

COMPATIBILITY OF PVC WITH POLYURETHANES OF DIFFERENT SOFT SEGMENTS

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ABSTRACT

Blends of PVC and polyurethanes with four different soft segments of molecular weight 1000 were prepared and studied by dynamic mechanical and DSC techniques. It was found that the compatibility of PVC with segmented polyurethanes was related to the mixing of PVC molecules and the soft segments of the polyurethanes. Polyester based polyurethanes are more compatible with PVC than polyether based polyurethanes. Solution cast blends of PVC with PCL-polyurethane (1/2/1) exhibit single and narrow glass transition, while the blends with PPO-polyurethane (1/2/1) are completely incompatible. The compatibility was found to decrease with increasing hard segment content for all the polyurethanes used. The methods of blend preparation may change the compatibility of PVC/PU blends through their influence on the mixing or demixing of the hard and soft segments.

INTRODUCTION

Considerable effort has been expended in recent years in studying polymer-polymer systems, the polyblends. Because of the commercial demand for permanent plasticizer, process aids and impact modifiers, the blends of PVC with other polymers were the focus of attention in many of such studies.

Segmented copolymers, including polyurethanes, are now more and more widely used for blending modification of PVC resins. Their advantage is the ease in obtaining a series of copolymers with continuously variable properties by selecting the copolymer components and the compositions to match the demands in different modification uses. As these copolymers themselves are microscopically multicomponent systems in nature, so their blends with other polymers are very complicated systems. The relationship between the chemical structure and composition of the components and the morphology and properties of the blends is difficult to be investigated in detail and remains not well known for us.

Nevertheless, it is clear that the compatibility between PVC and polyurethanes is decisive in affecting the morphology and properties of the blends. Polyurethanes of different soft segments have been used for studying the compatibility with PVC in the literature [1-8]. However the soft segment length and hard segment content of the polyurethanes used and the value of blend ratio with PVC were not the same for different polyurethanes, so their results were not comparable with each other.

In this paper, blends of PVC with polyurethanes of four different soft segments were

investigated at the same conditions and the influence of hard segments and the chemical structure of soft segments on compatibility was discussed.

EXPERIMENTAL

Materials

Segmented polyurethanes were synthesized by a two-step method involving endcapping the hydroxy-terminated polydiols with 4,4'-diphenylmethane diisocyanate (MDI) following by reaction in solution with the chain extender, 1,4-butanediol (BDO)^[9]. Four polydiols, namely hydroxy terminated polycaprolactone (PCL), polytetramethylene adipate (PTMA), polytetramethylene oxide (PTMO) and polypropylene oxide (PPO), of number average molecular weight 1000 were used. The composition and intrinsic viscosity of the polyurethane samples are listed in Table 1. The intrinsic viscosity was measured in N,N'-dimethylacetamide at 30°C. A suspension grade PVC of molecular weight $M_w = 15.3 \times 10^4$ and $M_n = 5.7 \times 10^4$ was used throughout the work.

Table 1 Segmented polyurethane samples

Sample	Soft segment	Polydiol/MDI/BDO mole ratio	Intrinsic viscosity, (dl/g)
PU-11	PCL	1/1/0	1.05
PU-12	PCL	1/2/1	0.95
PU-13	PCL	1/3/2	1.39
PU-14	PCL	1/4/3	0.88
PU-21	PTMA	1/1/0	1.01
PU-22	PTMA	1/2/1	0.75
PU-23	PTMA	1/3/2	1.17
PU-24	PTMA	1/4/3	1.05
PU-32	PTMO	1/2/1	1.05
PU-42	PPO	1/2/1	0.50

Blends of PVC and PU were made by solution mixing in tetrahydrofuran and casting into trays. The sheets were then placed under vacuum at 60°C for at least a week prior to use. For polyurethanes of high hard segment content dimethylformamide was used instead of tetrahydrofuran.

Instrumental

Dynamic mechanical data were obtained at 3.3 Hz by using an Iwamoto viscoelastic spectrometer. Samples were initially cooled to about -180°C, and measurements were performed with a heating rate of 2—3°C/min.

DSC thermograms over the temperature range from -70°C to 200°C were recorded using a Perkin-Elmer DSC-4 purged with nitrogen. Runs were conducted on samples of about 20mg at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

The storage modulus E' and the dissipation factor $\tan\delta$ of the polyurethanes used in this work are plotted as functions of temperature in Figures 1—3. Peak positions in the $\tan\delta$ curves of these

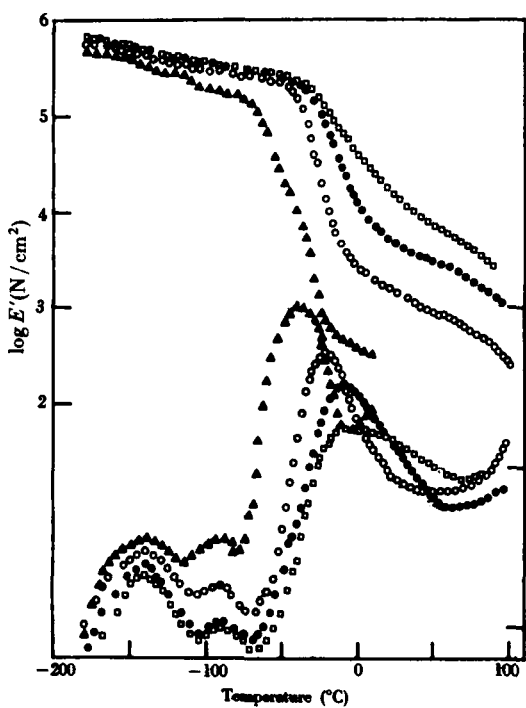


Fig.1 Storage modulus E' and $\tan\delta$ curves of PCL polyurethanes

▲ PU-11, ○ PU-12, ● PU-13, □ PU-14.

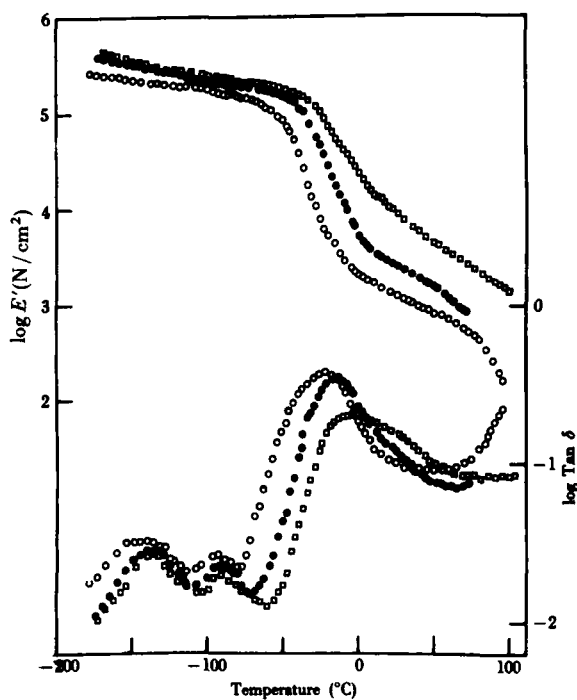


Fig.2 Storage modulus E' and $\tan\delta$ curves of PTMA polyurethanes

○ PU-22, ● PU-23, □ PU-24.

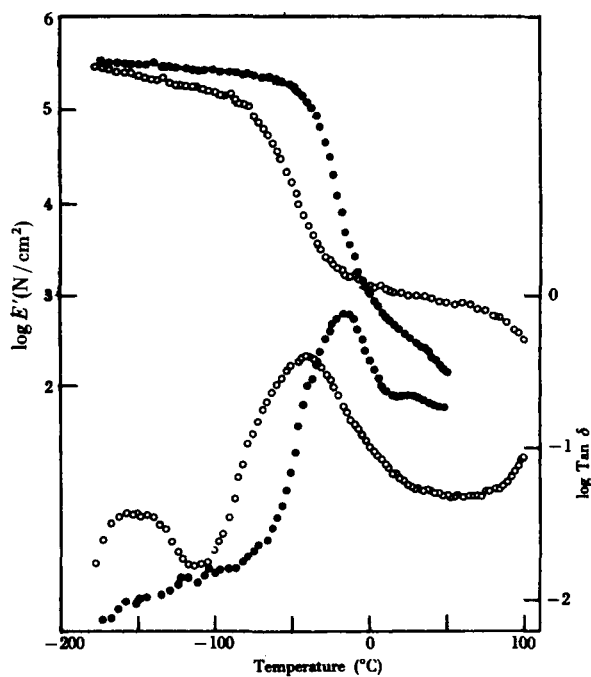


Fig.3 Storage modulus E' and $\tan\delta$ curves of PTMO and PPO polyurethanes

○ PU-32, ● PU-42.

Figures are summarized in Table 2. The high temperature loss peak, the α peak, is attributed to the motion of molecular segments in the noncrystalline regions which accompanies the glass transition and is located in the temperature range from -40°C to 0°C for different samples.

A γ peak was observed for polyurethanes with PCL, PTMA and PTMO soft segments at about -140°C , which remained almost unchanged for different soft segments. This secondary relaxation has been reported by many authors for segmented copolymers^[2-5,10-14] and also for related soft segment homopolymers [15, 16] and polyurethane homopolymers^[17,18] in the temperature range from -150°C to -100°C and was ascribed to motions of methylene sequences including oxygen — $\text{O}-(\text{CH}_2)_n-\text{O}$ ($n \geq 4$) mainly in the soft segments. The necessity of $n \geq 4$ was supported by our results for PPO-polyurethanes.

Table 2 Transitions of polyurethanes from dynamic mechanical and DSC measurements

Sample	$\tan\delta$			DSC			
	$T_g(^{\circ}\text{C})$	$T_{\beta}(^{\circ}\text{C})$	$T_{\alpha}(^{\circ}\text{C})$	$T_g(^{\circ}\text{C})$	$T_g^{*}(^{\circ}\text{C})$	$T_g^{**}(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
PU-11	-40	-90	-140	-31	-31	-31	—
PU-12	-20	-90	-140	-28	-19	-7	135
PU-13	-10	-90	-140	-20	-8	7	155
PU-14	0	—	-140	-13	0	10	180
PU-22	-20	-95	-140	-31	-19	-7	136
PU-23	-15	-90	-135	-20	-6	5	152
PU-24	-5	-90	-140	-15	3	13	174
PU-32	-40	—	-150	-55	-40	-29	155
PU-42	-18	—	—	-19	-8	-8	—

* After cooling from the melt, cooling rate $20^{\circ}\text{C}/\text{min}$.

** After quenching from the melt.

A small β peak at about -90°C was detected for polyurethanes of polyester soft segments. The mechanism of this secondary relaxation is not well known yet. Kajiyama and MacKnight^[18] reported a β_H peak at -80°C (3.5Hz) for three series of polyurethane homopolymers, but without any discussion. Huh and Cooper^[13] found a relaxation at -50°C (110Hz) for PTMA/MDI/BDO copolymers and assigned it to the motions of NH or C=O groups to which water molecules are attached by hydrogen bonding. Seefried et al.^[11] found a peak at -70°C (1-2Hz) in their studies of polyurethanes with PCL soft segments, and they supposed that it may arise from the disruption of associations between the hard and soft segments. As the peak was higher for polyurethanes with PTMA soft segments than for PCL polyurethanes, and it was not observed for polyurethanes with polyether soft segments, so it may be related to motions of the ester groups in the soft segments or motions of ester groups including the neighbouring methylene sequences. The latter has been suggested by Kajiyama and MacKnight^[17] for a peak at -120°C , which was labelled as one of their γ relaxations.

Figures 1 and 2 show the composition dependence of dynamic mechanical behavior of PCL-

and PTMA-polyurethanes respectively. The position of the secondary relaxations remains almost unchanged with increasing hard segment content for both series, while the peak value of them decreases slightly. This is consistent with the concept that these relaxations are mainly related to local motions of the soft segments. The α peak shifts to higher temperatures for samples of higher hard segment content. At the same time peak width and the temperature range of the related

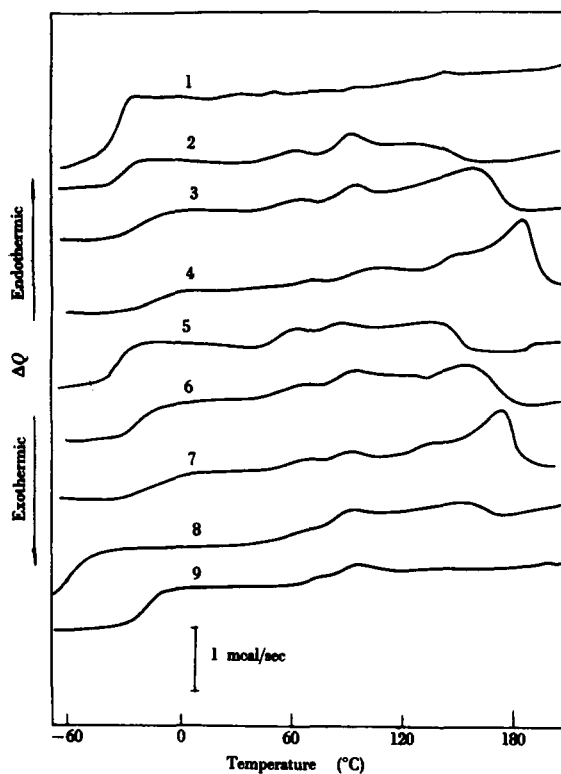


Fig.4 DSC curves of solution cast polyurethane samples. (1) PU-11, (2) PU-12, (3) PU-13, (4) PU-14, (5) PU-22, (6) PU-23, (7) PU-24, (8) PU-32, (9) PU-42.

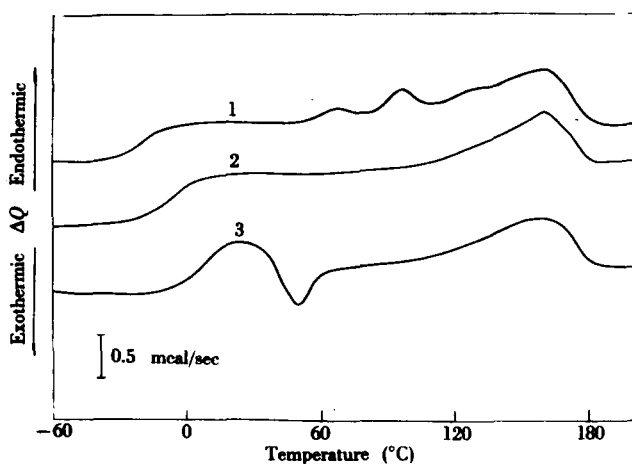


Fig.5 DSC curves of PU-13: 1. solution cast, 2. after slow cooling, 3. after quenching

modulus drop become very broad. These results indicate the mixing of more hard segments in the soft segment domains and the increase of heterogeneity of these domains with increasing hard segment content. Similar results have been reported for PTMO- and PPO-polyurethanes. The PTMO-polyurethane PU-32 has a very broad peak as compared to polyester based polyurethanes of the same hard segment content. It may imply a less compatibility of hard and soft segments in the soft segment rich domains in the case of PU-32.

The thermograms of solution cast polyurethane samples are given in Figure 4. The glass transition and a main endothermal peak T_m related to the melting of hard segment crystals were observed. The latter appeared at higher temperatures and had larger value of enthalpy changes for samples of higher hard segment content and was not observed for PU-11. The data of T_g and T_m are summarized in Table 2. Usually two or three small endopeaks were observed under T_m in the temperature range from about 50°C to 140°C, which may be related to the thermal effects of disordering and dissociation of hydrogen bondings between hard segments and various kinds of short range order within the hard segment domains^[19-21].

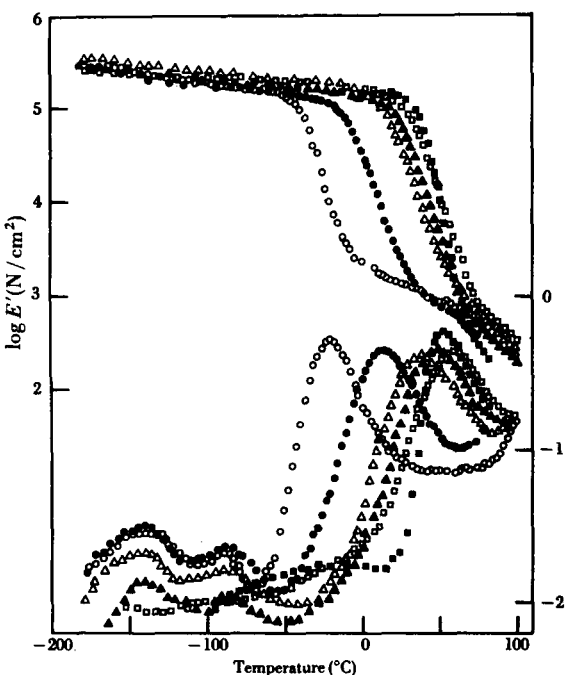


Fig.6 Storage modulus E' and $\tan\delta$ curves of solution cast PU-12/PVC blends with blend ratios

○ 100/0, ● 70/30, △ 50/50, ▲ 35/65, □ 20/80, ■ 0/100.

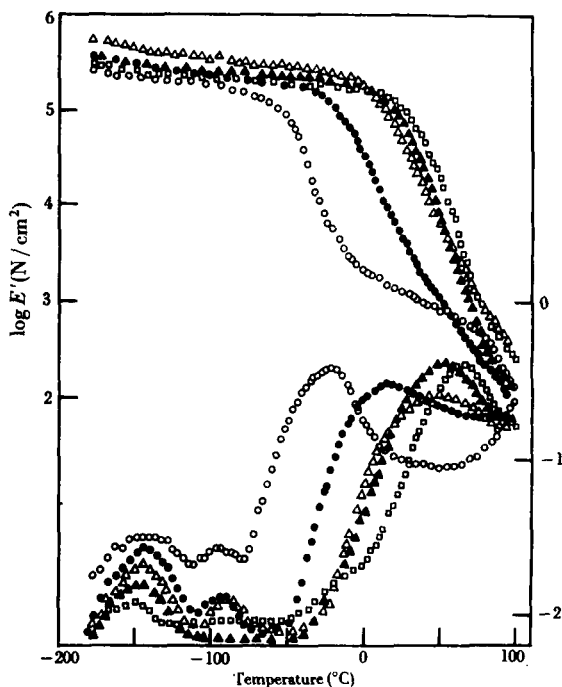


Fig.7 Storage modulus E' and $\tan\delta$ curves of solution cast PU-22/PVC blends with blend ratios

○ 100/0, ● 70/30, △ 50/50, ▲ 35/65, □ 20/80.

The DSC curves of samples PU-13 in second runs after quenching or slow cooling from the melt state are given in Figure 5. The significant difference between the T_g values obtained for samples of different thermal history indicates a better mixing of soft and hard segments at elevated temperatures and that the solubility difference of soft and hard segments in tetrahydrofuran will help the segregation of segments during solution cast. The results shown in Figure 5 were typical for the polyurethanes used in this work, and they may imply the large possibility in affecting the morphology and properties of the samples by means of varying the processing conditions. These

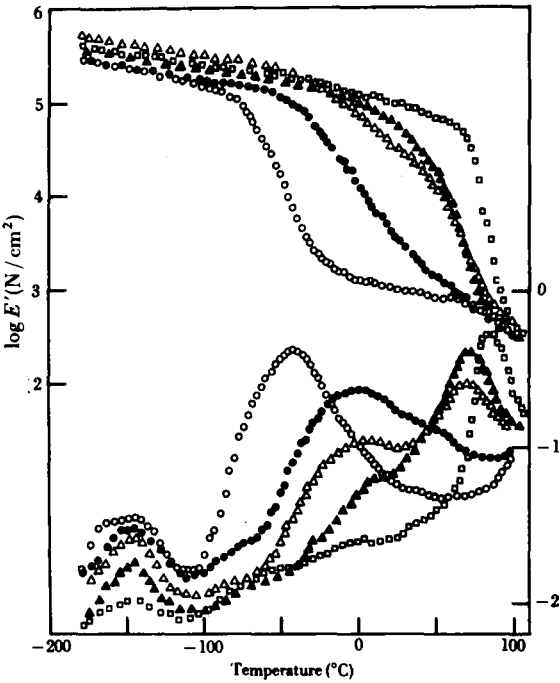


Fig.8 Storage modulus E' and $\tan \delta$ curves of solution cast PU-32/PVC blends with blend ratios
○ 100/0, ● 70/30, △ 50/50, ▲ 35/65, □ 20/80.

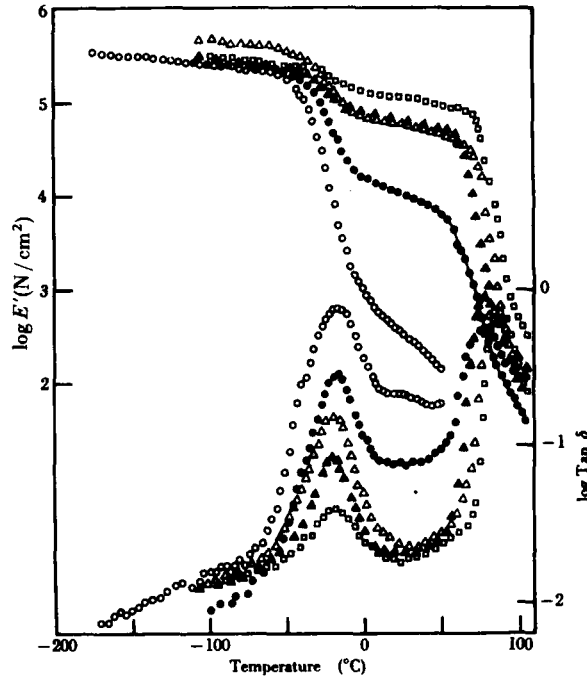


Fig.9 Storage modulus E' and $\tan \delta$ curves of solution cast PU-42/PVC blends with blend ratios
○ 100/0, ● 70/30, △ 50/50, ▲ 35/65, □ 20/80.

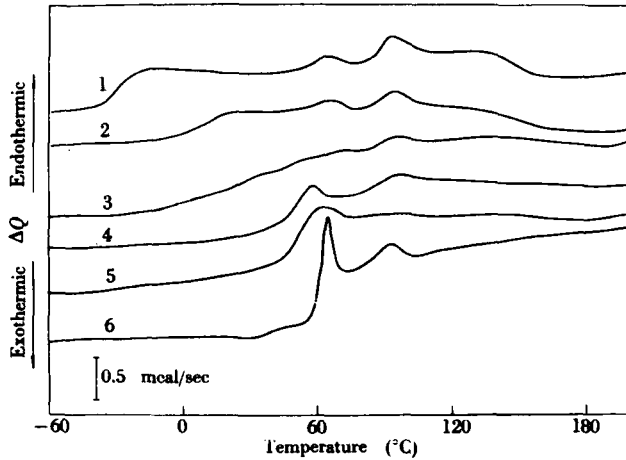


Fig.10 DSC curves of solution cast PU-12/PVC blends with blend ratios:
(1) 100/0, (2) 70/30, (3) 50/50, (4) 35/65, (5) 20/80, (6) 0/100

results are consistent with those of Wang and Cooper^[5] for a PTMO-polyurethane sample and the time dependent phase mixing and demixing behavior discussed by Wilkes et al.^[22]. The only exception is sample PU-11. The mixing of PCL segments and the single MDI units was not influenced by processing conditions.

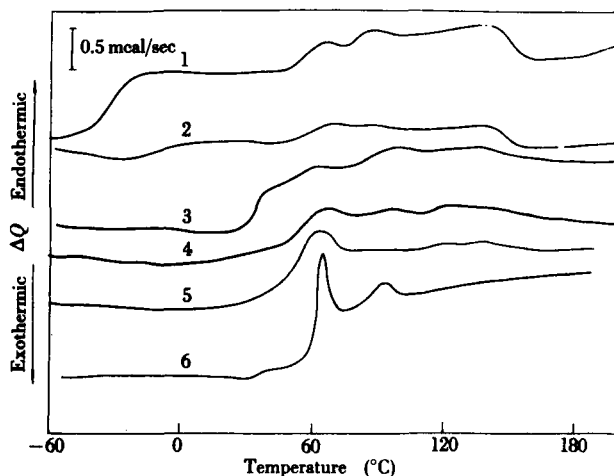


Fig.11 DSC curves of solution cast PU-22/PVC blends with blend ratios:
(1) 100/0, (2) 70/30, (3) 50/50, (4) 35/65, (5) 20/80, (6) 0/100

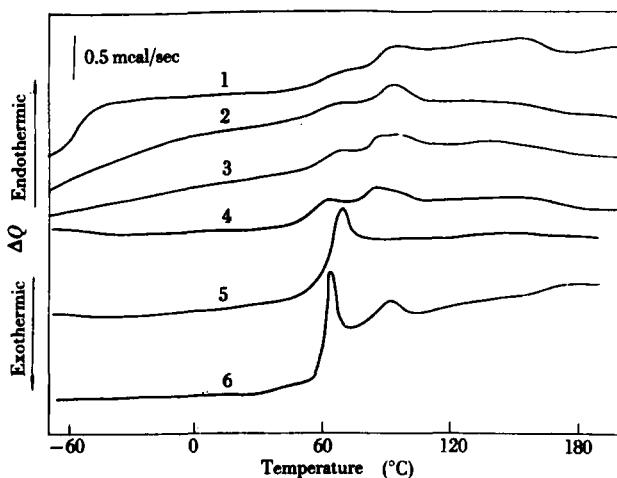


Fig.12 DSC curves of solution cast PU-32/PVC blends with blend ratios:
(1) 100/0, (2) 70/30, (3) 50/50, (4) 35/65, (5) 20/80, (6) 0/100

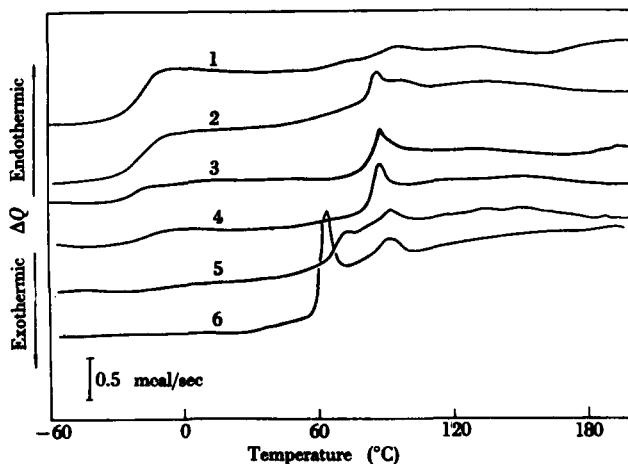


Fig.13 DSC curves of solution cast PU-42/PVC blends with blend ratios:
(1) 100/0, (2) 70/30, (3) 50/50, (4) 35/65, (5) 20/80, (6) 0/100

The T_g of PVC solution cast specimens determined by dynamic mechanical measurements was 55°C, and it became 78°C after annealing at 110°C for 3 h. DSC studies gave similar T_g value of 60°C for first run and 77°C in second run for solution cast specimens which were lower than that for the original powder specimens (92°C). The phenomenon of lower T_g value may be due to trace of THF in the specimens^[23].

Figures 6—9 show the results of dynamic mechanical measurements for blends of PVC with PU-12, PU-22, PU-32 and PU-42, and the corresponding DSC curves are given in Figures 10—13. Data of glass transitions are listed in Table 3. It is clear that the secondary transitions of polyurethanes are not affected after being blended with PVC, but the glass transition changes obviously and differently for polyurethanes of different soft segments. These four polyurethane samples have soft segments of the same molecular weight and content, but only different in chemical

Table 3 T_g (°C) of blends with different polyurethanes

Sample	Blend ratio (wt.)	tan δ		DSC		
		T_g	$\Delta T_{g, \frac{1}{2}}$	T_g	T_g^*	T_g^{**}
PU-12/PVC	100/0	-20	32	-28	-19	-7
	70/30	15	42	8	5	7
	50/50	40	46	25	8, 80	0
	35/65	50	44	45	10, 77	12, 80
	20/80	60	45	50	10, 76	11, 75
PU-22/PVC	100/0	-20	44	-31	-19	-10
	70/30	15	88	-8	-12, —	-6
	50/50	50	72	35	-10, —	-6, 81
	35/65	55	60	49	-12, 80	-9, 79
	20/80	65	48	52	-12, 70	0, 72
PU-32/PVC	100/0	-40		-55	-40	-32
	70/30	0, 55		-30, 55	-36, 88	-30, 88
	50/50	5, 70		-20, 65	-36, 88	-30, 88
	35/65	8, 72		—, 60	-36, 85	-30, 88
	20/80	5, 85		—, 60	—, 80	-30, 75
PU-42/PVC	100/0	-18		-19	-8	-8
	70/30	-18, 80		-18, 83	-7, 88	-7, 90
	50/50	-18, 85		-19, 83	-11, 88	-8, 88
	35/65	-20, 80		-19, 83	-11, 88	-9, 88
	20/80	-18, 88		-19, 70	-13, 83	-14, 84

* After cooling from the melt, cooling rate 20°C/min.

** After quenching from the melt.

structure. So it will be interesting to compare the compatibility of the four series polyurethanes with PVC according to data from these Figures.

A common method for determining the compatibility of two polymers is based on the singularity of the glass transition. If there is only one T_g in the blend, these two polymers are said to be compatible. If the T_g 's of the constituent polymers remain unchanged in the blend, the polymers are incompatible. However these criteria are too crude for practical uses, and additional descriptions are needed to include detailed difference of real polyblend systems. Polymer pairs, having some compatibility only within very limited blend ratios, may exhibit two T_g 's in the blend slightly deviated from the T_g 's of the individual polymers respectively approaching each other. For polymer blends, exhibiting a single T_g , the amount of mixing of one component in the another can be characterized by the position of T_g , and the heterogeneity or the degree of compatibility of the blend — the width of T_g transition expressed in temperature or frequency. Complete or well compatible polyblend systems will have a single narrow glass transition and the T_g value may be predicted using the various equations applied to random copolymers.

Two well separated glass transitions were observed in both dynamic mechanical and DSC measurements for PU-42/PVC blends of all the blend compositions used in this study. The T_g value of the two transitions remains constant during the change of compositions and equals to the value of T_g 's of the two constituents respectively. These results mean that the solution cast PU-42/PVC blends are incompatible systems. The glass transition temperature of PVC phase in these solution cast blends has much higher value than that of the solution cast PVC homopolymer and very close to the value accepted for PVC polymers. It seems that, as will also shown below, the existence of another polymer in the blend which is well soluble in THF and incompatible with PVC may prevent the influence of trace THF on the molecular motion of PVC after solution cast.

The blends of PVC with another polyurethane having polyether soft segments PU-32 also exhibit two peaks in $\tan\delta$ -T curves, although the peaks are not well separated as in the case of PU-42. It is accepted that DSC measurements is not very sensitive in detecting glass transitions. However the double T_g behavior was still observed for some of the PU-32/PVC blends. The lower glass transition temperature of the blends deviates significantly from that of PU-32, but it remains rather constant with varying blend ratios. It indicates that only limited amount of PVC can be mixed into the PTMO domains and the excess PVC molecules will segregate forming PVC domains in the blends.

The blends of PVC and polyurethanes with polyesters as soft segments were more compatible than the previous two, exhibiting single glass transition for solution cast specimens in the dynamic mechanical and also DSC measurements. The smooth shifting of T_g values of the blends with the composition between the T_g 's of the pure polyurethanes and PVC implies that the components of the blends may be mixed in any ratio. However there is still some difference in compatibility between blends of PVC and the two polyester based polyurethanes evidenced in the width of their glass transitions. It is not easy to quantitatively characterize the width of the glass transition, and no common accepted methods exist. In general, it can be determined as the temperature range of modulus drop ΔT_g accompanying the glass transition or the half height width of the glass transition peak in dynamic mechanical measurements. But the determination of these parameters may become infeasible in practice due to the overlapping of different transitions. In this work a modified parameter $\Delta T_{g,1/2}$ was used. It was defined as the half height width of T_g peaks with $\tan\delta=1 \times 10^{-1}$ as the base line. This method may avoid some influence of other transitions, and the $\Delta T_{g,1/2}$

value was found to be about half of ΔT_g determined for some samples, having very clear rubbery plateau after glass transition. The $\Delta T_{g,1/2}$ of PCL-polyurethane/PVC blends is not very different from that of the PCL-polyurethane and keeps almost constant during the variation of the blend ratio. It may imply that the compatibility between PU-12 and PVC is quite good in the solution cast specimens. At the same time the addition of PVC into PTMA-polyurethane raised obviously the $\Delta T_{g,1/2}$ value. It means that the onset of molecular motions accompanying the glass transition

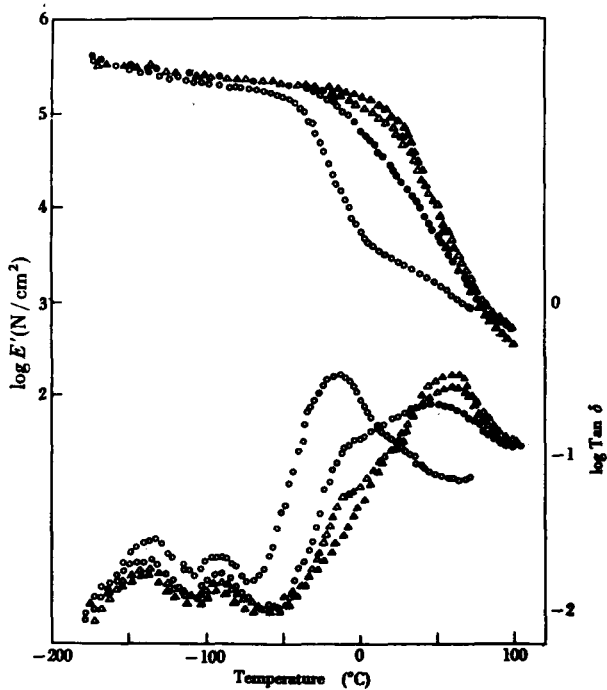


Fig.14 Storage modulus E' and $\tan\delta$ curves of solution cast PU-23/PVC blends with blend ratios:
○ 100/0, ● 70/30, △ 50/50, ▲ 35/65.

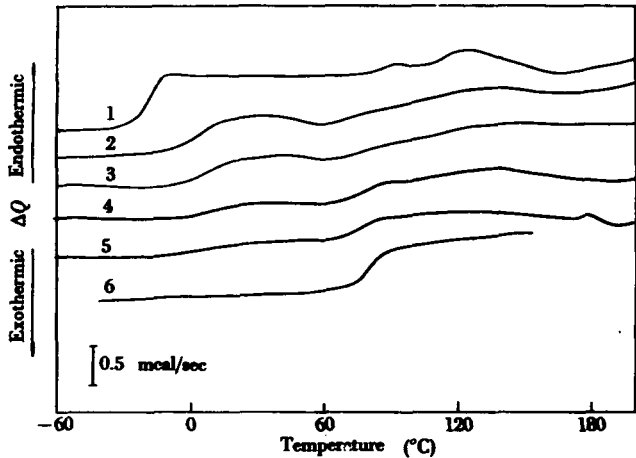


Fig.15 DSC curves of blends PU-12/PVC after cooling from the melt.
The blend ratios are (1) 100/0, (2) 70/30, (3) 50/50, (4) 35/65, (5) 20/80, (6) 0/100.

occurs at quite different temperatures, although single glass transition was observed. The relatively small $\Delta T_{g,1/2}$ value for specimens of blend ratio 20/80 is probably due to the limitation of the parameter $\Delta T_{g,1/2}$ which ignores the heterogeneities giving only small contributions to $\tan\delta$ at temperatures far away from the main peak position.

It is obvious from the foregoing that the compatibility between PVC and polyurethanes is mainly expressed as the mixing of PVC molecules and soft segments, and polyester segments, especially the PCL segments, are much more compatible with PVC than the polyether segments similar to the situation of polyester and polyether homopolymers. One of the important problems that will be interested for polymer modification by blending with segmented copolymers is to ascertain the influence of hard segments on the compatibility and hence the morphology and properties of blends. For this purpose the blends of PVC and polyester based polyurethanes of different hard segment content were studied.

Table 4 $T_g(^{\circ}\text{C})$ of blends with polyester polyurethanes of different hard segment content

Blend ratio (wt.)	$T_g(^{\circ}\text{C})$				
	PU-11/PVC	PU-13/PVC	PU-14/PVC	PU-23/PVC	PU-24/PVC
100/0	-40	-10	0	-15	-5
70/30	-5	0, 35	42	-10, 45	10, 60
50/50	20	0, 50	25, 60	-10, 60	10, 65
35/65	40	—, 55	0, 55	10, 60	10, 60
20/80	52	—, 50	—, 55		

Both the dynamic mechanical and DSC measurements show the influence of hard segments on compatibility. The T_g values are listed in Table 4 and the temperature dependence of modulus and $\tan\delta$ for PU-23/PVC blends are illustrated in Figure 14. Blends of PU-11/PVC still have single narrow glass transition, while the others exhibit two T_g 's or T_g peaks with obvious shoulders even for PCL-polyurethane/PVC systems. It means that although PCL homopolymer is well known one of the polymers that are compatible with PVC^[24,25], the introduction of short polyurethane sequence like $-\text{MDI}-(\text{BDO}-\text{MDI})_2-$ to connect PCL segments of $M=1000$ will make the PCL segments almost incompatible with PVC molecules.

The influence of hard segments on compatibility also found its evidence from comparing the behavior of specimens obtained by applying different preparation methods. T_g values for solution cast specimens and specimens after cooling from the melt state were determined by DSC technique for all the blend systems. Data for blends with polyurethanes of the same hard segment content are listed in Table 3, and the curves for blends PU-12/PVC in second run are shown in Figure 15. It is clear from Table 3 that these blends become less compatible or more incompatible after the melt treatment. This phenomenon can be understood, if the effect of solvent and melt treatment on the mixing of hard segments in the soft segment rich domains of the polyurethanes, as has been discussed before, is taken into account. The difference in solubility will result in better segregation of hard and soft segments during solution cast, that is favorable to the mixing of soft segments with

PVC molecules. Oppositely the improvement of segmental mixing of polyurethanes in the melt treatment will reject the approaching of PVC molecules to the soft segments.

CONCLUSIONS

The compatibility of PVC with segmented polyurethanes is related to the mixing of PVC molecules and the soft segments of the polyurethanes. Polyester based polyurethanes are more compatible with PVC than the polyether based polyurethanes. Solution cast blends of PVC with PCL-polyurethane (1/2/1), being well compatible, exhibit single narrow glass transition, while the blends with PPO-polyurethane (1/2/1) are completely incompatible.

The compatibility obviously decreases with increasing the hard segment content of the polyurethanes. The methods of sample preparation may change the compatibility of PVC/PU blends through their influence on the mixing or demixing of the hard and soft segments.

Keywords:

PVC blends, PU segmented copolymers, PVC/PU blends, Compatibility, DSC, Dynamic mechanical measurement.

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REFERENCES

- [1] Piglowski, J. and Laskawski, W., *Ang. Makromol. Chem.*, **1979**, 82,157.
- [2] Piglowski, J.; Skowronski, T. and Masiulonis, B., *Ang. Makromol. Chem.*, **1980**, 85,129.
- [3] Hourston, D.J. and Hughes, I.D., *J. Appl. Polym. Sci.*, **1981**, 26, 3467.
- [4] Kalfoglou, N.K., *J. Appl. Polym. Sci.*, **1981**, 26, 823.
- [5] Wang, C.B. and Cooper, S.L., *J. Appl. Polym. Sci.*, **1981**, 26, 2989.
- [6] Bandyopadhyay, P.K. and Shaw, M.T., *J. Appl. Polym. Sci.*, **1982**, 27, 4323.
- [7] Bandyopadhyay, P.K. and Shaw, M.T., *J. Vinyl. Technol.*, **1982**, 4(4), 142.
- [8] Shen, C.H. and Wang, Y.Y., *Ang. Makromol. Chem.*, **1984**, 121, 49.
- [9] 毛润生, 学位论文, 中国科技大学应化系 (Thesis, University of Science and Technology of China) 1985.
- [10] Nishi, T and Kwei, T.K., *J. Appl. Polym. Sci.*, **1976**, 20, 1331.
- [11] Seefried, Jr. C.G.; Koleske, J.V. and Critchfield, F.E., *J. Appl. Polym. Sci.*, **1975**, 19, 2493, 2503.
- [12] Ng, H.N.; Allegrezza, A.E.; Seymour, R.W. and Cooper, S.L., *Polymer*, **1973**, 14, 255.
- [13] Huh, D.S. and Cooper, S.L., *Polym. Eng. Sci.*, **1981**, 11, 369.
- [14] Ferguson, J.; Hourston, D.J.; Meredith, R. and Patsavoudis, D., *Eur. Polym. J.*, **1972**, 8, 369.
- [15] Willbourn, A.H., *J. Polym. Sci.*, **1959**, 34, 569.
- [16] Takayanagi, M.; Imada, K. and Kajiyama, T., *J. Polym. Sci.*, **1966**, C15, 263.
- [17] Kajiyama, T. and MacKnight, W.J., *Macromol.*, **1969**, 2, 254.
- [18] Kajiyama, T. and MacKnight, W.J., *Trans. Soc. Rheol.*, **1969**, 13, 527.
- [19] Seymour, R.W. and Cooper, S.L., *Macromol.*, **1973**, 6, 48.
- [20] Srichatrapimuk, V.W. and Cooper, S.L., *J. Macromol. Sci.*, **1978**, B15, 267.
- [21] Kwei, T.K., *J. Appl. Polym. Sci.*, **1982**, 27, 289.
- [22] Wilkes, G.L. and Emerson, J.A., *J. Appl. Phys.*, **1976**, 47, 4261.
- [23] Malac, J.; Altmann, V. and Zelinger, J., *J. Appl. Polym. Sci.*, **1970**, 14, 161.
- [24] Khambatta, F.B.; Warner, F.; Russell, T. and Stein R.S., *J. Polym. Sci. Polym. Phys. Ed.*, **1976**, 14, 1391.
- [25] Hubbell, D.S. and Cooper, S.C., *J. Polym. Sci. Polym. Phys. Ed.*, **1977**, 15, 1143.