

POLYURETHANE-POLYSTYRENE INTERPENETRATING NETWORKS

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ABSTRACT

A series of polyurethane based on liquid chloroprene-hydroxyethyl methacrylate copolymer (CP-co-HEMA)-polystyrene (PS) interpenetrating polymer networks (PU-PS IPN) were synthesized. Some physical properties were examined and density behavior was investigated. In 60% polyurethane (PU) system, the tensile strength and density increased greatly. Transmission electron micrographs showed that the phase separation existed and the sizes of PS domains dispersed in PU phase were about 500–4,000 Å. In comparison with correlative PU-PMMA IPN system, which has the higher compatibility, this system showed an extensive phase separation and clear boundaries. There was no phase inversion observed even for 60% PU system in which PS was still the dispersed phase and PU the continuous phase. This was due to the relatively faster rate of formation of PU than that of ST polymerization.

INTRODUCTION

The IPN, an important branch of multicomponent polymers, has been rapidly developed towards variety and practicality since Millar^[1] first synthesized IPN in 1960. In the IPN system, a network, to some extent, interpenetrates with another to form permanent physical crosslinking. Most of IPN systems consist of a rubber and a plastic and generally are incompatible systems. IPN systems can be altered from reinforced rubber to toughened plastic by adjusting compositions. Their morphologies (interpenetrating degree and phase separation extent) are related to the nature of the polymer pair, polymerization methods and so on, and the physical properties also depend partially on which phase is the continuous phase. The methods used for characterizing IPN are electron microscopy, thermal analysis, dynamic mechanical analysis, and various methods for determining compatibility, density behavior, stress-strain behavior, swelling behavior, and physical properties. But none of them can approach the quantitative level of the characterization.

Kim et al. investigated poly(caprolactone) glycol PU IPN^[2]. Hourston et al. systematically studied Adiprene L-100 PU IPN^[3-6]. Li et al. examined hydroxyl terminated butadiene-acrylonitrile copolymer PU IPN^[7,8].

In this paper, a series of PU-PS IPN were synthesized by sequential process. Liquid chloroprene-hydroxyethyl methacrylate copolymer (CP-co-HEMA) was used as original material for PU and divinyl benzene (DVB) as crosslinking agent for PS. The physical properties and density behavior were investigated. In 60% PU composition, both of them have been improved remarkably. The morphology has been studied with transmission electron microscope. The result indicates that there is phase separation in the IPN system. Domain sizes are about 500–4,000 Å. The solubility parameter of the pure PU is 9.9 (cal/cm³)^{1/2}. Therefore the system is an incompatible one (the solubility parameter of PS being about 9.0). As compared with correlative PU-PMMA IPN system which has higher compatibility, the phase boundary is clearer and the extent of the phase separation is larger. The domain size distribution is relatively uniform. The results as mentioned above indicate that entanglement of the two networks forces intermixing and inhibits further phase separation. The PS phase still has been the dispersed phase till up to 60% PU. This is due to the different relative reaction rates.

EXPERIMENTAL

Materials

CP-co-HEMA with average molecular weight of 2200 and hydroxy value of 8.00×10^{-4} (equ./g) was prepared by ourselves^[9]. 1,4-Butanediol (BD), 2,4-toluene diisocyanate (TDI) and dibutyl tin dilaurate (DBTDL) were used without further purification. Styrene and MMA were washed with alkaline solution and distilled water, then dried for use. DVB as a cross-linking agent and AIBN as an initiator were used.

Polymerization

CP-co-HEMA, TDI and BD were dissolved in a certain amount of ST or MMA with NCO/OH ratio of 1.0. Then DBTDL was added to promote the formation of PU (0.1 wt. % of PU). The mixture was fully stirred, degassed and poured into molds with caps. Finally, the molds remained at room temperature for 24 h, then the reaction temperature was raised to 60°C for 24 h followed by 6 h more at 90°C. AIBN was used at the amount of 0.5 wt. % of ST (MMA).

Characterization

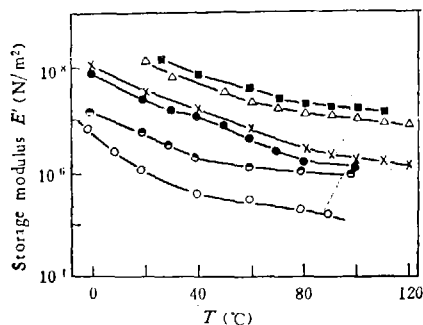
The physical properties data were obtained based on the standard techniques. The density data were obtained by volume measurement. The sample for morphological study was cut by microtome, exposed to the osmium tetroxide vapour to be stained, then it was observed under the H-500 electron microscope. The dynamic storage modulus (E') was measured with METRAVIB analyser.

RESULTS AND DISCUSSION

The physical properties of the PU-PS IPN system are listed in Table 1. The E' tempera-

Table 1 The physical properties of PU-PS IPN system

PU content (wt. %)	Tensile strength (kg/cm ²)	Elongation (%)	Hardness (A)
100	71	300	70
95	78	200	75
80	108	130	80
70	146	90	90
60	188	50	96

Fig. 1 The E' -temperature curves of the PU-PS IPN system

■ 50% PU; △ 60% PU; × 75% PU; ● 85% PU;
 ◐ 90% PU; ○ 100% PU.

ture curve is shown in Fig. 1. The tensile strength, hardness and E' increase and the elongation at break decreases with increase of ST content.

The enhancement and improvement of the moduli result from the entanglement and interpenetration at the boundaries of the dispersed phase. Sequentially, the domain with high modulus PS uniformly disperses in the PU phase and plays a role of reinforcement filler. The enhancement of the tensile strength is the most obvious in 60% PU composition.

There was a controversy about density behavior of IPN system; Millar^[1] found that the measured values of the density were higher than the theoretical values based on volume additivity in his IPN system. He explained that the phenomenon was attributed to the interpenetration between two networks filling the relatively loose and amorphous molecular structures and the formation of more compact molecular structure. However, in the similar IPN system, Shibayama^[10] and Frisch^[11] did not find the density effect. The experimental results in Kim's work^[12] revealed that there was the density effect and it was more apparent in PU-PS IPN system than in PU-PMMA IPN system. In the composition of 75% and 50% PU, the density increment was 0.032 g/cm³. If a IPN system consists of a rubber and a plastic and the interpenetration between two networks occurs, the density effect will appear. Therefore, the density effect may partially prove the presence of the interpenetration in some IPN systems.

Table 2 The density data of the PU-PS IPN system

PU content (wt. %)	Measured density (g/cm ³)	Calculated density (g/cm ³)	Increment
100	1.303	—	—
85	1.250	1.254	-0.004
75	1.218	1.227	-0.009
65	1.216	1.203	0.013
60	1.207	1.184	0.023
50	1.197	1.167	0.030
30	1.121	1.100	0.021

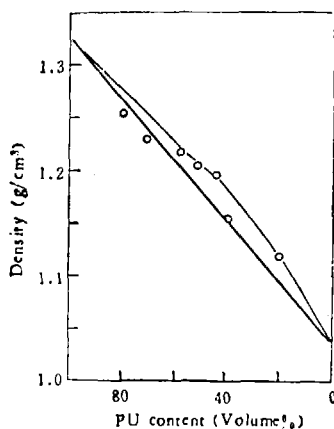


Fig. 2 The plot of the density and PU content (The fine line is the measured densities)

Table 2 lists the density data. In comparison with the theoretical values based on volume additivity, it is clear that the measured values tend to be larger than the theoretical ones. The minus values may be caused by the measurement error (average error range: 0.008–0.015). The maximum increments appear in the 60% and 50% PU compositions. The result is consistent with physical properties data.

The morphology of IPN system is very complicated. Different polymerization systems and conditions can form different morphologies. In the systems with large domain sizes (several μ), the morphology is composed of partial interpenetration at the boundaries of the dispersed phase. In the systems with small domain sizes (about 100Å), the main microstructure is super-molecular mixing and the domain size is in the same order of magnitude as the distances of the crosslinking points. The systems with middle sizes are those systems with domain sizes of about 1,000Å. On the other hand, polymerization conditions considerably influence the domain sizes and can change the general situations mentioned above besides natures of networks, such as compatibility. In sequential IPN system, the network first



Fig. 3 Micrograph of
100% PU
 $\times 10,000$



Fig. 4 Micrograph of
90% PU
 $\times 10,000$



Fig. 5 Micrograph of
80% PU
 $\times 10,000$



Fig. 6 Micrograph of
70% PU
 $\times 10,000$



Fig. 7 Micrograph of
60% PU
 $\times 10,000$



Fig. 8 Micrograph of
90% PU
 $\times 50,000$



Fig. 9 Micrograph of
80% PU
 $\times 50,000$



Fig. 10 Micrograph of
60% PU
 $\times 50,000$



Fig. 11 Micrograph of 60%
PU (PU-PMMA IPN)
 $\times 50,000$

formed will generally tend to be the more continuous phase, and the closer the relative reaction rates for network formation, the finer the domain sizes formed^[13]. Also the domain size is related to the crosslinking density, distance between crosslinking sites^[14].

Kim et al. investigated poly(caprolactone) glycol PU IPN^[2]. He found that the domain sizes were about 200–5,000 Å and the phase inversion occurred at 75% PU in his PU-PS IPN system, because the relative reaction rate of ST polymerization was faster than that of PU. In his PU-PMMA IPN system, the domain sizes were about 500–2,000 Å and the phase inversion was not so clear as that of PU-PS IPN system, though it occurred at 75% PU. In 60% PU system, PU phase still retained its own continuity. The reason is that PU-PMMA IPN system is a more compatible one in comparison with PU-PS IPN system.

The transmission electron micrograph of the pure PU shows the domain structure of the hard segments (see Fig. 3). The white parts are the hard segments which can not be stained. The domain is attributed to the soft-hard segment phase separation of PU caused by hydrogen bonding association^[15] or by partially crystallized area^[2]. In 90% PU, the hard segment domain (large one) still remains and the PS domain (small one) disperses in the PU phase. With the increase of the ST content, the hydrogen bonding association and crystallinity are inhibited and the pure hard domains of PU exists no longer, followed by the increase of ST domain concentration and a little change of the domain size. The domain sizes are about 500–4,000 Å (see Figs. 5–7). The solubility parameter of the pure PU in the system is 9.9 (cal/cm³)^{1/2} measured by swelling method. This system is similar to Kim's PU-PS IPN system (an incompatible one)^[2]. The two phase separation and boundaries can be seen clearly from Figs. 9 and 10. On the contrary, in Fig. 11, the boundaries can be identified indistinctly while the two phases retain their own continuities. This is due to the different compatibility. In Fig. 7, the PS phase still is the dispersed phase and the PU phase remains in continuous phase. This is different from Kim's system because in this system, the reaction of forming PU of CP-co-HEMA with TDI in the presence of the DBTDL as a promoter is faster than the polymerization of ST. Through the micrographs, we can see that ST domains disperse in the PU phase uniformly and the domain size distribution also is relatively even in spite of the presence of the two unfavorable factors in the system (incompatibility and different reaction rate). It is evident that the two networks entangle and interpenetrate with each other to form permanent physical crosslinking to some extent, and to force mixing. The results revealed on the micrographs are in accordance with their physical properties and density data, and the 60% PU composition is a one with high interpenetrating degree in this system.

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