

Synthesis, Properties, and Morphology Based on Polyurethane and Polymethyl Methacrylate AB-Crosslinked Copolymers

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SYNOPSIS

The AB-crosslinked copolymer was prepared as a transparent material from toluene diisocyanate (TDI) or hexamethane diisocyanate (HDI), triethylene glycol (TEG), hydroxyethyl methacrylate (HEMA), and methyl methacrylate (MMA). The optical transmission, impact resistance, thermal mechanical properties, and morphology of the copolymer were studied. The results indicate that this material has a microheterogeneous structure with the dispersed phase size no more than 0.1 μm . © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymethyl methacrylate (PMMA), polycarbonate (PC), CR-39 (poly[diethylene glycol bis (allyl carbonate)]), SAN (styrene-acrylonitrile copolymer), NAS (styrene-acrylate copolymer), and HIP (styrene-ethyl methacrylate-tribromostyrene copolymer), etc., are commonly used as transparent organic materials.¹ Although PC exhibits high impact strength, heat-resistance, and low moisture absorption, its surface hardness is not very high and, moreover, during the injection process the polymer chains tend to orient, so resulting in double refraction. PS has satisfactory low water absorption and high refraction index, but its surface also is not hard enough. HIP, SAN, and NAS cannot meet the needs, not only for transparency, but for surface hardness as well. With many excellent properties such as heat and solvent resistance, high hardness and transparency, CR-39 has been thought to be the most superior at the present day. However, the high contraction percentage of CR-39 is disadvantageous for its use,² in addition, it is very expensive. PMMA is well known for having the best transparency, better general properties and lower price, but also has drawbacks, e.g., the lower temperature resistance and surface hardness, poor resistance to the solvents, etc.

Many authors have tried to improve the properties of polymeric transparent materials. It is the objective of this work to prepare a transparent material with high surface hardness and impact strength and good properties in general using the technique of AB-crosslinked copolymerization.

Studies of an AB-crosslinked copolymer have been reported in many references.³⁻⁶ Synthesis of the AB-crosslinked copolymer from urethane oligomer and MMA has been limited to patents. Investigations on its morphology and thermomechanical properties haven't been reported yet. In this work, we synthesized an AB-crosslinked copolymer of urethane oligomer (from TDI or HDI, TEG, HEMA) and MMA as a transparent material. The morphology and properties of it were examined.

EXPERIMENTAL

Raw Materials and Treatment

MMA (analytically pure) was purified by reduced pressure distillation to remove any inhibitors. Azobisisobutyronitrile (AIBN, chemically pure) was recrystallized from alcohol. The water traces in TEG (chemically pure) and HEMA (Industrial grade) were eliminated under vacuum. Dibutyltin dilaurate (DBTL, chemically pure) was used as received. TDI (the ratio of 2.4-TDI/2.6-TDI is 80/20 by weight) and HDI were industrial products used without fur-

ther refinement. All of the other reagents were analytical.

Synthesis of the AB-Crosslinked Copolymer

To a 150 mL reaction vessel equipped with a magnetic stirrer, the calculated amounts of HEMA, TEG, MMA, TDI (or HDI), and AIBN were added, respectively. After being stirred and homogenized thoroughly, the reactants were allowed to react with each other for 1.5 h, followed by addition of 0.04 percent by weight DBTL, stirring for an additional 1.5 h, then the blend was degassed and poured into a glass mould, using silicone oil as release agent. The mould is transferred into an oven with reaction proceeding at 50°C for 15 h, then at 70°C for 2 h, 80°C for 1 h, 90°C for 3 h, 100°C for 1 h, 120°C for 2 h. In the end, the mould was cooled to room temperature gradually, and the transparent plate was obtained. The basic formulation used was as follows:

For the copolymer TP (prepared from TDI): MMA/(TEG + TDI + HEMA): 20/80 (by weight), OH/NCO: 1.05/1.00 (mole ratio), TEG/HEMA: 0.5/1.0 (mole ratio in hydroxyl group), AIBN: 0.20% (by weight).

For the copolymer HP: MMA/(TEG + HDI + HEMA): 20/80 (by weight), OH/NCO: 1.03/1.00 (mole ratio), TEG/HEMA: 0.8/1.0 (mole ratio in hydroxyl group), AIBN: 0.12% (by weight).

Property Tests

Optical transmission of the material was measured on a spectrophotometer Model 721 and the wavelength of the light used was from 360 to 720 nm.

The determination of Charpy impact strength (unnotched) and water absorption were conducted according to GB1043-79 and 1034-70, respectively. Surface hardness was measured with a ball tester for plastics according to GB3398-82. Using a thermomechanical analyzer (Model TM-700, Japan), the glass transition temperature (T_g) and linear expansion coefficient of the AB-crosslinked copolymer were determined at a heating rate of 5K/min. Finally we obtained the refractive index with an Abel refractometer at 20°C according to standard UD 678.5/8.

Morphology and Chemical Structure Determination

The morphological structure of the AB-crosslinked copolymer was observed by a transmission electron microscope (TEM) Model H-800 (Japan), using ruthenium tetroxide as staining agent. Infrared spectra were obtained on a Model IR-400 spectrometer (Japan).

RESULTS AND DISCUSSION

Infrared Spectra

Figures 1 and 2 give the infrared spectra corresponding to the samples TP (the AB-crosslinked copolymer prepared from TDI) and HP (the copolymer prepared from HDI), respectively. It can be seen that the absorptions at 2270 cm^{-1} , arising from a C=C double bond, and 1650 cm^{-1} arising from a —NCO group, have disappeared. This suggests that the

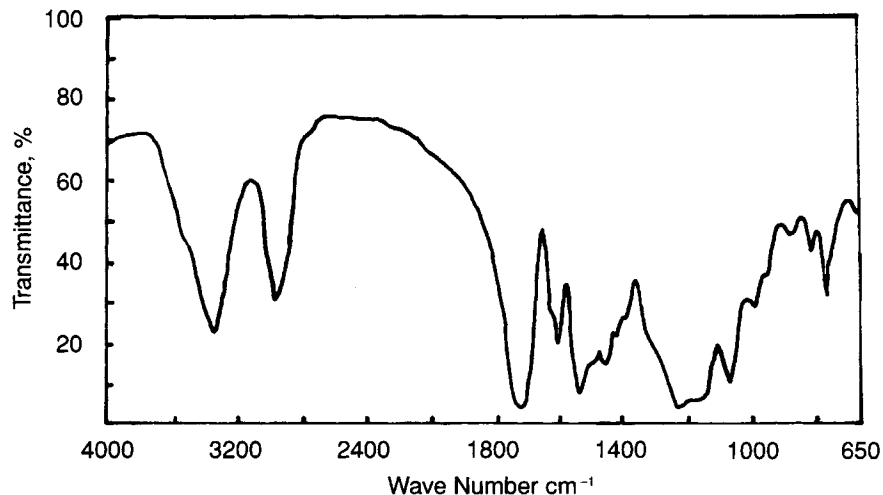


Figure 1 The infrared spectrum of material TP.

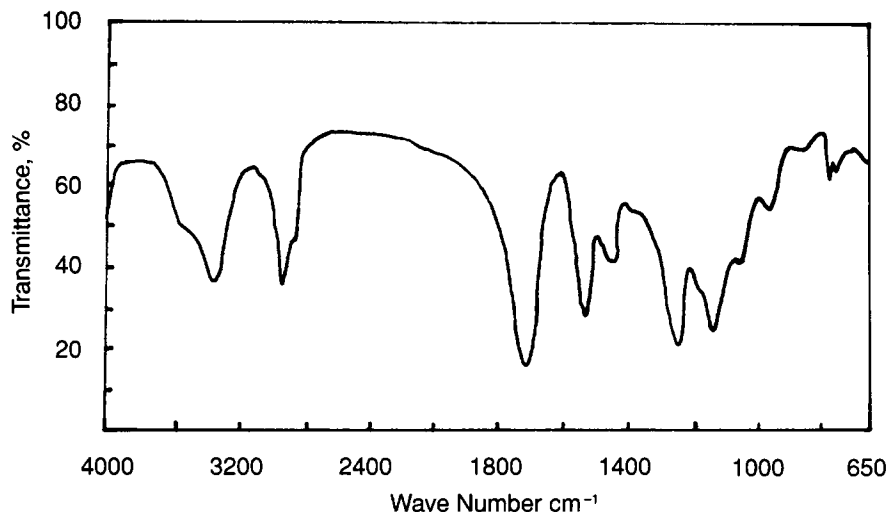


Figure 2 The infrared spectrum of material HP.

crosslinking and copolymerization are essentially complete.

Some Aspects of the Apparent Kinetics of Prepolymerization

At the stage of prepolymerization, the reaction taking place in the system includes mainly step polymerization between isocyanate and hydroxyl (from TEG and HEMA) because of the lower reaction temperature, in other words, the chain polymerization rate of MMA can be neglected. The apparent kinetics of the step polymerization in the presence

and absence of MMA have been made by a titrimetric analysis. Figure 3 shows the relationship between the reaction velocity (increment of the conversion of NCO groups per minute) and the reaction temperature at the initial stage of the prepolymerization. According to the Arrhenius equation, the apparent activation energies of the reaction are calculated to be 35.07 KJ/mol in the absence of MMA and 36.73 KJ/mol in the presence of MMA. The results are near to each other, indicating that the presence of MMA has little effect on the reaction between —NCO and —OH groups. So in the reaction system, MMA acts only as a diluent, that is,

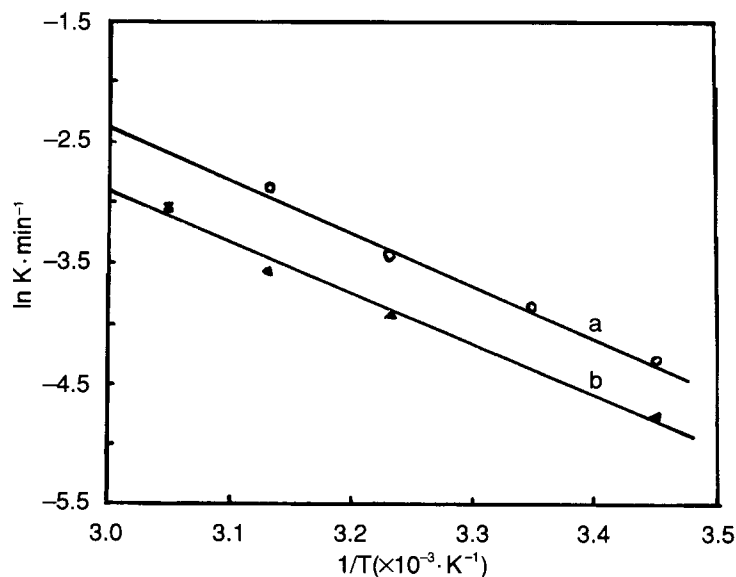


Figure 3 The relationship between the reaction velocity (K) and the temperature (T): (a) In the absence of MMA; (b) in the presence of MMA.

Table I Gelation Times with Different Amounts of AIBN and at Different Temperatures

Temperature, °C	AIBN %	0.2	0.4	0.6
50	Gelation time	475	171	125
60	Gelation time	79	30	22

it reduces the reaction velocity by decreasing the concentration of —NCO group, but the mechanism of the reaction is not changed.

For thermosetting polymers, gelation time is an important factor in production control. It is evident that the gelation time of TP depends little on the amount of HEMA, but mainly on the concentration of AIBN, the initiator, and the reaction temperature, as shown in Table I. Therefore, the key to preparing TP with excellent properties lies in the control of the AIBN concentration and reaction temperature.

Impact Strength and Surface Hardness

Increasing the amount of TEG leads to an increase of the impact strength, and has no distinct effect on the surface hardness for both TP and HP (Table II), at least in the range of this work. It is necessary to point out that the impact strength has a maximum value at the TEG/HEMA ratio of 0.75–0.80, especially for the material TP.

Effects of the MMA content on the impact strength and surface hardness are shown in Table

III. In general, the impact strength decreases with increasing the amount of MMA. But for the material TP, the maximum impact strength is achieved at a MMA content of 30%. This may relate to its microheterogeneous morphology, which exhibits the smallest domain size and a uniform distribution of the dispersed phase, the strongest joints between phases (Fig. 6c). It is also seen from Table III that the increase in MMA content makes the surface hardness decrease for TP, but increase for HP.

Table IV shows the changes in impact strength and surface hardness with the mole ratio of OH/NCO. Generally speaking, the impact strength and surface hardness reach a peak value when the ratio is close to 1. Specifically, the impact strength is highest at the ratio 1.20 and 0.91 for TP and HP, respectively. The reason is not clear yet, probably it has something to do with the crosslinking density.

Some Other Properties

Table V gives the comparison of refractive index between TP and other transparent polymers.¹¹ It is obvious that the value of TP is higher than that of PMMA or CR-39.

As mentioned above, PMMA is a highly transparent organic material, the optical transmissions of TH and HP are comparable to that of PMMA at the wavelength of visible light (Fig. 4). In the region of shorter wavelength, such as the ultraviolet region, the value decreases remarkably, especially for TP, that is, TP exhibits stronger absorption of light in the ultraviolet region.

Table II Impact Strength and Surface Hardness of TP and HP at Various Ratios of TEG/HEMA

TEG/HEMA ratio in hydroxyl moles		0.00	0.33	0.50	0.75	0.80	1.00
Impact strength (N/m ²)	TP	7.0	11.2	10.7	16.4		11.8
	HP	9.8		13.8		17.8	17.7
Surface hardness (kg/mm ²)	TP	24.5	23.3	24.8	23.9		25.0
	HP	15.0		15.4		15.0	14.4

Table III Effects of MMA Content on the Impact Strength and Surface Hardness

MMA content (%)		0.0	10.0	20.0	30.0	40.0
Impact strength (Kg/m ²)	TP		8.3	10.7	15.6	12.5
	HP	31.1	21.5	17.7	20.9	15.1
Surface hardness (Kg/mm ²)	TP	24.7	25.2	24.8	23.9	21.8
	HP	8.9	12.0	14.4	14.7	16.6

Table IV Relationship Between the Impact Strength, Surface Hardness and OH/NCO Mole Ratio

OH/NCO mole ratio		1.30	1.20	1.10	1.04	0.91	0.83	0.8	0.70
Impact strength (Kj/m ²)	TP	10.3	13.6	11.9	10.1		9.2		9.0
	HP	3.0	12.8	14.6	17.8	25.0		17.0	
Surface hardness (Kj/mm ²)	TP	23.5	23.9	24.6	24.8		24.5		22.7
	HP	10.1	13.6	13.4	15.0	14.9		13.9	

Table V Refractive Index of TP and Other Optical Plastics

Material abbreviation	TP	PMMA	CR-39	PC	PS	PAN	SAN
Refractive index (25°C)	1.55	1.49	1.50	1.59	1.59	1.51	1.57

Table VI lists data on water absorption of TP, HP, and a few other transparent materials.¹² Although the water absorption of HP is a little higher, the value of TP is lower than that of the other materials, such as CR-39, PS, PMMA, etc.

Thermomechanical Analysis (TMA)

Table VII gives the results of glass transition temperature (T_g), linear thermal expansion coefficient α_1 before T_g and α_2 after T_g for different compositions. It is evident that the T_g s of TPs are higher than those of the homopolymer of component I (PU) and II (PMMA), except for the case of TEG/HEMA > 0.75. With increasing TEG content, the glass-temperatures of both TP and HP tend to decrease,

because the crosslinking density decreases along with increasing of TEG/HEMA ratio.

In order to control the dimension precision for manufacture, it is always desirable to have the smallest linear thermal expansion coefficient in a transparent materials. The results in Table VII indicate that the linear expansion coefficient α_1 of TP is less than that of PMMA, and less than half of the CR-39's. HP's α_1 , although higher than PMMA's α_1 , is also lower than the CR-39's. α_2 has little importance practically because all the materials being discussed here will be used in the glassy state. So we can conclude: used as optical material, TP is superior to CR-39 and PMMA not only in respect to water absorption, but linear heat expansion coefficient as well.

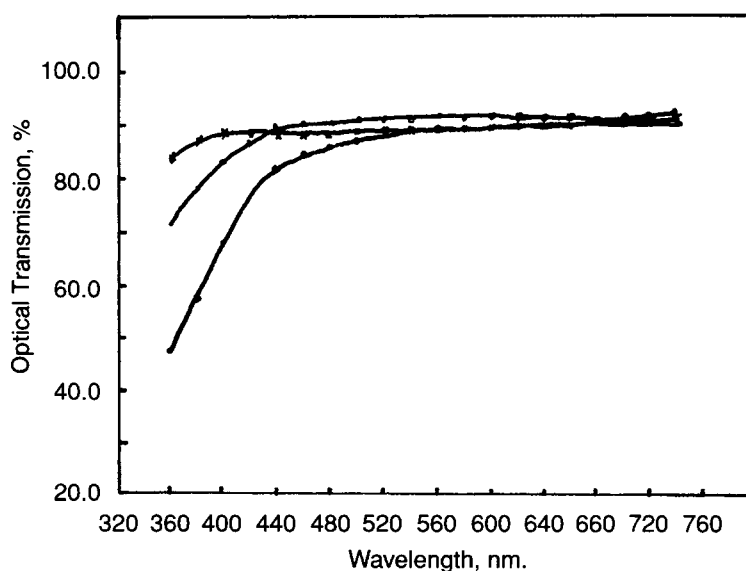
**Figure 4** The relationship between optical transmission and wavelength.

Table VI Comparison of Water Absorption Between the AB-Crosslinked Copolymer and a Few Optical Materials

Material abbreviation	TP'	TP	HP	CR-39	PS	PC	PMMA
Water absorption (%)	0.14	0.17	0.87	0.2	0.2	0.15–0.18	0.3–0.4

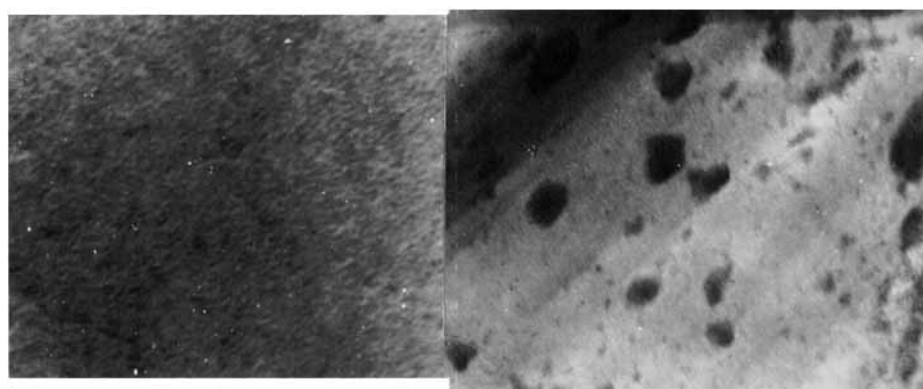
TP' contains 10% by weight MMA.

Morphology Structure

TEM micrographs of TPs and HP, with different MMA content, are shown in Figure 5 and Figure 6, respectively. The component of polyurethane was

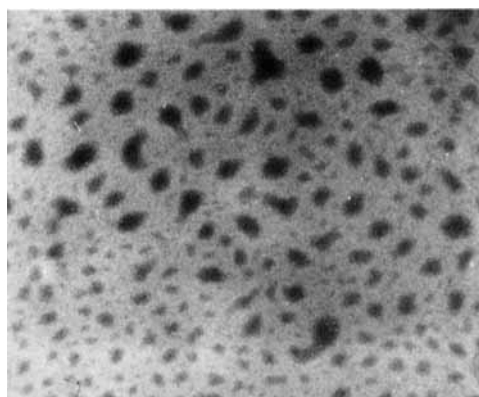
selectively stained with ruthenium tetroxide. All the micrographs, including homo-PU (prepared in the absence of MMA), exhibit two separated phases.

Morphological structure and the domain size of TP relates greatly to MMA content as shown in

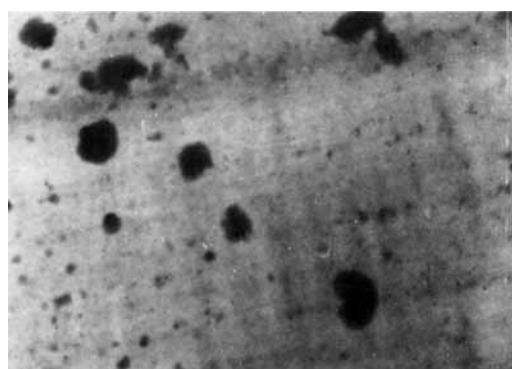


a. MMA%: 0.0
Magnification: 300,000
Average size of the dispersed phase: 0.0035 μm

b. MMA%: 20.0
Magnification: 40,000
Average size of the dispersed phase: 0.12 μm



c. MMA%: 30.0
Magnification: 42,000
Average size of the dispersed phase: 0.06 μm

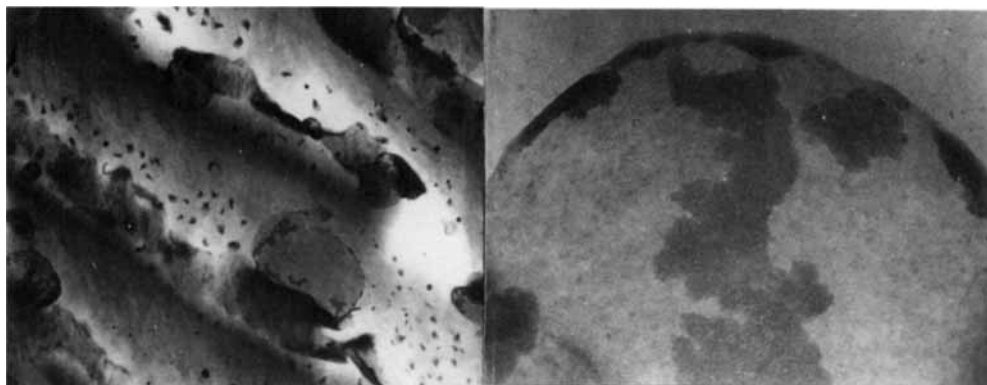


d. MMA%: 40
Magnification: 20,000
Average size of dispersed phase: 0.24 μm

Figure 5 TEM micrographs of TP with different MMA content.

Table VII The Transition Temperature and Linear Thermal Expansion Coefficient of TP, HP, PMMA, and CR-39

Sample Code			MMA Content %			TEG/HEMA Mole Ratio in Hydroxyl					
	PMMA	CR-39	TP1 10	TP2 20	TP3 30	TP6 0.33	TP7 0.75	TP8 1.00	HP1 0.5	HP2 0.8	HP3 1.0
$T_g, ^\circ\text{C}$	115		137	131	133	136	131	114	82	67	64
$\alpha_1 \times 10^6/\text{K}$	9.1	16.4	7.5	5.9	6.1	6.6	5.7	7.3	11.5	12.1	12.6
$\alpha_2 \times 10^6/\text{K}$	103.3		15.7	16.1	18.3	15.3	18.1	17.2	10.1	16.1	16.6



Magnification: 7,000

Magnification: 80,000

Figure 6 TEM micrographs of HP (OH/NCO: 0.91; Photograph b is the magnified image for the marked domain in photograph a).

Figure 5. In the range of this work, the PU component is the dispersed phase scattered in the matrix of PMMA, similar to the situation reported by other authors.^{4,15} Figure 5 also shows that the dispersed PU phases distribute most uniformly at the MMA content of 30% resulting in the highest impact strength as mentioned above. Looking at Figure 6 TEMs for the sample giving highest impact strength (Table IV), we can find that some of the dispersed particles have a sausage-like structure.

CONCLUSION

PU/PMMA-based AB-crosslinked copolymers with various compositions were synthesized as transparent materials. The morphological structure of the material is microheterogeneous with a domain size no more than $0.1 \mu\text{m}$. Because of the advantages of high transparency and surface hardness, low water

absorption, and linear thermal expansion coefficient, significant application prospects can be expected for these materials.

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