

Polycarbonate-Polyurethane Semi-Interpenetrating Polymer Networks: T_g Behavior and Morphology

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Synopsis

The dynamic mechanical properties, transition behavior, and morphology of polycarbonate (PC)-polyurethane (PU) semi-interpenetrating polymer networks (semi-IPNs) and linear blends were studied by means of Rheovibron, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). Two glass transition temperatures corresponding to polycarbonate and polyurethane were observed and microphase separation was further evident with TEM. In PC/PU semi-IPNs, two glass transition temperatures were shifted inwardly indicating that the interpenetrating network of polyurethane increases the mutual miscibility of PC and PU. The average phase domain was 500 Å in semi-IPNs and the phase domains were in the range 1000–6000 Å in linear blends of the corresponding polymers. The compatibilities of PC and PU were greatly influenced by the molecular weight of polyols in PU prepolymer and the ratio of NCO/OH; lower molecular weight polyols and higher NCO/OH ratio resulted in better compatibility, and finer phase domains in PC and PU linear blends and semi-IPNs.

INTRODUCTION

Interpenetrating polymer network (IPN) is a unique type of polyblend which can be classified as polymeric catenanes, if we envision a crosslinked polymer network to be composed of many macrocycles of varying sizes. IPN can be viewed as the crosslinking of one component which occurs in the presence of an already cross-linked polymer network. If only one polymer is crosslinked, the material is referred to as a pseudo-IPN¹ or semi-IPN.² Among immiscible (or partially miscible) systems, the degree of interpenetration depends on the miscibility of components. For systems of a high degree of a miscibility, the networks can be visualized as being interpenetrated and continuous throughout the entire macroscopic sample. However, if the components consist of chemically distinct polymers, some degree of phase separation occurs.^{3–7} There is no general method to prove the existence of interpenetration, nor to measure the quantitative level of interpenetration. Equilibrium swelling and the apparent cross-linked density measurements will serve the purpose only when the IPN is homogeneous and the statistical theory of rubber elasticity is applicable. It is helpful to measure the glass transition temperatures and the mechanical properties in the study of heterogeneous systems.

Interpenetrating polymer networks represent a new approach to the problem of mutual immiscibility of polymers. Sperling,^{8–10} Frisch,^{11–13} Lipatov,^{14–16}

TABLE I
Materials

Materials	Description	Source
PC	Polycarbonate, mol. wt. 30,000–50,000	Panlitel-1250Y (Japan)
PPG-400	Poly(oxypropylene) glycol, $\text{OH}_{\text{no.}} = 280 \pm 10$	Chiung-Long Co. (Taiwan)
PPG-1000	Poly(oxypropylene) glycol, $\text{OH}_{\text{no.}} = 160 \pm 10$	Chiung-Long Co. (Taiwan)
PPG-2000	Poly(oxypropylene) glycol, $\text{OH}_{\text{no.}} = 112 \pm 1$	Chiung-Long Co. (Taiwan)
MDI	4,4' Diphenylmethane diisocyanate	Ti-Jing Co. (Taiwan)
TMP	Trimethylolpropane	TDI Co. (Japan)
T-12 Cat.	Dibutyltin dilaurate	Merck

and co-workers have done pioneering research in the field of IPNs. They have also established that in many cases, the interpenetrations of the two phases yield materials with new or enhanced properties. Polycarbonate is outstanding in toughness, transparency, and temperature resistance. The polymer also displays good rigidity up to 140°C, and very good characteristics in electrical insulation, but its cost is very high, its ultraviolet (UV) and chemical resistance are limited, and it is notch sensitive and susceptible to strain crazing.

To modify the properties of polycarbonate, polyurethane was chosen to be linear blended or semi-interpenetrated with polycarbonate. In this paper we first discuss the T_g behavior and morphology of the linear blends and semi-IPNs. The influence of molecular weight of polyols in PU prepolymer and NCO/OH ratio on the T_g behavior and morphology is discussed also.

EXPERIMENTAL

Materials

The starting materials used and their descriptions are listed in Table I. All polyols were dried at 80°C for 8 h under a vacuum of 4–5 mmHg. 4,4-Diphenylmethane diisocyanate (MDI) and polycarbonate (PC) were used without further purification.

Preparation of Polyurethane (PU)

A resin kettle, under dry nitrogen, was charged with MDI, to which polyols of various molecular weights and ratio of NCO/OH were added slowly with stirring to obtain PU prepolymer. The reaction was carried out at 55–60°C until the theoretical isocyanate content (determined by the di-*n*-butylamine titration method)¹⁷ was reached. The prepolymer was stored inside a desiccator before use. Samples prepared are shown in Table II.

Preparation of Linear PU and Cross-linked PU

Linear polyurethane was polymerized by mixing PU prepolymer and 1,4-butanediol (1,4-BD) containing 0.02% T-12 catalyst. A homogeneous solution

TABLE II
Polyurethane Prepolymer of Different NCO/OH Ratio and mol. wt. of Polyols

Samples	Composition	NCO/OH	NCO% (Theory)	NCO% (exp.)
A1	PPG400 + MDI	1/0.3	15.89	15.56
A2	PPG400 + MDI	1/0.5	9.33	9.32
A3	PPG400 + MDI	1/0.7	4.75	4.60
B1	PPG1000 + MDI	1/0.3	10.69	10.51
B2	PPG1000 + MDI	1/0.5	5.60	5.48
B3	PPG1000 + MDI	1/0.7	2.65	2.58
C1	PPG2000 + MDI	1/0.3	6.92	6.87
C2	PPG2000 + MDI	1/0.5	3.36	3.30
C3	PPG2000 + MDI	1/0.7	1.53	1.50

of 1,4-BD and trimethylolpropane (TMP) in a 1/1 equivalent ratio was prepared (containing 0.02% T-12 catalyst). Cross-linked polyurethane was synthesized by mixing the homogeneous solution and PU prepolymer to give a NCO/OH ratio of 1.05. All samples were put into an oven at 120°C for 4 h then postcured at 80°C for 12 h. The samples were kept at room temperature for 7 h before testing.

Preparation of PU / PC Blends and Semi-IPNs

PU prepolymer, with different NCO/OH ratios, were dissolved in dried dichloromethane with PC in different weight percents producing a 17–19% concentrated polymer solution. 1,4 BD (containing 0.02% T-12 catalyst) and 1,4 BD plus TMP (in a 1/1 equivalent ratio, containing 0.02% catalyst) were added to the concentrated polymer solution, respectively, to form a casting solution. The casting solution was spread over a smooth glass plate to form a thin clear film. The film was allowed to desolve for a controlled period of time, ranging from a few seconds to as much as 5 min or more depending upon the thickness of the film. When a skin was formed, the film was immersed in a quenching bath for 3–4 h then dried at room temperature. After being dried, the samples were placed in a vacuum oven for 10 days and postcured at 80°C

TABLE III
Description of Polycarbonate-Polyurethane Samples

Samples	Description			
A13I	PPG400 + MDI,	NCO/OH = 1/0.3,	PU/PC = 9/91,	semi-IPNs
A23I	PPG400 + MDI,	NCO/OH = 1/0.5,	PU/PC = 9/91,	semi-IPNs
A27I	PPG400 + MDI,	NCO/OH = 1/0.5,	PU/PC = 25/75,	semi-IPNs
A33I	PPG400 + MDI,	NCO/OH = 1/0.7,	PU/PC = 9/91,	semi-IPNs
A37I	PPG400 + MDI,	NCO/OH = 1/0.7,	PU/PC = 25/75,	semi-IPNs
A23B	PPG400 + MDI,	NCO/OH = 1/0.5,	PU/PC = 9/91,	linear blend
A27B	PPG400 + MDI,	NCO/OH = 1/0.5,	PU/PC = 25/75,	linear blend
B13I	PPG1000 + MDI,	NCO/OH = 1/0.3,	PU/PC = 9/91,	semi-IPNs
B27I	PPG1000 + MDI,	NCO/OH = 1/0.5,	PU/PC = 25/75,	semi-IPNs
B27B	PPG1000 + MDI,	NCO/OH = 1/0.5,	PU/PC = 25/75,	linear blend
C13I	PPG2000 + MDI,	NCO/OH = 1/0.3,	PU/PC = 9/91,	semi-IPNs
C27B	PPG2000 + MDI,	NCO/OH = 1/0.5,	PU/PC = 25/75,	linear blend

for 12 h, then conditioned in a desiccator for 3 days before testing. Samples prepared are listed in Table III.

Measurements

The dynamic mechanical data were obtained with a Rheovibron dynamical viscoelastometer (Model DDV-III-C) at a heating rate $2^{\circ}\text{C}/\text{min}$ and 110 Hz from -80 to 180°C . The glass transition temperature, the melting temperature, and ΔH were measured with a DSC calorimeter (Mettler TA 300) from

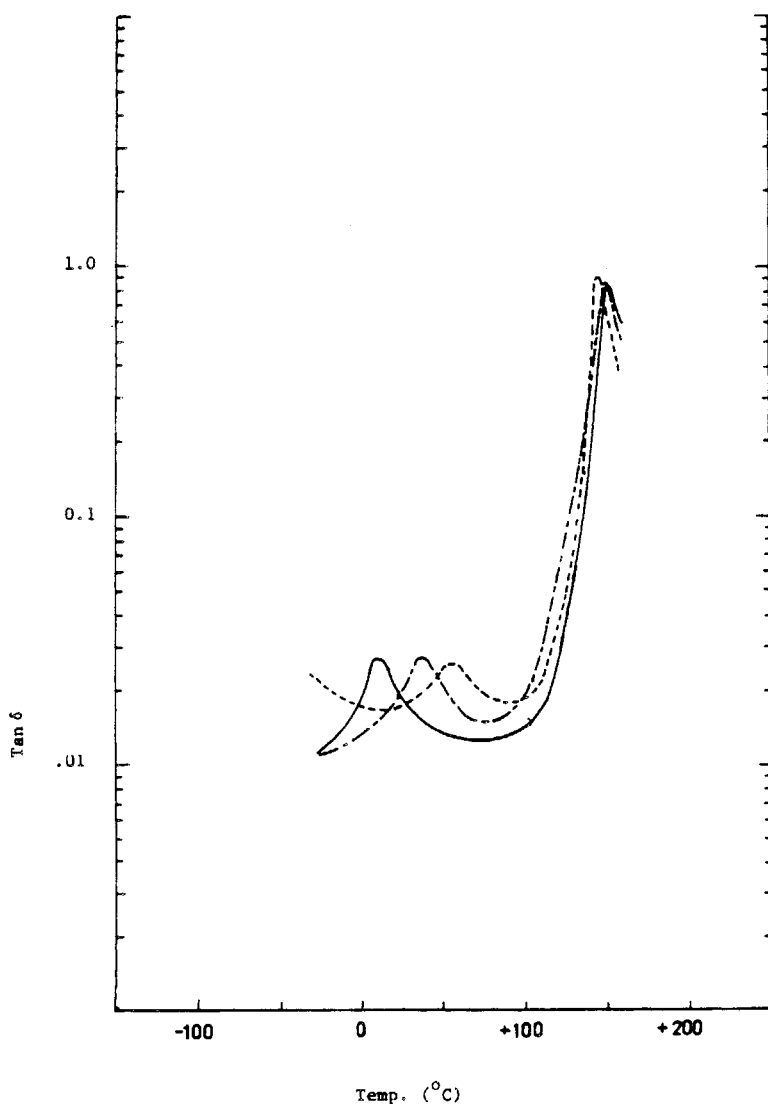


Fig. 1. Dissipation factor ($\tan \delta$) versus temperature at varying NCO/OH ratio. \cdots A13I, $-\cdots-$ A23I, $—$ A33I.

-100 to 300°C, under dry nitrogen at a scanning rate of 10°C/min. Specimen size was in the order of 10 mg. A transmission electron microscope (TEM) Model H-600 (Hitachi) was used to observe the morphology of the samples. Samples were prepared by solution casting method¹⁸ and were stained in OsO₄.

RESULTS AND DISCUSSION

Figure 1 shows the $\tan \delta$ versus temperature for various values of NCO/OH ratios. As the NCO/OH ratio increases, the lower PU peak shifts toward

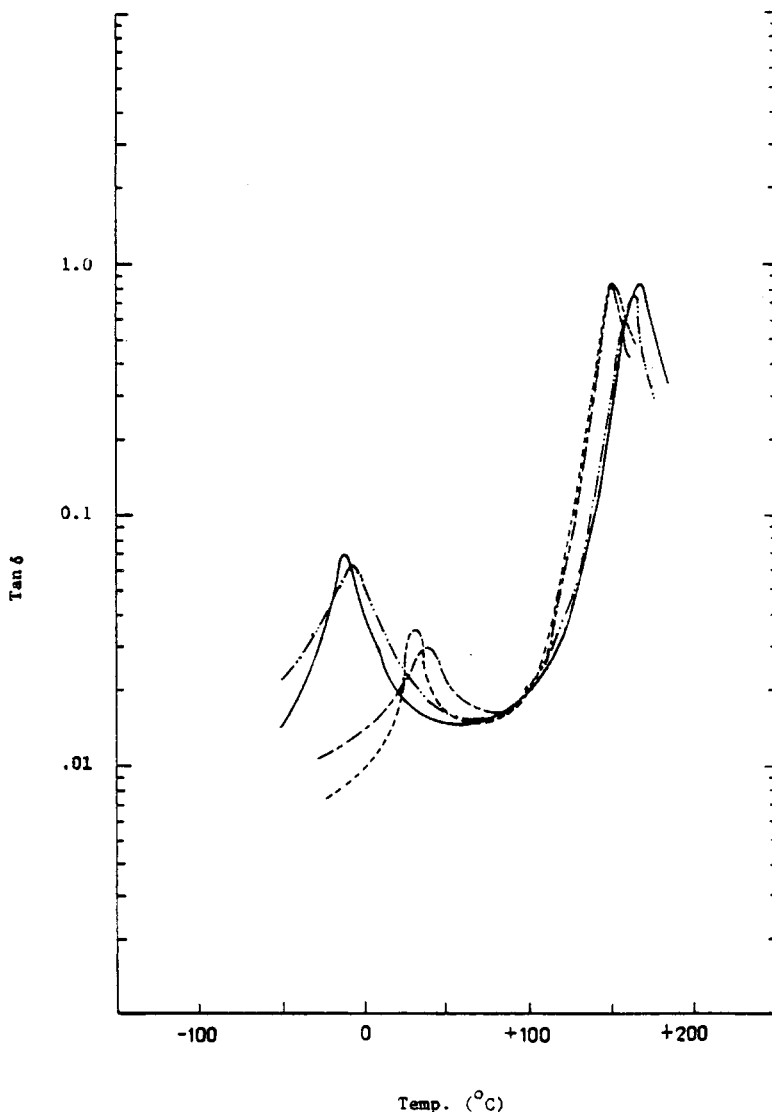


Fig. 2. Dissipation factor ($\tan \delta$) versus temperature. ···· A23B, ---- A23I, — B27B, -·-·- B27I.

higher temperature and the higher PC peak shifts toward lower temperature. Thus, the NCO/OH ratio governs the degree of crosslinking of polyurethane;¹⁹ the higher the NCO/OH ratio, the higher the degree of crosslinking, that is, the greater the miscibility between PC and PU. As the degree of crosslinking increased in the PU phase, the lower damping peak became lower and broader. Ueberreiter et al.²⁰ reported that it was generally assumed that the broadening and lowering of the transition region was caused by a distribution

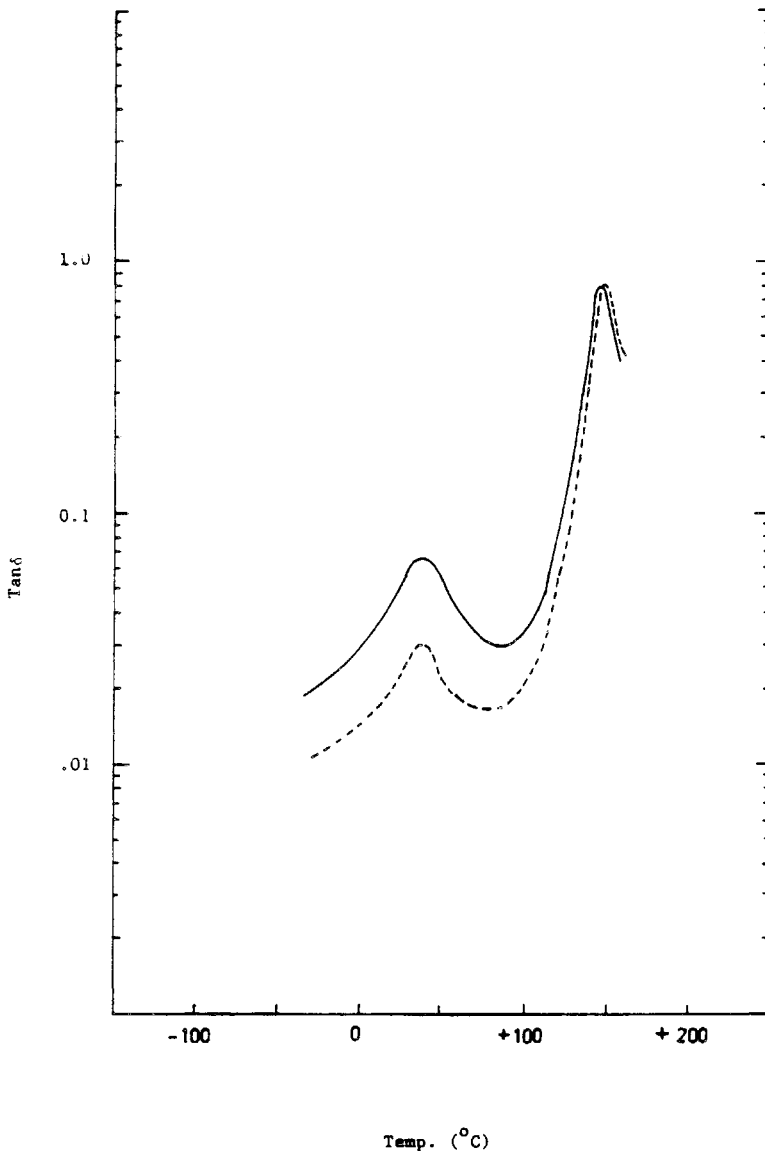


Fig. 3. Dissipation factor ($\tan \delta$) versus temperature at varying PU content. A23I, —A27I.

in the molecular weight between crosslinks or some other kind heterogeneity in the network structure. However Mason²¹ believed that it is caused by a broadening in the distribution of free volume between monomeric units. Figure 2 shows the inward shift of both PU and PC transition temperatures of semi-IPNs as compared to their linear blend. This may be taken as evidence that the intermixing of both PC and PU phases is increased by interpenetrating. Donald and Kaplan²² used damping peak to discuss the miscibility of two polymers. If two polymers are immiscible, an increase of one component will

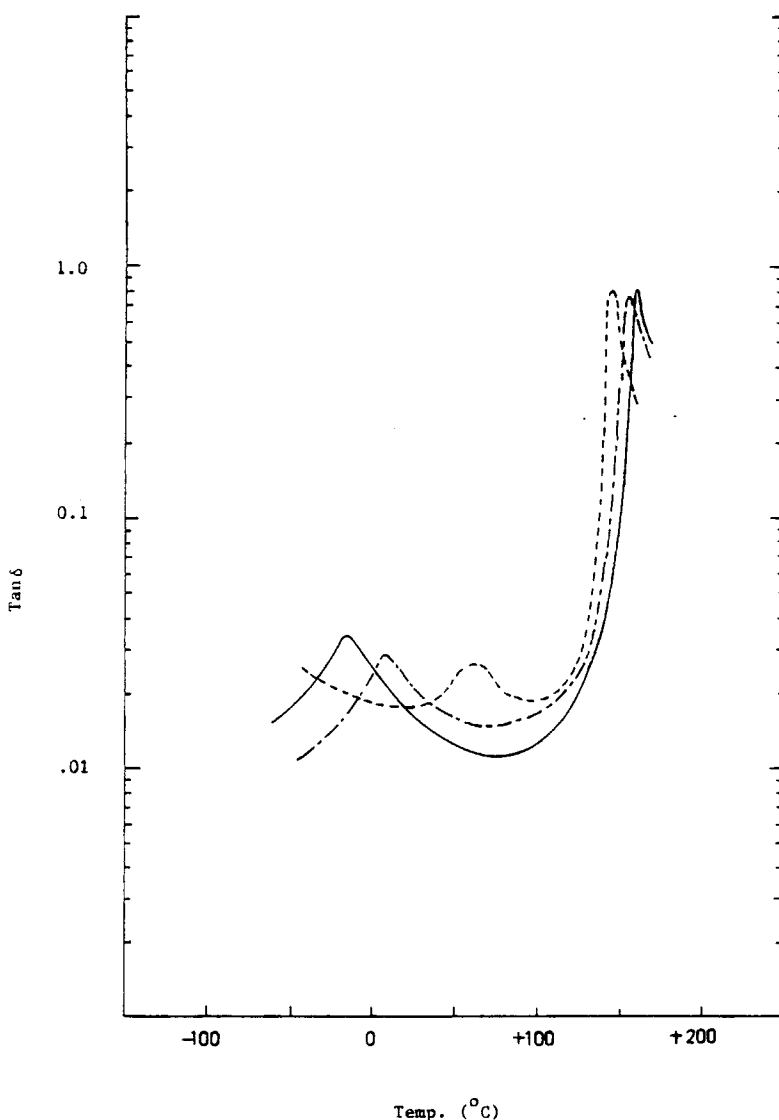


Fig. 4. Dissipation factor ($\tan \delta$) versus temperature at varying molecular weights of polyols in PU prepolymer. \cdots A13I, $-\cdots-$ B13I, $—$ C13I.

TABLE IV
 Data of DSC Measurements

Sample	Low T_g (°C)	High T_g (°C)	T_m (°C)	H (J/G)
A2C	44.12			
A2L	31.09			
B2C	-1.83			
B2L	-20.10			
C2C	-12.76			
C2L	-45.48			
B27I	25.53	135.49	216.9	5.51
B27B	-18.93	137.84		

Abbreviations: C = Crosslinked; L = Linear.

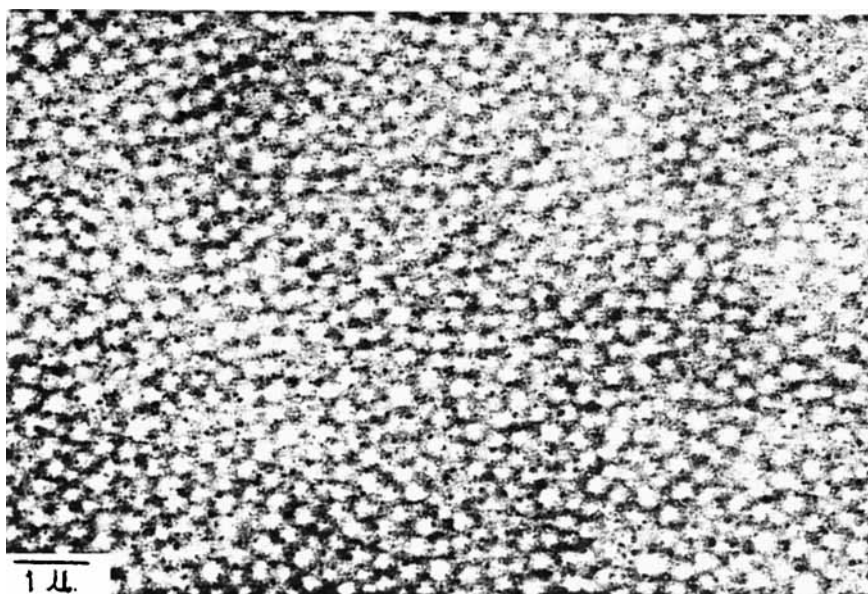
change the height of the damping peak, but will not shift it. However, if two polymers are miscible, an increase of one component will shift its transition temperature. Figure 3 shows that when the PU content increases only the height of the lower damping peak will change, but there is no transition temperature shift. This indicates that the miscibility of PC and PU is not good. The miscibility of PC/PU semi-IPNs also is greatly influenced by the molecular weight of polyols in the PU prepolymer. As shown in Figure 4, a system containing the lowest molecular weight polyol (PPG 400) has the highest amount of inward transition temperature shift; that is, a decrease in molecular weight of polyol in PU prepolymer will increase the miscibility of PC and PU.

Table IV shows the data determined by DSC in which we find that cross-linked PU polymer has a higher T_g temperature than linear PU. The T_g difference between cross-linked PU and linear PU is greatly affected by the molecular weight of polyols in PU prepolymer. A thermodynamic approach is used to state the effect of cross-link density on T_g .²³ The final relation may be written:

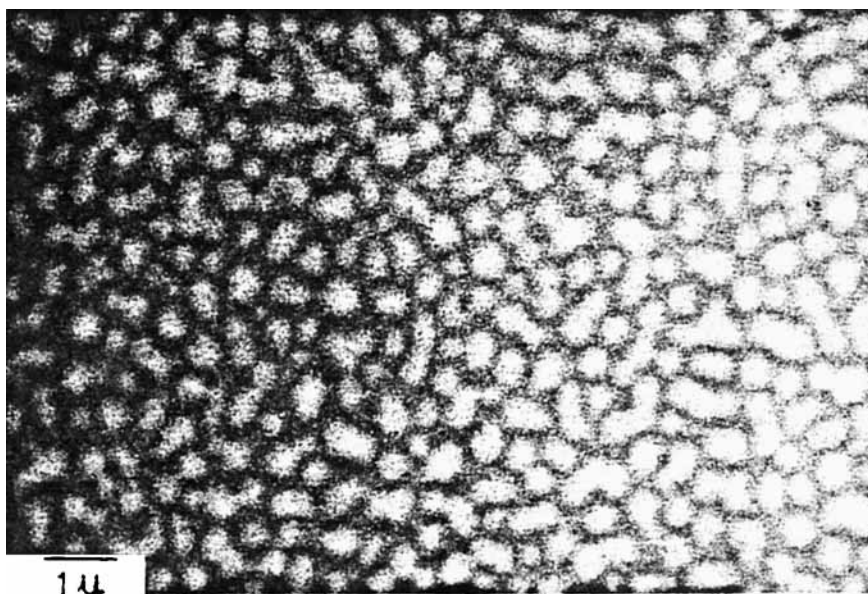
$$\frac{T(X') - T(0)}{T(0)} = \frac{KM X' / r}{1 - KM X' / r}$$

Where X' is the number of crosslinks per gram, M is the mer molecular weight, and r is the number of flexible bonds per mer, backbone, and side chain. K is a constant which is found by experiment. $T(X')$ is the T_g of X' crosslinks per gram and $T(0)$ is the T_g of no crosslinks. It is well known that T_g increases with increasing cross-linking density. Also, we find that the T_g difference between A2C and A2L is 13°C, while the T_g difference between B2C and B2L is 19°C. It is obvious that the glass transition temperature of high molecular weight, long chains of polyol synthetic polyurethane is easily raised by adding crosslinking agent. Both lower PU-phase T_g and upper PC-phase T_g of semi-IPNs shift inward compared to the corresponding linear blends. The results are the same as for those from dynamic behavior studies.

In general, the polyurethane-polycarbonate linear blend and semi-IPNs were heterogeneous: the polyurethane phase showed staining by osmium tetroxide. Jiang and Huang²⁴ and Eastmond and Phillips²⁵ reported that in electron micrographs of PC/PU system, PC appears dark without staining. Klemmner et al.^{1,26-28} reported that in PU blends with different polymers, the

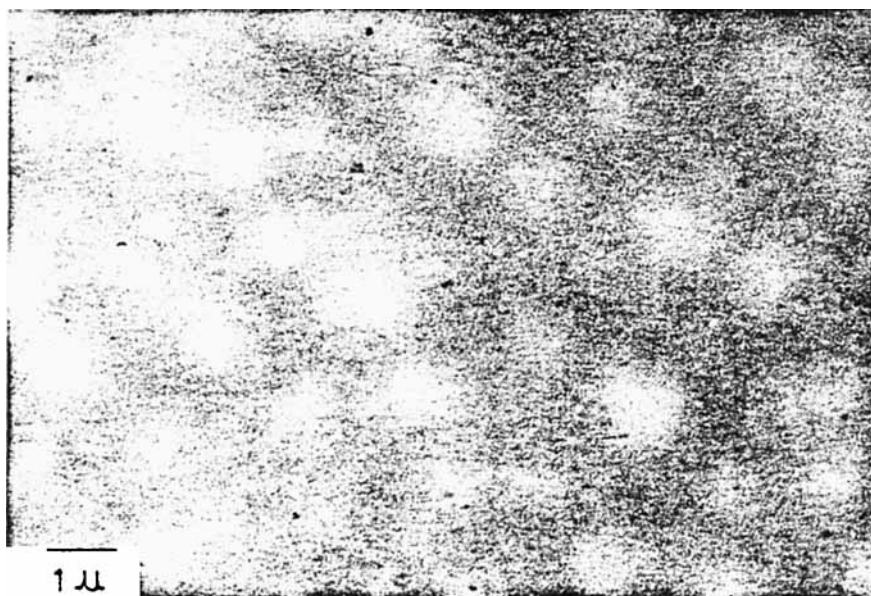


(a)



(b)

Fig. 5. Electron micrographs of the effect of polyols molecular weight in PU prepolymer on morphology of PC/PU linear blends. (a) A27B, PU phase domain: 1000 Å; (b) B27B, PU phase domain: 3000 Å; (c) C27B, PU phase domain: 6000 Å.



(c)

Fig. 5. (Continued from the previous page.)

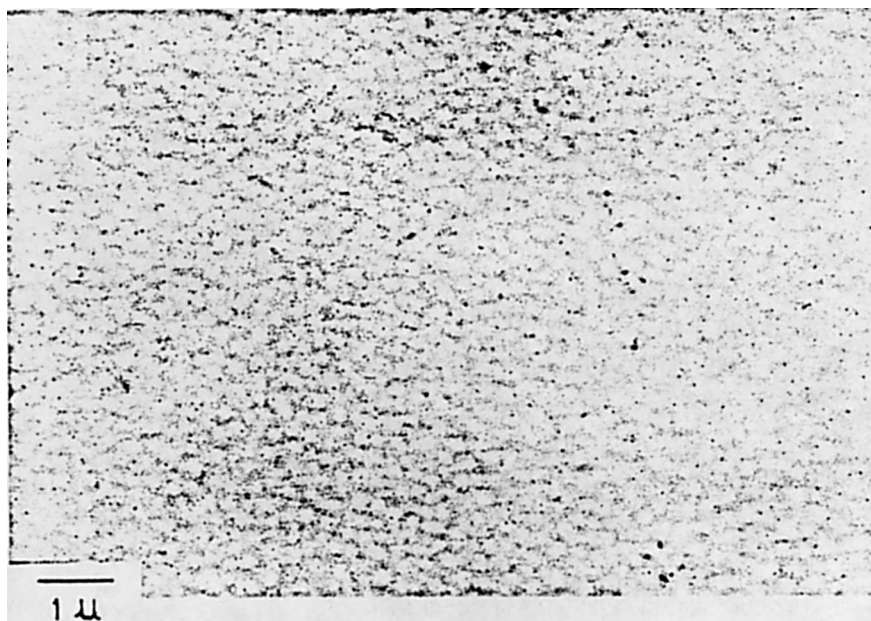


Fig. 6. Electron micrographs of A27I, PU phase domain: 500 Å.

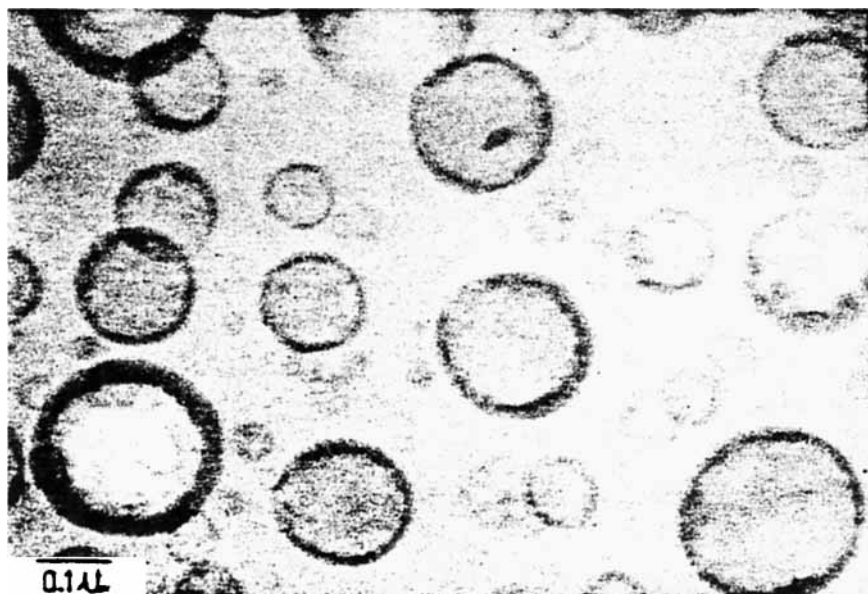


Fig. 7. Electron micrographs of A37I, PU phase domain: 500–1500 Å.

PU was stained by OsO_4 . When the staining time is short, the PU does not stain and PC will be dark as shown in Figures 5(a)–(c) and 6. When the staining time exceeds 8 h, PU will be stained, and will consist of dark domains as indicated in Figure 7.

Comparing Figures 5–7, we find that the phase domain sizes of the linear blend are in the range of 1000–6000 Å, but the domain size of the corresponding semi-IPNs is only about 500 Å. This is caused by interlocking of chains during polymerization and crosslinking of PU, which prevents to a certain extent, the demixing of the component networks. The relative molecular weight of polyol affects greatly the degree of phase separation of both PC/PU blends and semi-IPNs. Figure 5(a)–(c) shows the domain sizes of linear blends increases from 1000 to 6000 Å as the molecular weight of polyols increases from PPG 400 to PPG 2000. As mentioned above, the ratio of NCO/OH also greatly influences the compatibilities of PC and PU. Comparing Figures 6 and 7, we can see that PC/PU semi-IPNs with higher NCO/OH ratio exhibited smaller phase domain. This may indicate that higher density of crosslinking may improve the mutual miscibility of PC and PU. The electron microscopy study showed the existence of microphase separation, this is in agreement with the results obtained by Rheovibron and differential scanning calorimetry measurement.

CONCLUSION

The study of the transition behavior and morphology has established that microphase separation exists in PC/PU blends and semi-IPNs. The mutual compatibility of PC and PU can be improved by combining them as interpenetrating networks. The compatibilities of PC and PU can be further

improved by using higher NCO/OH ratio, and lower molecular weight polyols in PU prepolymer. The compatibility of PC and PU is not greatly affected by changing the PU composition.

Cross-linked PU has a higher T_g temperature than linear PU. The difference of glass transition temperature between cross-linked PU and linear PU is greatly influenced by the molecular weight of polyols in PU prepolymer. The T_g temperature difference between crosslinked PU and linear PU synthesized using higher molecular weight polyols is larger than that synthesized by lower molecular weight polyols. This suggests that the cross-linking agent has a greater influence on PU synthesized by high molecular weight, long chain of polyol.

The authors wish to thank the National Science Council of the Republic of China for financial support.

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Received September 8, 1986

Accepted March 19, 1987