Morphological Structure and Mechanical Properties of Polyurethane Modified with Methyl Methacrylate

ZHENG-QING WANG, LI-YI SHI, ZHI-PING ZHANG

East China University of Science & Technology, Shanghai, 200237, People's Republic of China

ABSTRACT: Three kinds of polyurethane-poly(methyl methacrylate) (PU–PMMA), that is, linear polymer, block copolymer, and interpenetrating polymer network (IPN), were synthesized by a simultaneous polymerization process, respectively. The effects of several factors such as ultraviolet (UV) setting, heat setting, chemical composition, and physical structure on the morphological structure and mechanical properties of polymers were studied by scanning electron micrograph, dynamic mechanical loss spectrum, and mechanical tests. The results show that PU–PMMA is a partially compatible system with a two-phase structure; the linear polymer has the highest elongation at break, and IPN has the strongest tensile strength, while the block copolymer has poor mechanical properties. In addition, the UV setting block copolymer and IPN system, with regular microphase domain structures, have higher tensile strength and elongation at break than those of heat setting polymers. With MMA content and hard segment in PU increasing, the tensile strength increases, and the elongation decreases. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1363–1369, 1998

Key words: polyurethane; polymethyl methacrylate; interpenetrating polymer network; block copolymer; structural behavior

INTRODUCTION

Polyurethane (PU) is well known for its wear resistance, high toughness, and compatibility with various polymers. Yet it is difficult to synthesize; moreover, it has a low product modulus and poor heat resistance. However, if it is modified by poly(methyl methacrylate) (PMMA) with a higher T_g, the strength and the modulus of the resulting polymers will be obviously improved. In addition, the introduction of PMMA into the system will also efficiently decrease the viscosity and prolong the durable time of the material. The PU–PMMA system has been one of the focus of interpenetration polymer network (IPN) study. In 1970s, Kim et al.[1] studied the structural morphology; and in 1980s, Jin et al.[2] reported the polymerization kinetics.

In this article, three kinds of PU–PMMA, that is, linear polymers, block copolymers and IPN, were synthesized by the simultaneous polymerization process, respectively. The effects of several factors, such as ultraviolet (UV) setting, heat setting, chemical composition, and physical structure on morphological structure and mechanical properties of polymers were studied, which provides a new way to study mutual relationship among the polymerization method, morphological structure, and mechanical properties of polymers.

EXPERIMENTAL

Raw Materials

The raw materials used in the experiment were listed in Table I. The chemical agents were all chemical-pure. Poly(oxypropylene) glycols (PPO) and Ethylene gycol (EG) were dehydration and dried before

Table I   Names of Raw Materials, Abbreviations, and Manufacturers

Name of Raw Material	Abbreviation	Formula	Manufacturer
Hexamethylene diisocyanate	HMDI	$OCN-\bigcirc-CH_2-\bigcirc-NCO$ (with CH_3 substituents on the cyclohexyl rings)	Bayer A.G.
Poly(oxypropylene) glycols	PPO	$HO-CH(CH_3)-CH_2-O-[CH_2-CH(CH_3)-O]_n-CH_2-CH(CH_3)-OH$	Dow Chem. Co.
Ethylene glycol	EG	CH_2-OH , CH_2-OH	Shanghai Chemical Agent Factory
Trimethylol propane	TMP	$CH_3-CH_2-C(CH_2OH)(CH_2OH)-CH_2OH$	Shanghai Chemical Agent Factory
β-Hydroxyl ethyl acrylate	HEA	$CH_2=CH-COOCH_2CH_2OH$	JiangSu DanYang Chemical Factory
Methyl methacrylate	MMA	$CH_2=C(CH_3)-COOCH_3$	FoShan Chemical Factory
Trimethylol propane triacrylate	TMPTA	$CH_3CH_2C(CH_2OOCCH=CH_2)(CH_2OOCCH=CH_2)-CH_2OOCCH=CH_2$	Shanghai Chemical Agent Factory
Dibutyltin diaurate	T-12	$CH_3(CH_2)_{10}COO-Sn(C_4H_9)(C_4H_9)-COO(CH_2)_{10}CH_3$	Shanghai Chemical Agent Factory
Azo-*bis*-isobutyronitrile	AIBN	$NC-C(CH_3)(CH_3)-N=N-C(CH_3)(CH_3)-NC$	Shanghai Chemical Agent Factory
Benzoinether	BEE	$Ph-CH(OCH_2CH_3)-C(=O)-Ph$	Shanghai Chemical Agent Factory

Table II   The Composition and Physical Properties of the Samples

No.	Structure	MMA Content (%)	Hard Segment Content (%)	Tensile Strength (MPa)	Elongation (%)	Hardness (A)	Appearance	Setting Method
1	Linear	25	50	16.5	377.3	90	Translucence	Heat
2	Block	25	50	14.8	68.3	90	Transparent	Heat
3	IPN	25	50	18.6	69.1	93	Transparent	Heat
4	IPN	50	50	30.2	55.5	97	Translucence	Heat
5	IPN	75	50	30.6	21.1	99	Translucence	Heat
6	IPN	25	35	13.8	224.0	85	Translucence	Heat
7	IPN	25	20	7. + 3	182.5	75	Milky	Heat
8	IPN	25	50	22.6	201.0	91	Transparent	Light
9	Block	25	50	18.6	131.6	92	Transparent	Light
10	Linear	25	50	16.0	351.0	90	Transparent	Light

Notes: The equivalent ratio of the block copolymer is as follows: HMDI : PPO : HEA = 2 : 1 : 1. The crosslink agent content of IPNs are as follows: TMP (10% W_{PU}); TMPTA (10% W_{MMA}).

use. Methyl metacrylate (MMA) was vacuum-distilled after being washed by NaOH solution and dried. AIBN was refined by recrystallization.

The Synthesis of the Samples

Add PPO, HMDI, and catalyst T-12 on ration into a reactor equipped with a thermometer, a stirrer, and an N_2 conduit. Raise the temperature up to 50°C under stirring at 0.13 MPa for 60 min. Begin to cool down to room temperature when there were no bubbles appearing in this system. Under stirring, introduce EG, MMA, and the heat initiator, AIBN, into system and extract the gases until the reactant mixture turned from turbid to clear. Then pour the mixture immediately into a quartz champing plate painted with a release agent and keep under N_2 protection at 50°C for 4 h and at 80°C for 2 h, then demold the sample. When the

Figure 1 Mechanical properties of the heat-setting polymer in which the MMA content is 25% and the hard segment content in PU is 50%: (1) linear polymer; (2) block copolymer; (3) IPN.

UV setting was required, AIBN was replaced by the light-sensitive agent BEE. The sample was put under a 1000-W high-pressure mercury lamp in a distance of 50 cm and radiated for 8 min, then demolded. Heat setting or UV setting PU–PMMA linear polymer was then synthesized. With the same process as stated above, PU–PMMA block copolymer can be synthesized by adding HEA into the system and PU–PMMA IPN by adding both TMP and TMPTA.

Test of the Samples

Mechanical Properties

An Instron Model 1185 versatile material test machine was used, and the test was carried out at room temperature. The speed of the cross was 250 mm min. The samples were cut into a dumbbell shape, and the hardness of the samples was tested by the LX-A rubber tester.

Polymerization Speed

Nicolet 520 SX Fourier transform infrared (FTIR) was used, the resolving power was 4 cm^{-1}, and the scanning frequency was 10. Test samples were prepared by casting the solution onto a plate to make a film. The light strength was measured by a UV-2 radiant meter.

Polymer Morphology

The samples were immersed into THF solvent and etched for 2 h at reflux temperature. After being dried, the surfaces of the samples were sprayed
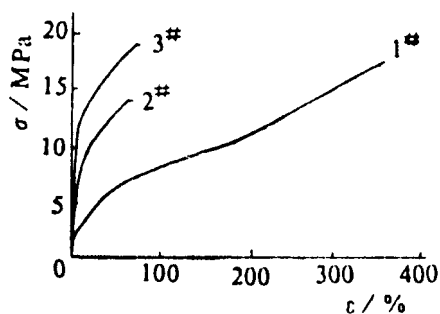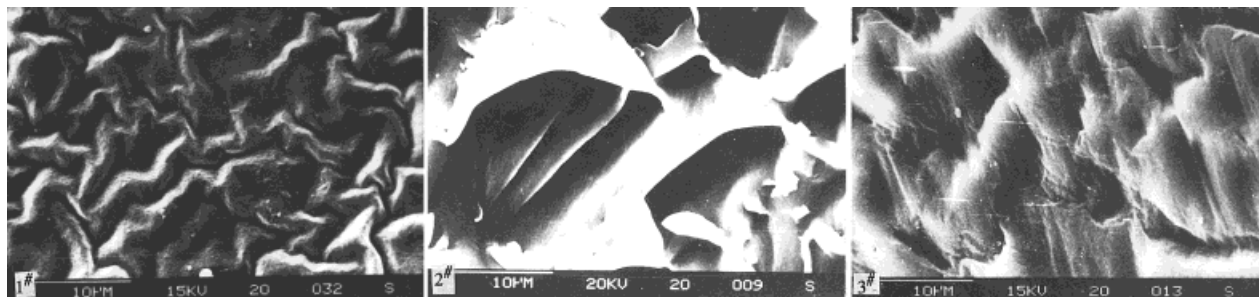
Figure 2 SEM photos of heat setting PU–PMMA (2000 times), in which the MMA content is 25% and the hard segment content in PU is 50%: (1) linear polymer; (2) block copolymer; (3) IPN.

with gold and were observed; photos were taken by a Cambridge S-250MKII SEM.

Dynamic Mechanical Properties

Japanese DDV-IIC dynamic loss spectrum was used. The thickness of the sample was 0.01–0.015 cm. The range of the test temperature was −100–200°C and rose at a rate of 2°C min. The frequency was 110 Hz.

Composition and Physical Properties

The compositions, physical properties, and setting methods are listed in Table II.

RESULTS AND DISCUSSION

The Effect of Bonding Structure on the Polymer Morphology and Mechanical Property

Figure 1 shows the stress (σ)–strain (ε) curve of heat setting PU–PMMA linear polymer, block copolymer, and IPN, which have similar compositions and different bonding structures. It can be seen from the curve that the elongation at break of the linear polymer is the biggest, about 380%, while those of IPN and block copolymer are quite small, with 69 and 68%, respectively. The tensile strength of the IPN is the largest, about 18.2 MPa; the second is linear polymer, with the tensile strength of about 16.5 MPa. The block copolymer has the smallest tensile strength, about 14.8 MPa. The electron micrograph (Fig. 2) shows that the phase of the block copolymer is large, and the boundary of the phase is smooth. So when stretched, it is easy to break. Because there exists a relative slide movement among molecular chains of the linear polymer, its elongation at break is quite large. On the other hand, the

boundary of IPN is vague, and the structure of its hard segment is sticking out. Because of the chemical crosslinking and physical tangling effect, the tensile strength of IPN is the largest.[3,4]

The Effect of MMA Content on the Polymer Morphology and Mechanical Property

Figure 3 shows the $\sigma - \varepsilon$ curve of IPNs with different MMA contents. It can be seen from the curve that when the MMA content rises from 25 to 75%, the tensile strength increases from 18.6 to 30.6 MPa, while the elongation at break decreases from 69 to 21%. The reason is that PMMA has a high T_g, which is a benefit to increase the strength of he polymer. The electron micrographs (Figs. 2
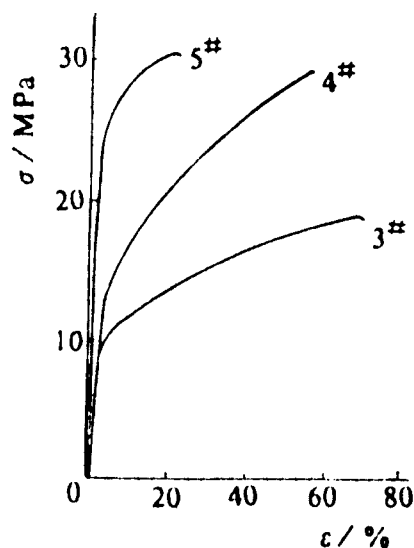

Figure 3 The effect of MMA content on physical properties of IPNs, in which the hard segment content in PU is 50% in the heat setting method. The MMA content is as follows: (3) 25%; (4) 50%; (5) 75%.
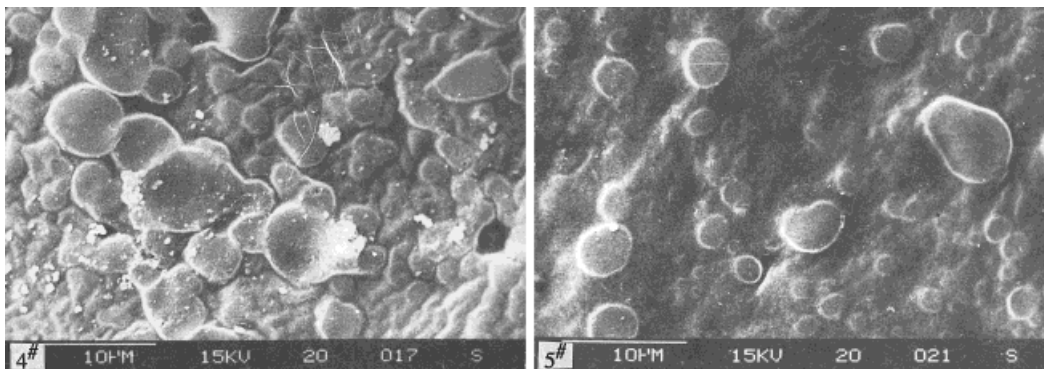
Figure 4 SEM photos with different MMA contents. Hard segment content in PU: 50%. Heat-set method: IPN and MMA content: (4) 50%; (5) 75%.

and 4) show that by increasing the MMA content, there exists a phase conversion. The IPN converts from the continuous phase to the disperse phase. This phenomenon was also observed by Kim et al.[1] The phase conversion can verify our former conclusion that by increasing the MMA content, the tensile strength of the polymers increases, while the elongation at break decreases.

The Effect of Hard Segment Concentration in PU on Polymer Mechanical Properties

The crosslinking PU is composed of the PPO soft segment, HMDI, EG, and TMP hard segments. Figure 5 is the $\sigma-\varepsilon$ curve of the IPN with different hard segment contents. It can be seen from the curve that as the hard segment content in PU increases, the tensile strength of the polymer increases rapidly, and the elongation at break obvi-
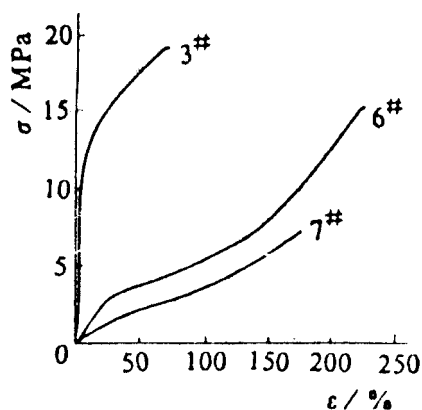
ously decreases. This property is the same as that of pure PU.[5] But when the hard segment content decreases to 20%, the tensile strength and elongation at break decreases at the same time. The reason is that the structure of the hard segment area is regular, and there exists a strong hydrogen bonding,[6] which makes the IPN easy to orientate and crystallize. The decrease of the hard segment content results in the decrease of physical crosslinking points in PU and affects the physical properties of the polymer.

The Effect of the Setting Methods on the Polymer Morphology and Mechanical Properties

The polymerization speed of PU–PMMA can be changed by UV light setting.[7] Figure 6 is the $\sigma-\varepsilon$ curve of the light setting linear polymer, block co-

Figure 5 The effect of hard segment content on the physical properties in which the MMA content is 25% in the heat setting method. Hard segment contents in PU are as follows: (3) 50%; (6) 35%; (7) 20%.
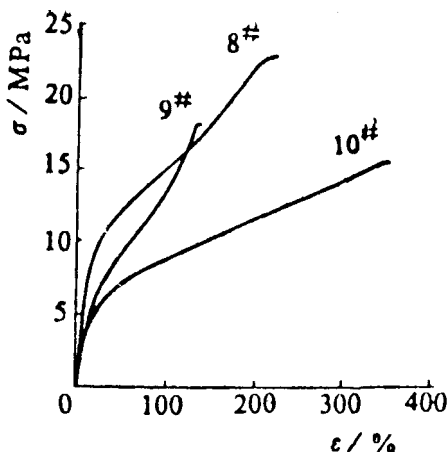

Figure 6 Physical properties of the light-setting polymers in which the MMA content is 25% and the hard segment content in PU is 50%: (8) IPN; (9) block copolymer; (10) linear polymer.
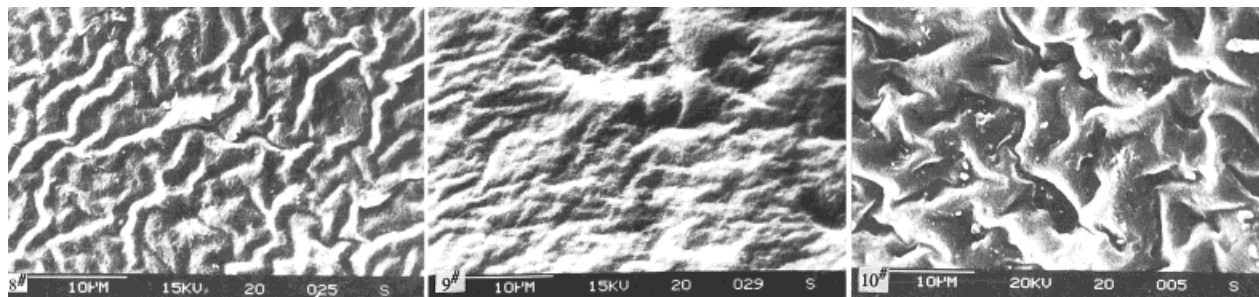
Figure 7 SEM photos of light-setting PU–PMMA in which the MMA content is 25% and the hard segment content in PU is 50%: (8) IPN; (9) block copolymer; (10) linear polymer.

polymer, and IPNs. Compared with the heat setting samples with the same composition, the tensile strength and elongation at break of both the block copolymer and IPN obviously increases, while the difference of the linear polymer is not obvious. It can also be observed from the electron micrograph (Fig. 7) of the light setting polymer that the phase structure of the light setting block copolymer and IPN is homogeneous, and the phase area is relatively small, which means that the compatibility of the polymers is good. Because of the coordination effect, the tensile strength and elongation at break increases at the same time. As the phase structure of the light setting linear polymer is similar to that of the heat setting, their mechanical properties are almost the same. It can be seen from Figure 8 that there is a strong absorption peak of NCO group at 2265 cm^{-1}. The change of the absorption peak can indicate the polymerization speed of PU, while the polymerization speed of PMMA can be indicated by the change of the C=C

vibration absorption peak at 1635 cm^{-1}. Figure 8 shows that after keeping the temperature at 50°C for 130 min, the strong absorption peak of NCO group at 2265 cm^{-1} disappear completely and the C=C absorption peak at 1635 cm^{-1} remains almost unchanged, which means that the PU has quite high reaction activity and polymerizes first during heat setting. During light setting, the light-sensitive agent splits to active radicals, which makes MMA polymerize rapidly. After being irradiated for 200 s, the C=C peak at 1635 cm^{-1} disappears completely, while the absorption peak of NCO group at 2265 cm^{-1} remains the same. In the view of Park et al.[8] and Sperling et al.,[9] the polymer morphology is controlled by the networks, which polymerize first since such networks have a tendency to form a continuous phase structure. Because MMA polymerizes first during light setting process, the physical properties of the light setting block copolymer and IPN are better than those of heat setting ones.
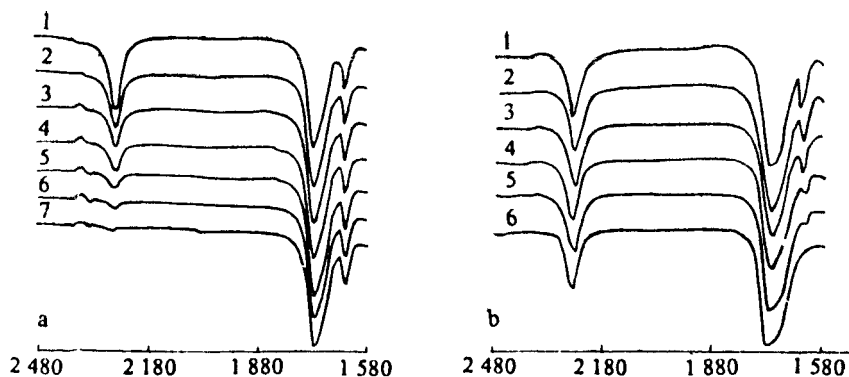

Figure 8 FTIR spectra of PU–PMMA polymer (MMA–PU = 50/50). (a) Heat-setting, 50°C; number, 1, 2, 3, 4, 5, 6, 7; time/min., 0, 20, 30, 40, 57, 92, 130. (b) light-setting, UV; number, 1, 2, 3, 4, 5, 6; time/s, 35, 45, 60, 90, 150, 200.

The Effect of the Polymer Structure on Dynamic Mechanical Properties

The dynamic mechanical properties of the light setting polymer, block copolymer, and IPN are shown in Figure 9. The corresponding T_g data are listed at Table III. There exists a plate area between two T_g, which means that the system appears to be a two-phase structure. Among the curve, there is a sharpest temperature change area between two T_g in block copolymer, which means that the compatibility of the block copolymer is good. Due to the existence of the crosslinking network structure, which limits chain move-
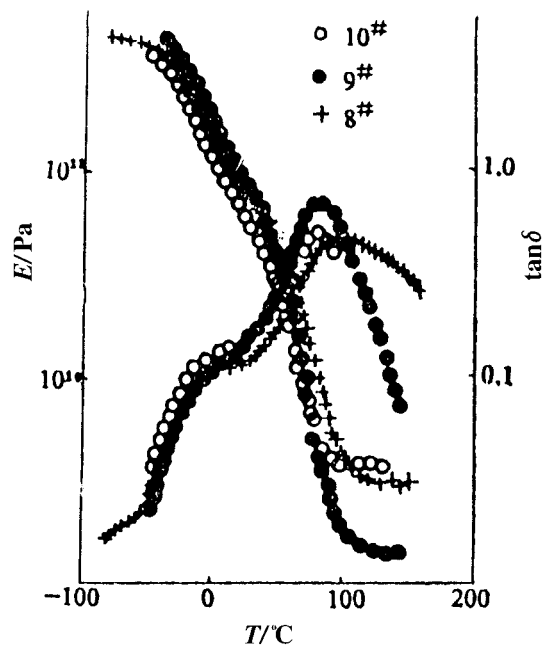
Table III   The T_g of Polymers Measured by DDV

No.	T_{g_1}/°C	T_{g_2}/°C
8 (IPN)	1.3	97.3
9 (Block copolymer)	0.6	82.6
10 (Linear polymer)	−1.6	78.7

Notes: The T_{g_1} of the soft segment in PU is −44.8°C; the T_{g_2} of the hard segment in PU is 58.1°C; the T_g of PMMA is 110°C.

ment and results in the wideness and decrease of the tan σ_{max}. The tan σ curve of the IPN has quite a wide platform between two converse peaks. Moreover, there is a move in the T_g transition peaks on the tan σ curves of the three samples, which shows that the PU–PMMA is a partially compatible two-phase system corresponding to the observation of the electron micrographs.

Figure 9 The mechanical property of the polymer MMA content is 25% and the hard segment content in PU is 50%: (8) IPN; (9) block copolymer; (10) linear polymer.

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