of crosslinking or not the second component on the optical transmission of the IPNs [8]. Thus, the obtaining of satisfactorily transparent sheets is by far more difficult than for the corresponding full IPNs. Usually, the semi-1 IPNs, when prepared in exactly the same way as the latter, show a slight turbidity or a blue haze. The phenomenon depends also on the PUR content: it becomes less pronounced with increasing PUR content. However, by adjusting some experimental parameters, transparent materials can be obtained and a detailed procedure will be described in a later paper. This result clearly shows that the crosslink degree of the second phase has less influence on the optical properties than that of PUR. This observation is in agreement with the now classical result that, in IPNs, the network formed first influences to the greater extent the end-properties of the material [9]; but, depending on its "quality" (amount of free or pendant chains) it is able to prevent more or less segregation of a species of the second phase in too large domains before its polymerization. Thus, the less "ideal" the PUR network, the more the crosslinking of the PAc phase beomes necessary: it contributes to a better phase dispersion which in turn enhances the transparency. Other authors have reached the same conclusion. Thus, Kim *et al.* [10] have reported that, in their semi-IPNs, the domain size is markedly greater than in the corresponding IPNs. In a somewhat different approach, Kanig and Neff [11] have demonstrated that crosslinking limits the degree of phase separation of two incompatible polymers in the same way as copolymerization [12]. Their results emphasize also that even a small amount of crosslink agent prevents visible demixing. The present results on semi-1 IPNs lead to another conclusion: as the origin of the turbidity in either full or semi-IPN combinations, *viz.* the incompatibility between POPG and PMMA, remains the same, it is certain that even with appropriate K values the PUR network is never completely formed.

Table 4. The appearance of turbidity in sheets of PMMA networks containing various fillers

Sample	Weight percent of filler at which turbidity appears
Crosslinked PMMA containing:	
POPG ($\overline{M}_n$ = 400)	20%
POPG ($\overline{M}_n$ = 2000)	5%
POPUR	15%
50% crosslinked PUR	37%*

* No loss of transparency; IPNs with higher PUR content have not been prepared.

The interaction of POPG and PMMA has also been investigated directly [13]. Thus, acrylic networks containing POPG of various molecular weights or POPUR, the α, ω-diphenylurethane derivative of POPG, have been prepared. Increasing amounts of either filler were combined with the host network, and the onset of turbidity noted. Table 4 first shows a marked difference in solubility with the molecular weight: 20% of POPG of $\overline{M}_n$ = 400 may be integrated into the PMMA network (crosslinked with 5% TRIM) before precipitation begins. For the glycol with $\overline{M}_n$ around 2000, the transparency disappears with less than 5% filler. When POPUR is utilized, the amount of filler can be increased up to 15%. It is not likely that such a change simply originates from the replacement of the hydroxyls; it may rather be ascribed to some hydrogen bonding between the hydrogen atom of the urethane groups and the ester functions of the acrylic phase. A result of such an interaction is enhanced dispersion of the polyoxypropylene chains in the acrylic medium, which prevents their aggregation. But in an IPN containing 50% by weight of PUR, 37% of the total weight consists of POPG, and the sheet is nevertheless transparent, so that hydrogen bonding alone cannot be the origin of the high transparency. The mode of dispersion imparted by the crosslinking of both phases thus appears to be essential. In fact, all these parameters contribute to the transparency of PUR/PAc blendings. A further cause, intersystem grafting, may also favour compatibility but it has been shown not to exist in the present system [5].

CONCLUSION

Although PUR and PMMA have nearly identical refractive indices, their combinations as IPNs or as semi-IPNs are not always transparent. The loss of transparency is due to incompatibility between POPG and PMMA. It can be avoided by preparing PUR networks with as few as possible pendant or free POPG chains. The crosslinking of the acrylic phase

facilitates the obtaining of transparent sheets. It appears that any means which allows a better dispersion of the phases leads to an enhanced, although in some way "forced" compatibility, which in turn yields transparent blends.

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