Morphology and Properties of Polyurethane/Poly (Methyl Methacrylate) Interpenetrating Polymer Networks by Co^{60}-γ Ray*

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SYNOPSIS

PU/PMMA IPNs were first synthesized using Co^{60}-γ radiation. The morphology, glass transition behavior, and mechanical properties of the formed IPNs have been studied by TEM, DSC, and electron tensile testing machine. The TEM micrographs and the results of DSC showed that Co^{60}-γ radiation was effective for obtaining small volume sizes of phase domains in IPNs. The structure with two continuous phases occurs in the content range of 40% to 70% PU. The ability of interpenetration enhanced with increasing the content of the crosslinking agents. The mechanical properties of IPNs reflected very good synergistic behavior.

INTRODUCTION

The interpenetrating technique of polymers could cause almost all polymer networks to be compatible by entanglements of polymer chains, which would induce little phase separation, and by which a variety of modified material with excellent properties could be synthesized.[1-2] The method is easy to carry out at low cost with high interest. Recently, the study of IPNs has been active.[3-5] In an effort to enhance the extent of interpenetration between incompatible polymers, Lee[6] synthesized PU/PMMA and PU/PSt IPNs under high pressure (> 10,000 kg/cm^2). They found that the two T_gs of the samples shifted inwardly and even exhibited only one glass transition. In the PU/PSt IPN samples, prepared by Kim[7] at low temperature, only one broadened transition region appeared. Although the high pressure method and the low temperature method are effective for getting high extent of interpenetration, it is difficult to apply those techniques in practice.

No articles have been published concerning the synthesized PU/PMMA IPNs by Co^{60}-γ radiation. Free radicals can be supplied steadily and continuously for IPNs system by radiation. By changing dose rate and radiation dose, the reaction rate and the reaction extent of MMA in the IPN system were controlled. The PMMA and PU networks could be formed simultaneously, then the extent of interpenetration between PMMA and PU networks was enhanced. The IPNs formed have properties with good transparency, high tensile strength, high impact strength and good heat resistance. In this work, PU/PMMA IPNs have been synthesized by Co^{60}-γ radiation. The morphology and mechanical properties of IPNs have been studied.

EXPERIMENTAL

Materials

Poly (propylene oxide), endcapped with ethylene oxide (PPO-EO), with functionality 3.05 and Mn = 3100, supplied by Dow Chemical Corp., was dried under vacuum in the presence of molecular sieves. Toluene diisocyanate (TDI) was produced by Olin. Chemical Corp. Stannous octoate (OcSn) was produced by M.T. Corp. Trimethylol propane (TMP)

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was obtained from Dow Chemical Corp. and vacuum dried over P_2O_5. Methyl methacrylate (MMA), produced by Shanghai Chemical Agent Factory, was washed with 5% solution of sodium hydroxide in water, followed by distilled water and dried over CaH_2. Trimethlyol-1,1,1-propane trimethacrylate (TMPTMA), supplied by Dalian Qinhua Institute, was dried over CaH_2. Azobisiobutyronitrile (AIBN)

was produced by Xian Chemical Agent Factory and refined by recrystallization.

Precisely weighted amount of various reagents were mixed thoroughly by ultrasonic wave. The mixture was cast into a mold made by two glass plates, sealed with rubber, and polymerized by Co^{60}–γ radiation at appropriate radiation dose and dose rate, and then put in a oven at 100°C for 4 h.
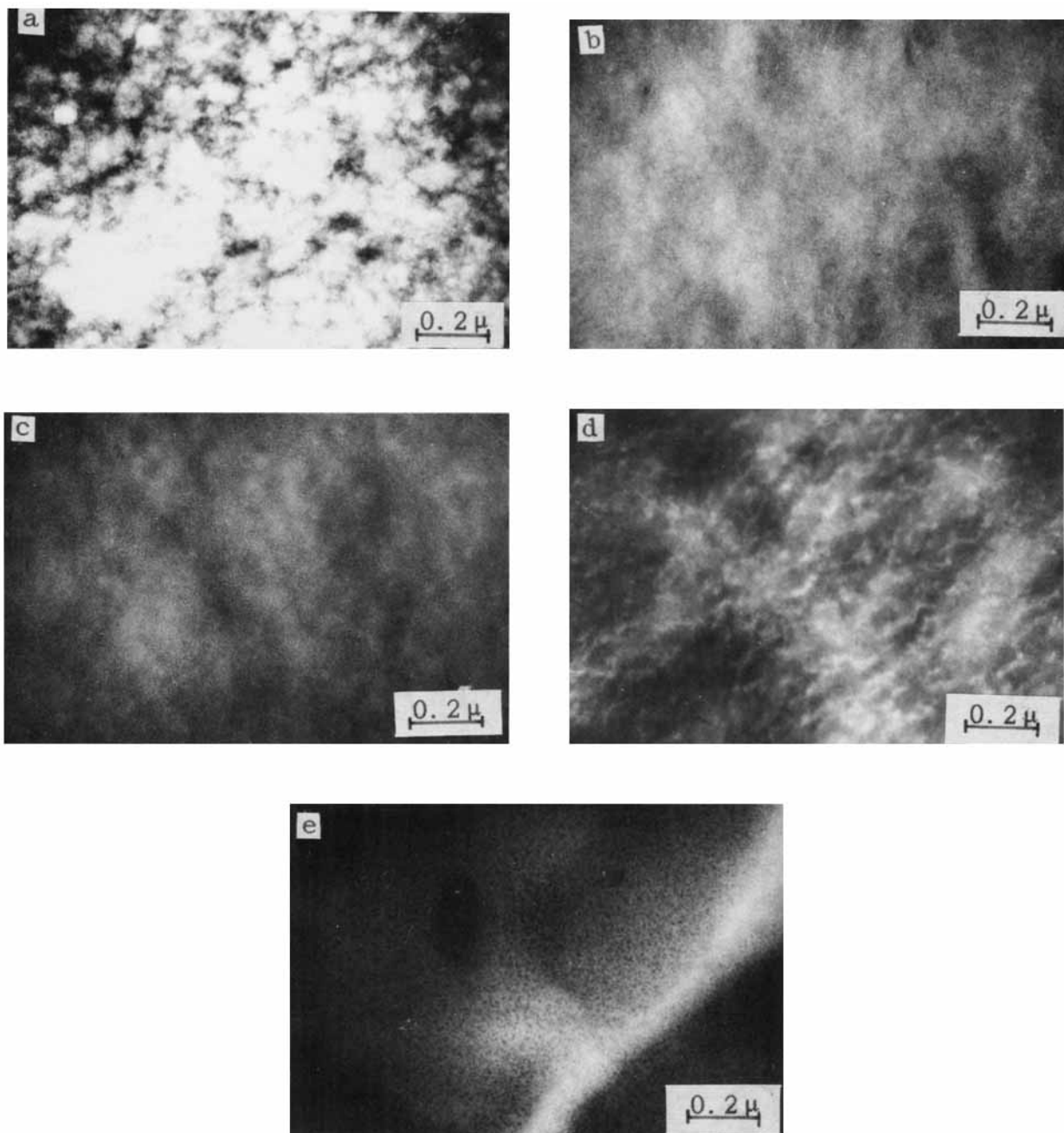

Figure 1 TEM micrographs for IPNs with the PU/PMMA ratio (by wt) of: (a) 25/75; (b) 40/60; (c) 50/50; (d) 70/30; (e) 75/25.

Transmission Electron Microscopy

The electron micrographs were obtained with JEM–200CX transmission electron microscopy. The specimens were wrapped in epoxy resin and cut into ultra-thin sections and stained by RuO_4.

Differential Scanning Calorimetry

The glass transition temperatures were measured on a Du Pont 1090 thermal analyzer. A constant heating rate of 10°C/min was employed over a temperature range of −100°C to 240°C. The sample weight was approximately 10 mg.

Mechanical Properties

Mechanical properties were performed at room temperature (25°C) using an AG-2000A electron tensile testing machine at an elongation rate of 50 mm/min.

RESULTS AND DISCUSSION

Morphology of IPNs

The staining rates of RuO_4 in PU (polyether) and PMMA differ. The soft segments of PU (polyether) can be stained faster. By controlling the staining time, the soft segments of PU can be stained but PMMA can not. It is reasonable to think that the dark regions in TEM micrographs represent PU phase and the bright regions are PMMA phase.

Figure 1 showed the electron micrographs for IPNs with the different PU/PMMA ratios (by wt). For the IPN with the PU/PMMA ratio less than 40/60, the PMMA phase is continuous, while the PU phase is dispersed (See Fig. 1a) and the domain size is about 300 Å in diameter. When the PU/PMMA ratio range is between 40/60 and 70/30, the IPN sample showed two continuous phase structure (See Figs. 1b, 1c, 1d). If the ratio of PU/PMMA increased above 70/30, the PU phase would remain continuous whereas the PMMA phase would
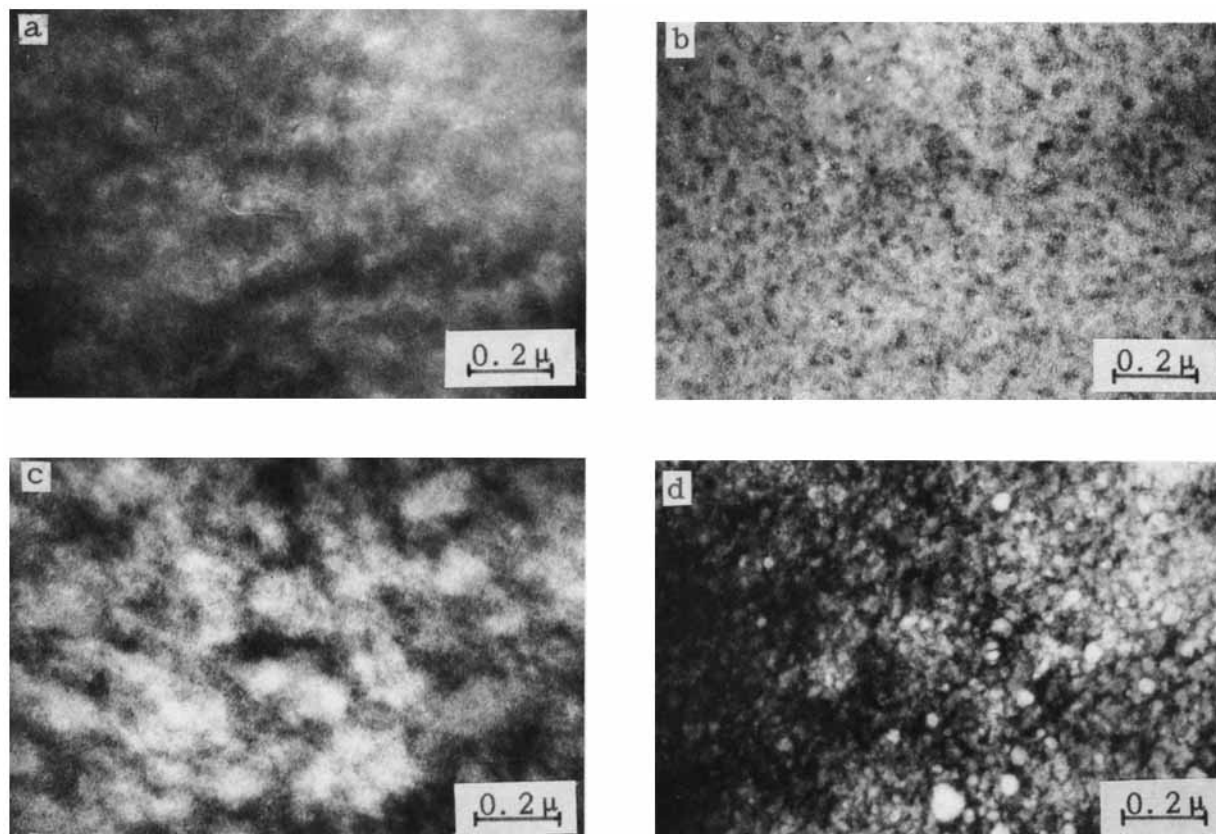

Figure 2   TEM micrographs for IPNs with different contents of TMPTMA or TMP: (a) TMP/(Polyether + TDI) = 1/100, TMPTMA/MMA = 3/100; (b) TMP/(Polyether + TDI) = 5/100, TMPTMA/MMA = 3/100; (c) TMP/(Polyether + TDI) = 3/100, TMPTMA/MMA = 1/100; (d) TMP/(Polyether + TDI) = 3/100, TMPTMA/MMA = 5/100.

Table I The Glass Transition Temperatures and Mechanical Properties for IPNs of Different PU/PMMA Ratio (by Wt)

PU/PMMA	T_g1 (K)	T_g2 (K)	Fracture Stress (MPa)	Ultimate Elongation (%)
0/100	—	401	58.2	3.0
25/75	226	395	28.7	33.5
40/60	227	389	24.1	94.5
50/50	228	386	22.8	213.4
75/25	228	392	15.4	308.4
100/0	227	378[a]	8.5	201.5

[a] The T_g of hard segment of pure PU is 378K.

become dispersed. The fact of the indistinguishable interface (Seen in Figs. 1b, 1c, 1d) reflected that the extent of interpenetration is maximum at the PU/PMMA ratio 50/50.

The electron micrographs for IPNs with different content of TMPTMA and TMP are shown in Figure 2. It can be seen that the extent of interpenetration increases with increasing the TMPTMA (cross-linking agent of PMMA) and TMP (crosslinking agent of PU) contents. This was because the increase in the content of crosslinking agents enhanced the crosslinking extent. With the increase of crosslinking degree, the entanglement and the interlocking of the networks increased and restricted the phase separation due to the increase of molecular weight during the polymerization.

The two continuous phase structure of IPNs, prepared by two incompatible polymers, is difficult to attain. By the control of radiation dose, dose rate, and reaction temperature during the radiation process, the formation rates of PU and PMMA could be kept almost the same, and the two networks could be formed simultaneously. Thus, in proper composition range, the IPN with two continuous phase structure could be prepared.

Glass Transition of IPNs

The glass transition temperatures (T_gs) of PU/PMMA IPNs are listed in Table I. The T_gs in low temperature range (T_g1), relating to the soft segment of PU network, are almost the same. This is because interpenetration of PU and PMMA, which is actually the interpenetration of PMMA and the hard segment of PU as PU network was produced from the crosslinking of the hard segment, have little influence on the soft segment of PU. Only one glass transition in the high temperature range (T_g2) appeared; it was located between the T_g of pure PMMA (401 K) and the T_g of hard segment in pure PU (378

K). In other words, the T_g2 shifted inwardly. This suggested that the high extent of interpenetration could be obtained by means of radiation.

Mechanical Properties of IPNs

The stress–strain curves of different components of PU/PMMA IPNs are shown in Figure 3. The fracture stress and ultimate elongation of PU/PMMA IPNs are listed in Table I. From Table I it can be seen that with increasing PU content in the system, the ultimate elongation increased while the fracture stress decreased; the fracture stress, however was still higher than that of pure PU. Furthermore, the ultimate elongation of the IPNs with appropriate composition could be higher than that of pure PU. This was due to the synergistic behavior of interpenetrating networks. The function of PMMA in the IPNs was the reinforcement on PU elastomers.
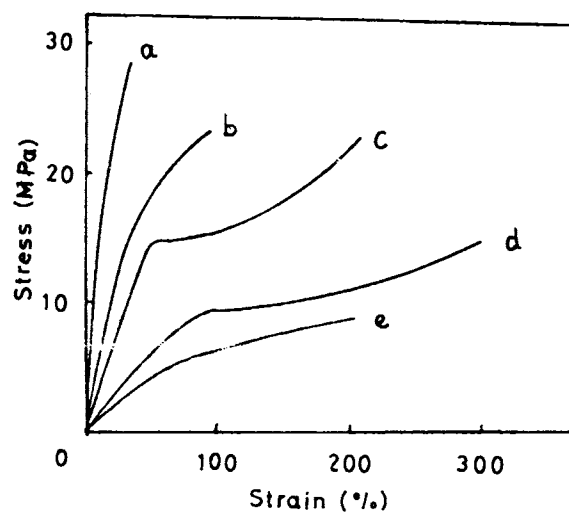

Figure 3 Stress vs. strain for IPNs with the PU/PMMA ratio (by wt) of: (a) 25/75; (b) 40/60; (c) 50/50; (d) 75/25; (e) 100/0.

Table II   Effect of TMPTMA and TMP Content on Mechanical Properties of IPNs with PU/PMMA = 50/50

Contents of Crosslinker		Fracture Stress (MPa)	Ultimate Elongation (%)
TMP/(Polyether + TDI)	TMPTMA/MMA		
3/100	1/100	21.4	221.6
3/100	3/100	22.8	213.4
3/100	5/100	24.1	199.1
1/100	3/100	18.7	294.2
5/100	3/100	24.5	191.3

The reinforcement through interpenetration is generally better than filler reinforcement. Filler reinforcement effect was produced by physical cross-linking among polymer chains, which resulted from surface absorption of filler particles on polymer chains. The filler reinforcement could disperse stress originally concentrated on one macromolecular chain to other chains. The reinforcement of IPNs was produced by the interlocking of dual crosslinking networks in IPNs system. The combining force of interlocking is much greater than the surface absorption force. The concentrated stress can be converged to macromolecular chains homogenously through interlocking networks. Even if there are cracks somewhere, IPNs can limit the enlargement of cracks through interlocking networks. This induces the fracture stress of PU/PMMA IPNs higher than that of pure PU and the ultimate elongation of IPNs at proper composition greater than that of pure PU.

The data of mechanical properties for IPNs with different content of TMPTMA and TMP is listed in Table II. The fracture stress for IPNs increased, but the ultimate elongation decreased with increasing the content of the crosslinking agents (TMPTMA and TMP). With increasing the content of the crosslinking agents, the crosslinking extent increased and the entanglement of the networks also increased, so the slipping among macromolecular chains can be prevented. Thus the rigidity and fracture stress of IPNs were enhanced while ultimate elongation decreased.

CONCLUSION

The morphology, glass transition behavior, and mechanical properties of PU/PMMA IPNs synthesized by radiation, have been studied. TEM micrographs showed that radiation initiated polymerization was a effective way to obtain PU/PMMA IPN with high extent of interpenetration. The IPNs with two continuous phase structure were obtained in the PU/PMMA ratio range of 40/60 to 70/30. The ability of interpenetration increased with increasing the content of the crosslinking agents. The glass transition temperature at high temperature range shifted inwardly due to interpenetration. With increasing PU content in the system, the fracture stress decreased and the ultimate elongation increased. Furthermore, the ultimate elongation of the IPNs containing more than 50% PU (by wt) would be greater than that of the pure PU. With increasing the content of the crosslinking agents (TMPTMA and TMP), the fracture stress increased while the ultimate elongation decreased.

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