

STUDY ON CASTOR OIL POLYURETHANE/ POLY (METHYL METHACRYLATE) AB CROSSLINKED POLYMERS*

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ABSTRACT

Castor oil polyurethane/poly(methyl methacrylate) AB crosslinked polymers (ABCP) were synthesized by free radical copolymerization of MMA and vinyl-terminated castor oil polyurethane which was obtained from isocyanate-terminated castor oil polyurethane and hydroxyethyl methacrylate.

The mechanical properties, transition and relaxation, as well as compatibility and morphology of the ABCP were investigated by changing the component. The results show that the ABCP is a semi-compatible system and the compatibility of the two components decreases with increasing content of the hard segment. The mechanical and damping properties of the ABCP are obviously superior to that of their homopolymers. The damping value is mainly controlled by crosslink density of the ABCP but the T_g value by component.

The multicomponent polymer material, referred to as AB crosslinked polymers (ABCP), consists of chains of polymer A crosslinked with chains of polymer B. The difference between ABCP and interpenetrating polymer networks (IPN) is that the latter consists of two independent networks, but the former only one network. Besides the excellent damping properties, ABCP has other unique advantages, such as the simple synthesis method, controllable molecular structure and so on, however, so far ABCP is not understood widely as IPN.

The synthesis of ABCP can be approached as two ways. One way was first proposed by Bamford and his colleagues involving free radical polymerization of halogenated prepolymer and vinyl monomer initiated by organometallic derivative of a transition metal in a low oxidation state^[1-3]. In the second method, the free radical copolymerization of vinyl-terminated prepolymer and vinyl monomer initiated by common initiators was also used. We have investigated some ABCP systems based on polyether urethane and vinyl monomers in this respect^[4].

In this paper, ABCP with lower cost based on castor oil polyurethane/polymethyl methacrylate (COPU/PMMA ABCP) was synthesized by using the second method. The mechanical properties, transition and relaxation behaviors, compatibility and morphology of the ABCP were studied in detail by changing the component and crosslink density. The activation energies of each relaxation process were calculated.

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EXPERIMENTAL

Materials

Castor oil was dewatered in vacuum. Methyl methacrylate (MMA) was washed with 10% NaOH and then distilled. 2,4-Toluene diisocyanate (AR) (TDI) was obtained from Shanghai Reagent Factory. Hydroxyethyl methacrylate (HEMA) was made by Tokyo Chemical Industry Co., Ltd.

Syntheses

Isocyanate-terminated prepolymer (ITP) was synthesized by condensation of castor oil and TDI at 40 °C. The product was then heated to 60 °C and reacted with HEMA with OH/NCO ratio being 1.3 for 1.5h, then the vinyl-terminated prepolymer (VTP) was obtained.

COPU/PMMA ABCP was prepared by the free radical copolymerization of the VTP and MMA monomer using peroxy-cyclohexanone and cobaltous naphthenate as initiator at 30 °C for 20 h and 100 °C for 1.5 h to remove the unreacted monomer.

Characterization

Isocyanate group content of the ITP was measured by chemical method and its molecular weight was measured by cryoscopic method. IR spectra were obtained on Perkin-Elmer 580B spectrograph and NMR spectra were recorded with JEOL FX-100 NMR spectrometer.

$\bar{M}_c$ of the cured samples were evaluated with swelling method. The gel fraction was measured by weighing the polymer extracted by methyl ethyl ketone. Dynamic mechanical data were obtained from VIBRON DDV-II-EA. Stress-strain measurement was carried out on INSTRON-1121 at room temperature with a crosshead speed of 100mm/min. The toughness of the ABCP was calculated from the area of the stress-strain curve. Dielectric property was measured on TRS-10C dielectric loss instrument at 30Hz to 10KHz. Transmission electron micrographs (TEM) were taken from HITACHI H-500 electron microscope. The samples were cut under refrigeration and stained by OsO₄.

RESULTS AND DISCUSSION

Structure of the prepolymers

Table 1 shows the isocyanate group content and molecular weights of prepolymer ITP and VTP. The IR and NMR spectra of the preolymers are shown in Figure 1 and 2, respectively.

Table 1 NCO group contents and molecular weights of prepolymers

Prepolymer	NCO content (wt%)		Molecular weight	
	Calculated	Measured	Calculated	Measured
ITP	8.66	8.22	1455	1397
VTP	0	0.22	1805	1128*

* The lower value is due to the presence of excessive HEMA in the system.

From the data of Table 1, it is obvious that the NCO contents and molecular weights of the prepolymers are very close to the calculated values, which

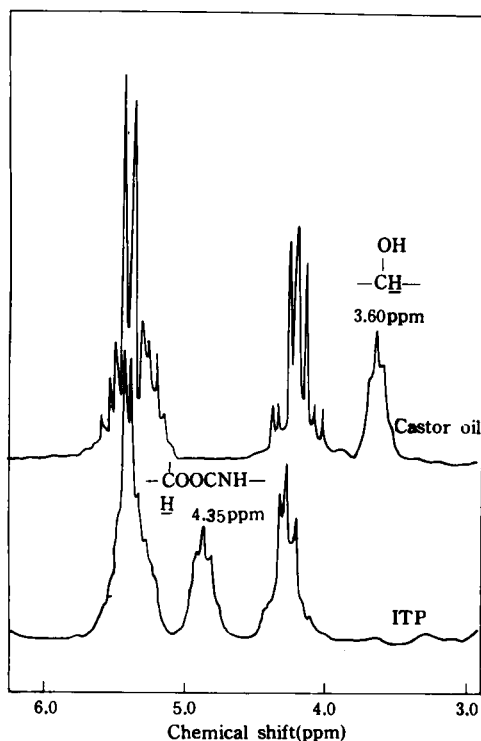
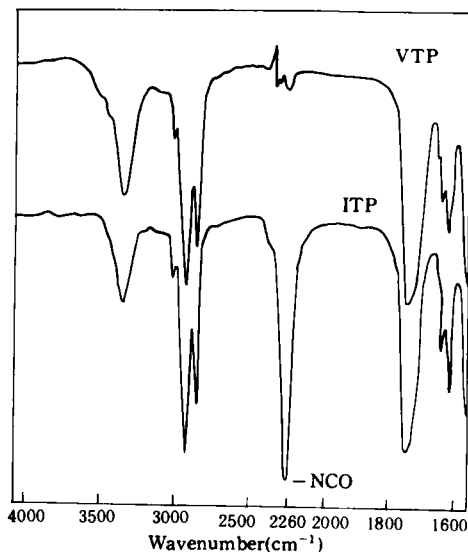
Fig.1 ^1H -NMR spectra of castor oil and ITP

Fig.2 IR spectra of ITP and VTP

indicates the reactions for obtaining the prepolymers are nearly complete. The results of Figure 1 and 2 also support the above conclusion. The disappearance of the resonance peak at 3.6 ppm ($-\text{CH}(\text{OH})-$) and the appearance of the peak at 4.85 ppm ($-\text{HNCOOCH}-$) mean that castor oil reacted with TDI completely. The disappearance of absorbance at 2260 cm^{-1} ($-\text{NCO}$) in Figure 2 indicates that the NCO groups of ITP almost completely condensed with OH groups of HEMA after the given reaction time.

Table 2 presents the characteristic data of the crosslinked polymers prepared by the copolymerization of VTP and vinyl monomer MMA. The average molecular weights between crosslink points ($\overline{M}_c$) measured by swelling method are essentially conformable with the values calculated from the following equation^[5]:

$$\overline{M}_c = (M_{\text{copu}} + W_{\text{mma}} / W_{\text{copu}}) / 2 \quad (1)$$

where M_{copu} : (molecular weight of VTP) / 3

W_{copu} and W_{mma} are weights of VTP and MMA, respectively.

The higher gel fraction of the polymer also means that the polymer obtained is a crosslinked one.

Table 2 Characteristic data of crosslinked polymers

Ratio of COPU / MMA	90 / 10	70 / 30	50 / 50	30 / 70	10 / 90
$\overline{M}_c$ calculated	334	429	601	1002	3005
$\overline{M}_c$ measured	308	406	578	937	—
Gel fraction (wt%)	94.4	95.9	95.5	95.0	95.6

Transition and relaxation

Dynamic mechanical properties of a series of ABCPs with different composition listed in Table 2 are shown in Figure 3. Increasing hard segment content and decreasing crosslink density (increasing $\bar{M}_c$) of the ABCPs result in the increase of the glass temperature, the magnitude of $\tan\delta$ peak and the degree of phase separation. Figure 4 shows the dielectric relaxation spectra of the ABCPs listed in Table 2 and homopolymers, COPU and PMMA. The T_g of homopolymers COPU and PMMA are 0 and 100 °C, respectively. With increasing MMA content, the T_g of samples shifts from 0 °C to higher temperature, $\tan\delta$ peaks increase in magnitude and the forms of the peaks change from symmetric to unsymmetric with a shoulder. The shoulder peak just appears at the position of $\tan\delta$ peak for COPU, which means the shoulder relates mainly to the glass transition of soft segment. Besides, the secondary relaxation of PMMA (0 to 40 °C) resulted from the side group of MMA also has some contribution to the appearance of shoulder peak with increasing PMMA content. The results are identical with that of dynamic mechanical spectra.

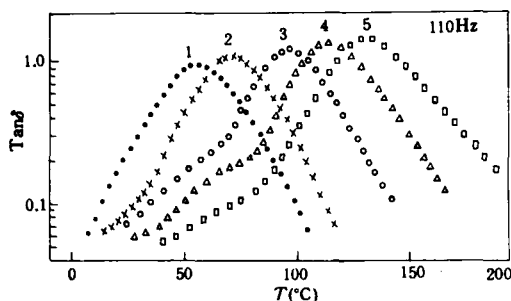


Fig. 3 The dynamic mechanical spectra of ABCPs
COPU / AMMA:

1, 90 / 10; 2, 70 / 30; 3, 50 / 50;
4, 30 / 70; 5, 10 / 90

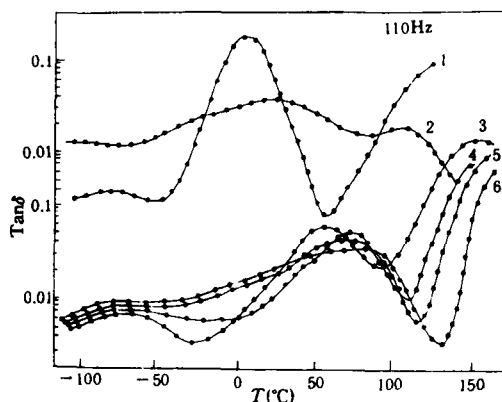


Fig. 4 The dielectric relaxation spectra of ABCPs
COPU / PMMA:

1, 100 / 0; 2, 0 / 100; 3, 90 / 10;
4, 70 / 30; 5, 50 / 50; 6, 30 / 70

In order to investigate more clearly the effects of crosslink density of the ABCP materials on their compatibility, divinyl benzene was added as crosslinked agent in the curing systems to adjust the average molecular weights between crosslinked points. Figure 5 presents the effect of crosslink density on the dynamic mechanical properties when COPU / PMMA = 30 / 70. With increasing crosslink density of ABCPs, the compatibility of the components and T_g values increase but $\tan\delta$ value and breadth of the peak decrease.

The following conclusions would be drawn by synthesizing the results of Figures 3 and 5: Phase separation to certain extent exists in the COPU / PMMA ABCP systems. The compatibility of the two components decreases with increasing hard segment content and decreasing crosslink density. The breadth of transition peak is mainly effected by the crosslink density but T_g value is chiefly controlled by the composition.

The dielectric relaxation spectra at different frequencies are shown in Figure 6.

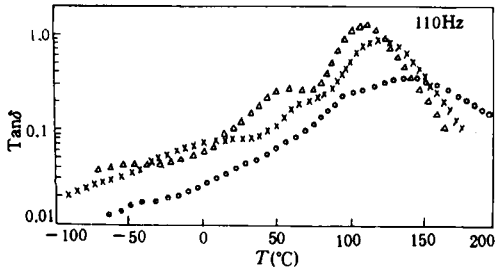


Fig.5 The effect of crosslink density on the dynamic mechanical properties .

COPU/PMMA=30/70, Calculated M_c :

Δ — 1000 ; $\times$ — 600 ; $\circ$ — 429

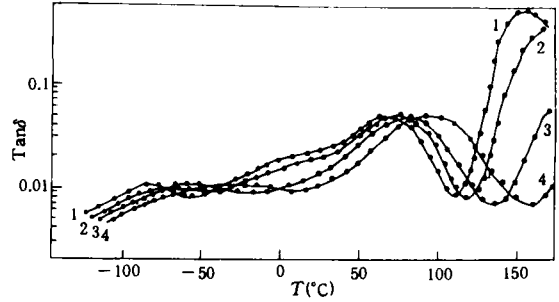


Fig.6 The dielectric relaxation spectra at different frequencies

COPU/PMMA=50/50. Frequencies (Hz):

1, 30 ; 2, 110 ; 3, 1000 ; 4, 10000

Three relaxation processes are observed from the curves of dielectric loss with temperature. The α relaxation, that is glass transition, appears in the range of 70 to 100 °C and the second relaxation is observed in the range of -80 to -40 °C. Besides, a shoulder exists at about 0 °C in the relaxation curves. Over the higher temperature side of α relaxation peak, the $\tan\delta$ value increases rapidly with increasing temperature, which results from the interface polarization and relates to the motion of dispersed phase domains.

In order to observe the change of energy in relaxation process, the activation energy of each relaxation process are calculated. For the transition and relaxation with a constant activation energy the dependence of relaxation time on temperature should be satisfied with Arrhenius equation :

$$\tau = \tau_0 \exp(E/RT) \quad (2)$$

where τ and τ_0 are the relaxation times at temperature T and reference temperature T_0 .

The second relaxation process conforms to equation 2, so that according to the data of τ and T obtained at a distinct frequency and equation 2, a straight line is obtained, from which the second relaxation activation energy could be calculated being 37.20KJ/mol.

In the α relaxation range for polymers, the relationship of $\ln \tau$ and $1/T$ is usually not linear and molecular motion activation energy is a function of temperature. The dependence of relaxation time on temperature follows WLF equation:

$$\text{Log } a_T = \text{Log } \frac{(T)}{(T_0)} = \frac{-C_1(T-T_0)}{C_2+T-T_0} \quad (3)$$

where a_T is the displacement factor, C_1 and C_2 are all constant. For convenience sake, the equation was adapted into equation 4:

$$\frac{1}{-\text{Log } a_T} = \frac{1}{C_1} + \frac{C_2}{C_1} \cdot \frac{1}{T-T_0} \quad (4)$$

The C_1 and C_2 values in WLF equation were calculated from the plot of $-1/\text{Log } a_T$ against $1/(T-T_0)$ being 10 and 80, respectively. According to the definition of the elastic relaxation activation energy^[4],

$$E_a = R \frac{d(\ln a_T)}{d(1/T)} \quad (5)$$

Equation 6 is obtained, from which the relationship of E_a and T could be expressed as Figure 7.

$$E_a = \frac{2.303 C_1 C_2 R T^2}{(C_2 + T - T_0)^2} \quad (6)$$

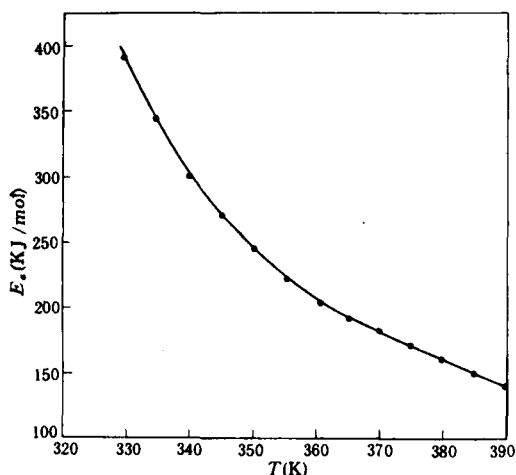


Fig. 7 The relationship of E_a and T

Mechanical properties

Figure 8 shows the stress-strain curves of COPU / PMMA ABCPs listed in Table 2 and homopolymers COPU and PMMA, which indicate that the mechanical properties of the materials appear elastic, tough or brittle behaviors, respectively, with different hard segment contents. For example, curve 1, the drawing curve for COPU, shows the drawing behavior of the polymer with high-elastic

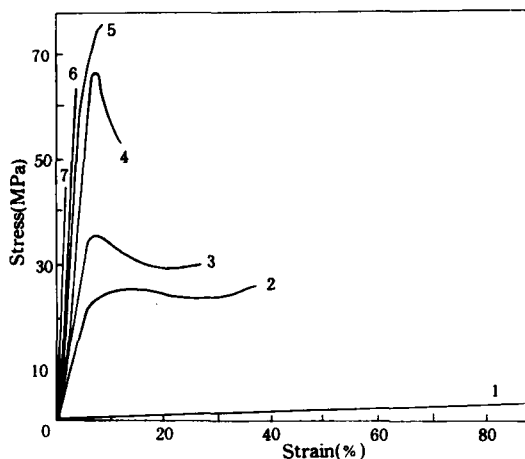


Fig. 8 Stress-strain curves of ABCPs
COPU/ PMMA: 1, 100/ 0; 2, 90/ 10; 3, 70/ 50;
4, 50/ 50; 5, 30/ 70; 6, 10/ 90; 7, 0/ 100

deformation . Curve 2 to 4 display the behaviors of tough materials which have a yield point with greater deformation and stress . Curve 5 shows the behavior of material at “soft glass state” . Curve 6 and 7 are typical drawing curves of the materials at “hard glass state” . At this state , during drawing stress rapidly reaches to a great value but elongation is small and breaks immediately . This is a typical behavior of “brittle break” for hard and brittle materials .

The mechanical property data of samples are listed in Table 3 . As shown , an increase of hard segment content leads to a great increase of Young’s modulus, meanwhile , due to AB crosslinking , the tensile strength of ABCP increases obviously and it surpasses that of their homopolymers far away in suitable ratio of COPU /PMMA . AB crosslinking also make the materials toughness be superior to their homopolymers obviously . The best result could be obtained at the ratio of COPU /PMMA being 70 /30. So the mechanical properties of COPU /PMMA ABCPs can be adjusted in great range according to the different requirements .

Table 3 Mechanical properties of ABCP samples*

COPU /PMMA ratio (wt%)	100 /0	90 /10	70 /30	50 /50	30 /70	10 /90	0 /100
Young’s modulus (MPa)	—	333.7	532.6	968.4	1131.0	1370.1	—
Tensile strength (MPa)	1.9	22.2	31.5	64.4	74.5	59.6	37.4
Toughness (J /cm ³)	1.31	6.38	7.05	4.11	2.45	1.41	0.75

* $\overline{M}_c$ of the ABCP samples are the same as that listed in Table 2 .

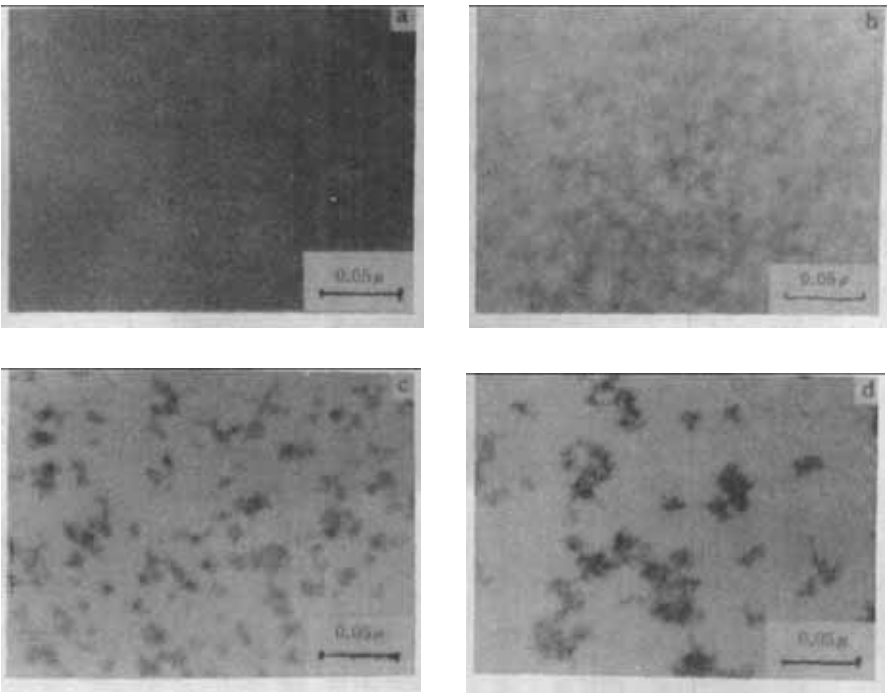


Fig.9 TEM micrographs of ABCPs
COPU /PMMA: a , 90 /10 ; B , 70 /30 ; c , 50 /50 ; d , 10 /90 .

Morphology

The photographs of transmission electron microscope (TEM) of ABCPs with different hard segment content indicated as in Table 2 are shown in Figure 9. With increasing hard segment content, the compatibilities of the ABCP systems changed from approximate compatible to semi-compatible and the domain sizes changed. For example, in Figure 9 (a) the COPU soft segment forms continuous phase (stained part) and the phase separation is not clear. In the case of COPU/PMMA being 70/30 (Figure 10 b), a double continuous phase structure is formed and the domain size increases to about one hundred angstroms, that means the ABCP with 30% PMMA is a semi-compatible system. When PMMA content is over 50%, phase inversion occurs (Figure 10 c and d) and the domain size reaches to hundreds angstroms. These results are conformable with that of dynamic mechanical spectra and dielectric relaxation spectra.

Keywords :

AB crosslinked polymers; Castor oil polyurethane; PMMA;
Dynamic mechanical properties; Dielectrical relaxation spectrum; TEM.

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