Studies on the morphology of blends of poly(vinyl chloride) and segmented polyurethanes

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Solution-cast specimens of poly(vinyl chloride)/polyurethane (PVC/PU) blends were studied by means of infra-red, differential scanning calorimetry and dynamic mechanical measurements. Polyurethanes with polycaprolactone, poly(tetramethylene adipate), poly(tetramethylene oxide) and poly(propylene oxide) of the same molecular weight (1000) were used. The results indicate that it is possible to change the morphology of the blends significantly by proper selection of the structure of the soft segments. The polyester soft segments are more compatible with PVC than are the polyether ones. Hydrogen bonding of NH groups with the urethane carbonyl of the hard segments and with the ester carbonyl and ether oxygen of the soft segments was studied by applying a curve resolution technique to the NH and carbonyl stretching vibration absorption peaks of the blends. Information about the distribution of hydrogen bonding between the different acceptors was used to discuss the segregation and mixing of the hard and soft segments at different PVC contents of the blends. Morphological models were proposed for blends of different compatibility between PVC and the soft segments.

(Keywords: poly(vinyl chloride); polyurethane; blends; morphology; infra-red spectroscopy; dynamic mechanical measurements; differential scanning calorimetry; hydrogen bonding)

INTRODUCTION

The concept of physically blending two or more existing polymers is one of the most important measures in obtaining new products or for problem solving. The current and potential importance of polymer blends, developed in the last decades, is remarkable. Much research work has been carried out to investigate the relationships between composition, morphology and properties of blends. However, in most cases the detailed studies only concern two-component blend systems.

There is a growing trend to use block copolymers for modification of other polymers for blending purposes. The advantage is the ease of obtaining a series of copolymers with continuously variable properties by selecting their components and composition properly to match the demands of various applications. Blends of poly(vinyl chloride) (PVC) with segmented polyurethanes (PU) are examples in this respect[1-8]. Polyurethanes with soft segments of different chemical structure, average length and content have been used by various authors. As these polyurethanes themselves consist of alternating soft- and hard-segment units, and are thus microscopically multicomponent systems, so the morphology of their blends with PVC is much more complicated than that of a two-component blend. The complete morphological features of multicomponent blends can only be described on the basis of information about segregation of all the components and interactions and mixing among them. In previous papers, discussion has usually only been given on compatibility between PVC and the soft segments or on compatibility between PVC and the polyurethanes in general. Wang and Cooper[5] reported the interaction between PVC molecules and the hard segments of polyurethanes dispersed in soft-segment regions and suggested morphological models for specimens cast from solutions of different solvents.

In the present work, blends of PVC and four segmented polyurethanes with polyether and polyester soft segments of the same average molecular weight and content were studied, and the influence of soft-segment structure on the morphology of these multicomponent blends 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) followed by reaction in solution with the chain extender, 1,4-butanediol (BDO)[9]. The polydiols used were hydroxy-terminated polycaprolactone (PCL), poly(tetramethylene adipate) (PTMA), poly(tetramethylene oxide) (PTMO) and poly(propylene oxide) (PPO) of number-average molecular weight 1000. The composition and intrinsic viscosity of the polyurethanes are listed in *Table 1*. The intrinsic viscosity was measured in *N*,*N*′-dimethylacetamide at 30°C. A suspension-grade PVC was used, the molecular weight ($M_w = 15.3 \times 10^4$, $M_n = 5.7 \times 10^4$) of which was determined from g.p.c. measurements.

Blends of PVC and polyurethanes were prepared by solution mixing in tetrahydrofuran and they were cast into trays for dynamic mechanical and d.s.c. measurements, or onto the surface of clear rock salt sheets

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Table 1 Segmented polyurethane samples

Sample	Soft segment	Polydiol/MDI/BDO mole ratio	Intrinsic viscosity (dl g^{-1})
PU-12	PCL	1/2/1	0.95
PU-22	PTMA	1/2/1	0.75
PU-32	PTMO	1/2/1	1.02
PU-42	PPO	1/2/1	0.50

for infra-red spectroscopic studies. Specimens were then dried in vacuum at 60°C for at least a week prior to use.

Methods

Dynamic mechanical measurements were performed at 3.3 Hz using an Iwamoto viscoelastic spectrometer. Samples were initially cooled to about −180°C, and measurements were conducted with a heating rate of 2–3°C min^{-1}.

D.s.c. thermograms of the samples were recorded over the temperature range from −70°C to 200°C using a Perkin–Elmer DSC-4. Runs were conducted on samples of about 20 mg at a heating rate of 20°C min^{-1}.

Infra-red spectra (600–4000 cm^{-1}) were obtained by using a Bruker IFS-113V *FT*i.r. spectrometer with an MCT detector. One hundred scans at a resolution of 2 cm^{-1} were signal-averaged and stored on a magnetic disc system.

Infra-red analysis

Two infra-red regions are of interest in the studies of the PU/PVC blends, i.e. the NH (3600–3000 cm^{-1}) and C=O (1800–1640 cm^{-1}) stretching vibration absorption regions. Both the NH and carbonyl absorption peaks are total contributions of overlapping bands of their free and hydrogen-bonded groups, respectively. For polyester-based polyurethanes the carbonyl peaks are even more complicated, being composed of bands of free and bonded carbonyl groups of both soft and hard segments. So it is necessary to get separated bands from these peaks by resolving the experimental curves in order quantitatively to discuss hydrogen bonding in the polyurethanes. The shape of the bands was assumed to be a combination of the Lorentzian and Gaussian functions. The experimental curves were fitted by a least-squares method. The position, height and width of the bands were all optimized in the iteration procedure.

RESULTS

Dynamic mechanical properties

The storage modulus E' and the dissipation factor tan δ of the four series of blends are plotted in *Figures 1–4* as functions of temperature. The pure polyurethanes exhibit a main loss peak accompanied by a drastic modulus drop in the temperature range from −18°C to −40°C for different samples These peaks are attributed to motion of molecular segments during the glass transition of the samples. A small peak was observed at about −140°C for polyurethanes with PCL, PTMA and PTMO soft segments. This secondary relaxation has been reported by many authors for segmented copolymers and was believed to be related to motions of methylene sequences including oxygens mainly in the soft segments[2–5,10–14]. Another small peak of secondary relaxation was detected for polyurethanes of polyester soft segments at about −90°C, and it has been assumed[15] to be related to motions of the ester groups in the soft segments in our previous paper.

The secondary transitions of the polyurethanes are not affected after being blended with PVC, while the temperature of the glass transition obviously changes with blending, and the changes were quite different for polyurethanes of different soft segments. The T_g values of all the blends are listed in *Table 2*. Two well separated

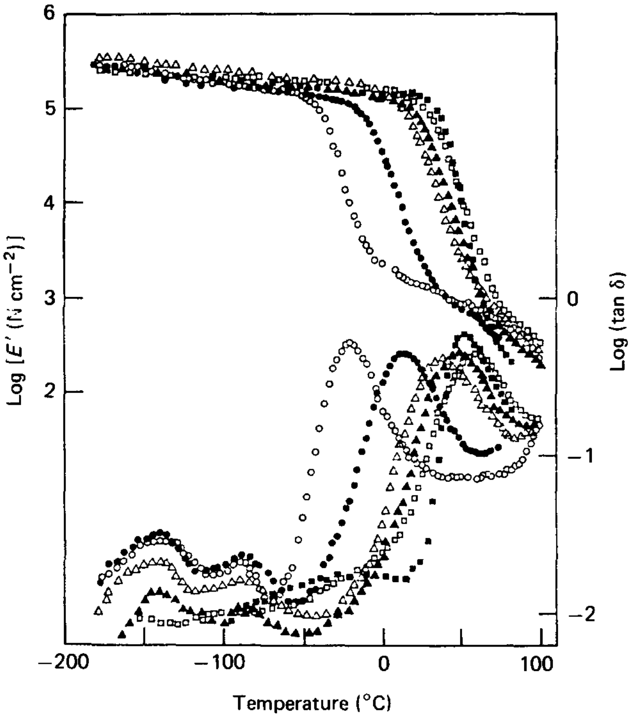


Figure 1 Temperature dependence of storage modulus and loss tangent for PU-12/PVC blends: ○, 100/0; ●, 70/30; △, 50/50; ▲, 35/65; □, 20/80; ■, 0/100

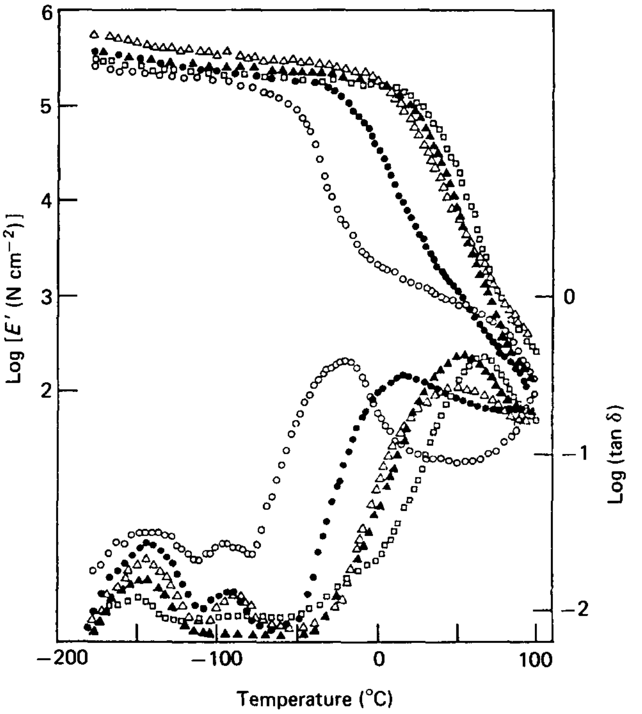


Figure 2 Temperature dependence of storage modulus and loss tangent for PU-22/PVC blends: ○, 100/0; ●, 70/30; △, 50/50; ▲, 35/65; □, 20/80

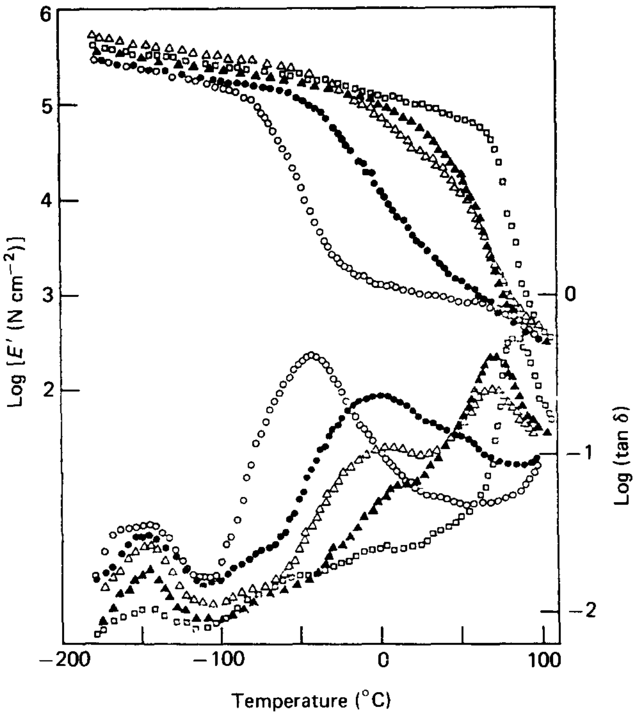


Figure 3 Temperature dependence of storage modulus and loss tangent for PU-32/PVC blends: ○, 100/0; ●, 70/30; △, 50/50; ▲, 35/65; □20/80

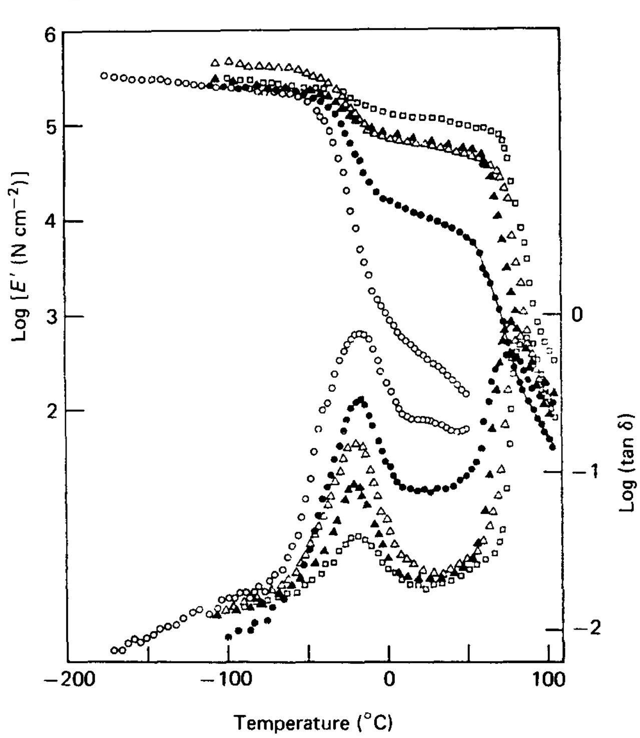


Figure 4 Temperature dependence of storage modulus and loss tangent for PU-42/PVC blends: ○, 100/0; ●, 70/30; △, 50/50; ▲, 35/65; □, 20/80

glass transitions were observed for PU-42/PVC blends of all blend compositions used in this work. The T_g value of the two transitions remains constant during the change of blend composition and equals the value of T_g of the two constituents respectively. Blends of PVC with another polyurethane, PU-32, having polyether soft segments also exhibit two T_g peaks in tan δ vs. T curves, although these peaks are not well separated as in the case of PU-42. Blends of PVC and polyester-based polyurethanes show a single glass transition, the temperature of which shifts to higher temperatures with increasing PVC content of the blends. The loss peak width of blends with PU-22 is larger than that of PU-12/PVC blends. The T_g of a solution-cast PVC specimen was found to be lower than that of the original powder specimens. This phenomenon may be due to traces of tetrahydrofuran in the specimens[16].

Differential scanning calorimetry

The thermograms of polyurethanes show the glass transition and a main endothermic peak T_m related to the melting of hard segment crystals. Usually two small endothermic peaks were observed below T_m in the temperature range from about 50°C to 140°C, which may be related to the thermal effects of dissociation of hydrogen bonding between the segments and disordering of various kinds of short-range order within the hard-segment regions[17–19]. Blends of PVC with polyester polyurethanes exhibit a single glass transition, while those with polyether soft segments usually show two T_g values. The T_g data of the blends obtained from d.s.c. measurements are given in *Table 2*, and *Figure 5* shows the thermograms for blends (50/50) of the four series.

Infra-red measurements

The infra-red spectra in the region 3600–3000 cm^{-1} for blends of PVC with different polyurethanes are given in *Figures 6–9*. The major NH absorption peaks were observed at about 3325 cm^{-1} and 3335 cm^{-1} for blends with polyurethanes of polyether and polyester soft segments respectively. A small shoulder on the high-frequency side of the peak appears around 3420 cm^{-1}. The main peak shows some skewness, especially for blends with polyether polyurethanes, having a wider distribution on the low-frequency side. In some cases an obvious shoulder at 3270 cm^{-1} was detected. Two additional small peaks in this region were observed at 3190 cm^{-1} and 3120 cm^{-1} respectively. The assignments of spectra in this region have been reported by many authors[18,20–25]. The band at 3120 cm^{-1} was considered to be an overtone of the band representing the NH

Table 2 Glass transition temperature of the PU/PVC blends

Sample	Blend ratio	T_g (°C)	
		tan δ	D.s.c.
PU-12/PVC	100/0	−20	−28
	70/30	15	8
	50/50	40	25
	35/65	50	45
	20/80	60	50
PU-22/PVC	100/0	−20	−31
	70/30	15	−8
	50/50	50	35
	35/65	55	49
	20/80	65	52
PU-32/PVC	100/0	−40	−55
	70/30	0, 55	−30, 55
	50/50	5, 70	−20, 65
	35/65	8, 72	–, 60
	20/80	5, 85	–, 60
PU-42/PVC	100/0	−18	−19
	70/30	−18, 80	−18, 83
	50/50	−18, 85	−19, 83
	35/65	−20, 80	−19, 83
	20/80	−18, 88	−19, 70

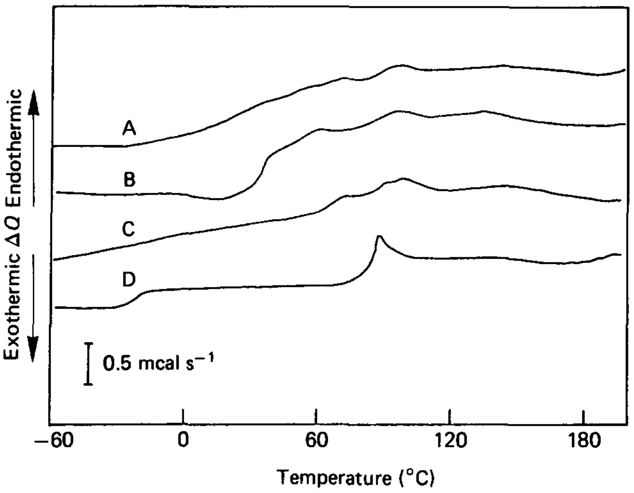


Figure 5 Thermograms for blends (50/50) of different polyurethanes: A, PU-12; B, PU-22; C, PU-32; D, PU-42

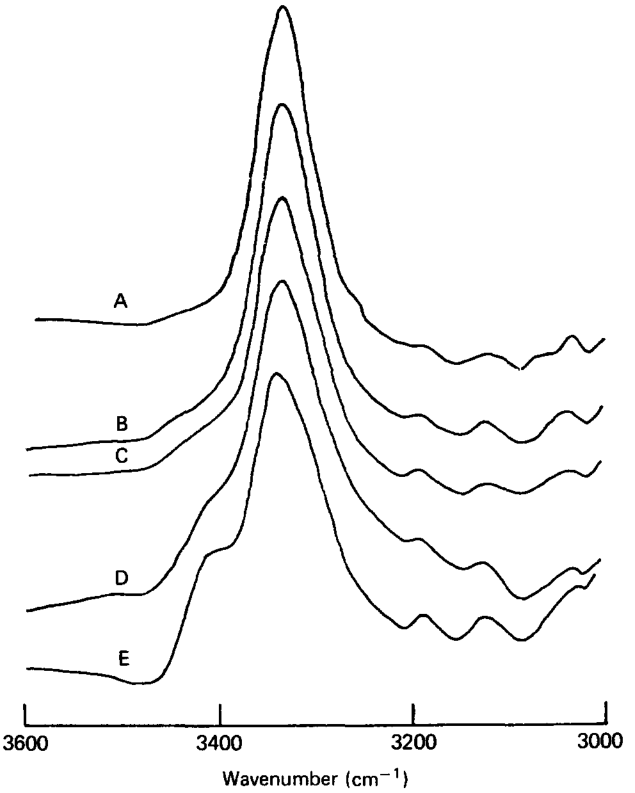


Figure 6 The NH stretching vibration absorption for PU-12/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

bending mode mixed with the C–N stretching mode at 1530 cm^{-1}. The other four bands at 3420, 3330, 3270 and 3190 cm^{-1} are all related to the NH stretching vibration and will be designated as $(NH)_1$, $(NH)_2$, $(NH)_3$ and $(NH)_4$ respectively in this paper. $(NH)_1$ was assigned to the free NH, while $(NH)_2$, $(NH)_3$ and $(NH)_4$ should be related to hydrogen-bonded NH, although there was some difference in their detailed assignment to *trans* or *cis* isomerism of the amide groups or to hydrogen bonding of NH groups with carbonyl or ether oxygens. The results show that most of the NH groups are hydrogen-bonded, but the amount of free NH increases with increasing PVC content of the blends.

In the region of carbonyl stretching vibration two well separated peaks of comparable intensity were observed for polyether polyurethanes and their blends (*Figures 10* and *11*) at about 1732 and 1705 cm^{-1}, which can be assigned to the free and bonded carbonyl groups respectively[18,22,23]. *Figures 12* and *13* show the carbonyl absorption for polyester polyurethanes and their blends. The absorption of bonded carbonyls is much less than that of free ones and appears as a small shoulder on the

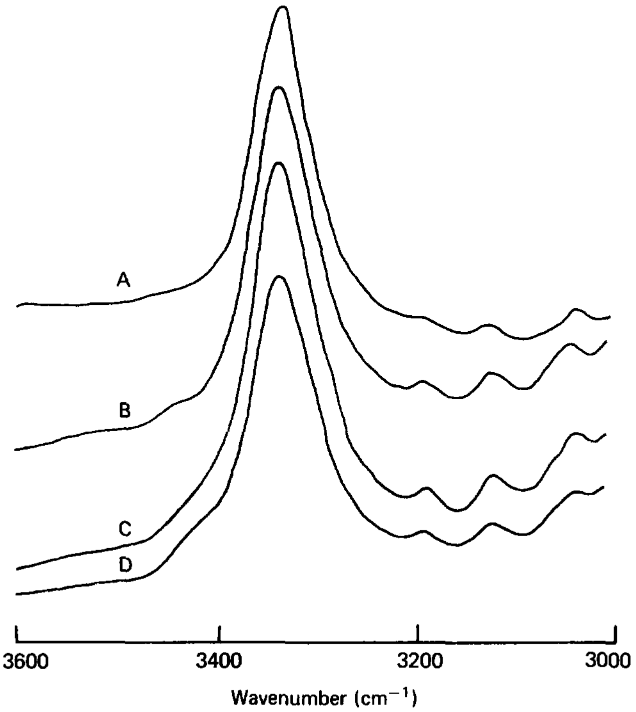


Figure 7 The NH stretching vibration absorption for PU-22/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65

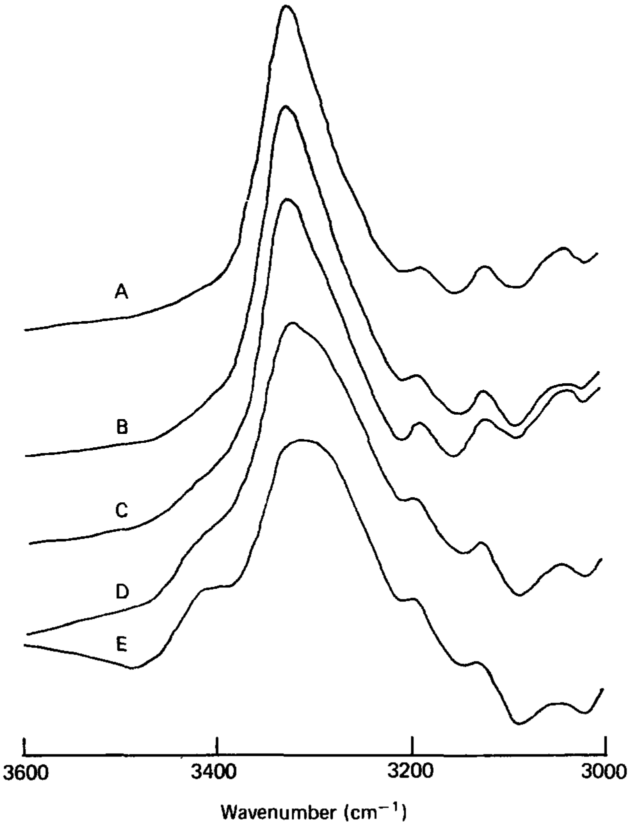


Figure 8 The NH stretching vibration absorption for PU-32/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

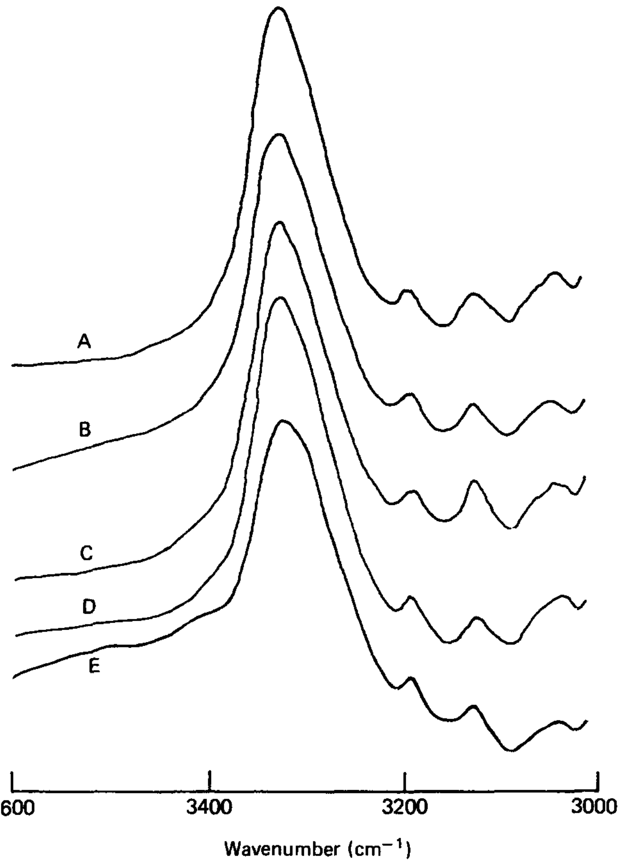


Figure 9 The NH stretching vibration absorption for PU-42/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

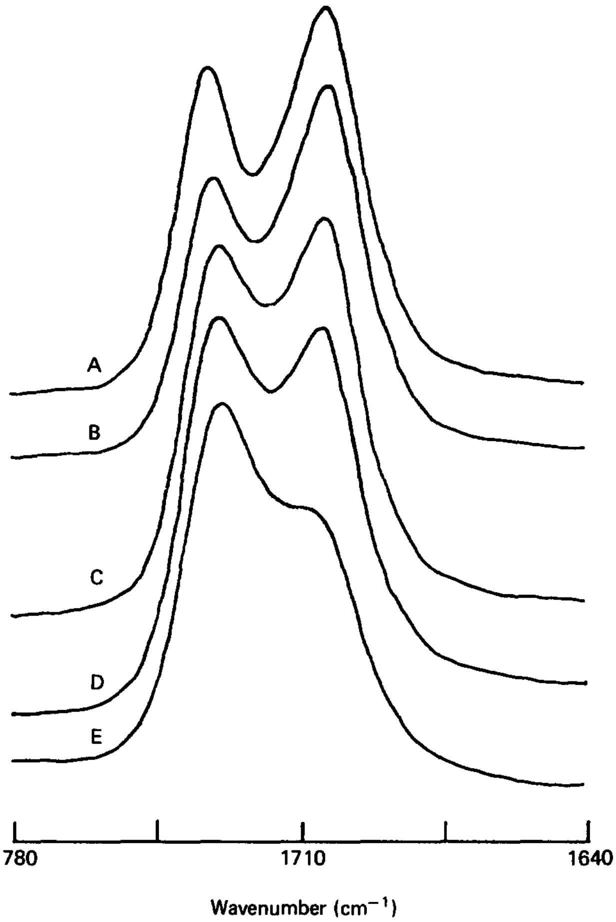


Figure 11 The carbonyl stretching vibration absorption for PU-32/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

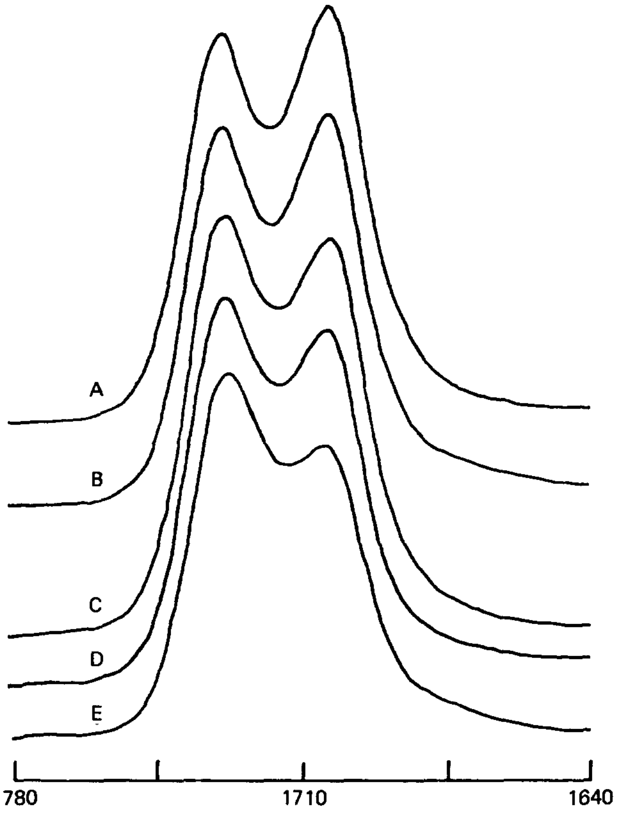


Figure 10 The carbonyl stretching vibration absorption for PU-42/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

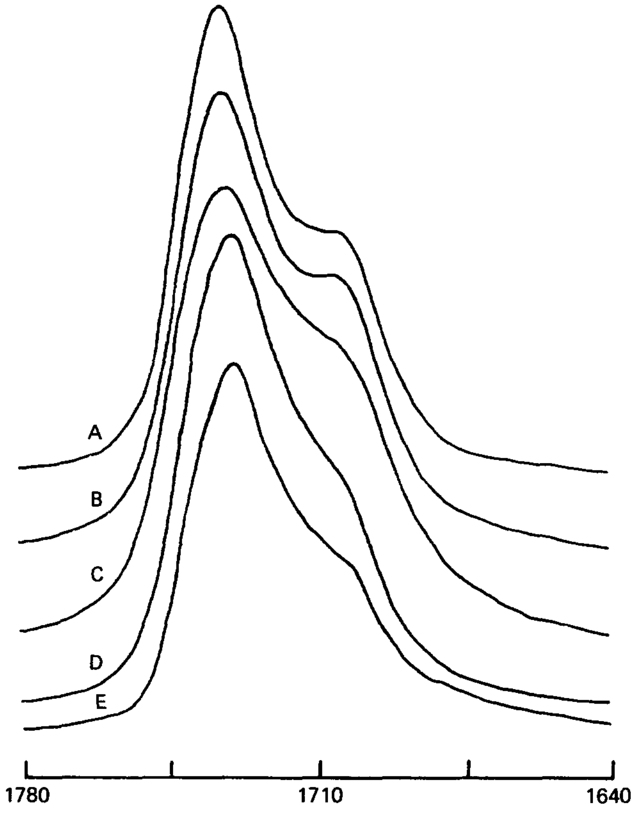


Figure 12 The carbonyl stretching vibration absorption for PU-22/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

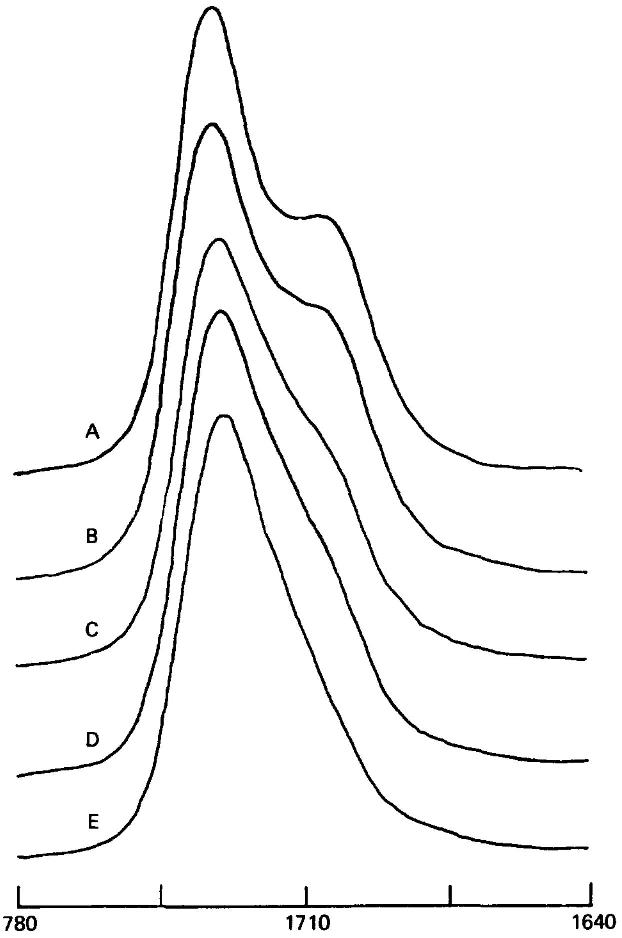


Figure 13 The carbonyl stretching vibration absorption for PU-12/PVC blends: A, 100/0; B, 80/20; C, 50/50; D, 35/65; E, 20/80

lower-frequency side. In general, four peaks in the carbonyl region would be expected for a polyester polyurethane, i.e. the free and bonded peaks of carbonyl groups of both hard and soft segments. The experimental results imply the close overlap of these bands.

Quantitative analysis of the NH and carbonyl absorptions was made on the basis of curve resolution. The experimental spectra in the region of 3500–3100 cm^{-1} were fitted with a combination of five symmetric bands. The band at 3120 cm^{-1} was included owing to its overlap with the $(NH)_4$ band. The initial band positions used in the iteration procedure were given according to the position of maxima or shoulders in the spectra and the literature data. *Figure 14* shows a typical NH peak resolution. The content of fractions of NH groups contributing the $(NH)_1$, $(NH)_2$, $(NH)_3$ and $(NH)_4$ bands is designated as X_f, X_{b_1}, X_{b_2} and X_{b_3} respectively and can be calculated by assuming that the ratio of relative absorptivity of the hydrogen-bonded NH group to that of the free one is constant for $(NH)_2$, $(NH)_3$ and $(NH)_4$ and equals 3.46 as determined from model compounds[26,27]. The results are summarized in *Table 3*. It is obvious that the NH groups are almost hydrogen-bonded, and the content $X_b = X_{b_1} + X_{b_2} + X_{b_3}$ decreases with increasing amount of PVC in the blends.

Figure 15 shows a typical resolution of carbonyl absorption for polyether polyurethane blends. As only hard-segment carbonyl groups exist in these samples, the two peaks related to free and bonded carbonyl groups are separated by a curve-fitting method. The resolution of carbonyl absorption for a polyester polyurethane blend is given in *Figure 16*. The initial peak positions (1730 cm^{-1} and 1701 cm^{-1}) were used for free and bonded carbonyls of hard segments in the iteration procedure according to our results for an –MDI–BDO– hard-segment homopolyurethane sample. The corresponding values for soft-segment carbonyls were selected as 1735 cm^{-1} and 1706 cm^{-1} respectively. The former was obtained from the spectrum of an amorphous PCL sample, while the latter was more arbitrary with the assumption of a similar band shift due to hydrogen bonding for the amide and ester carbonyls. The content of bonded carbonyl in the hard segments $X_{b'}$ was calculated from the area of peaks

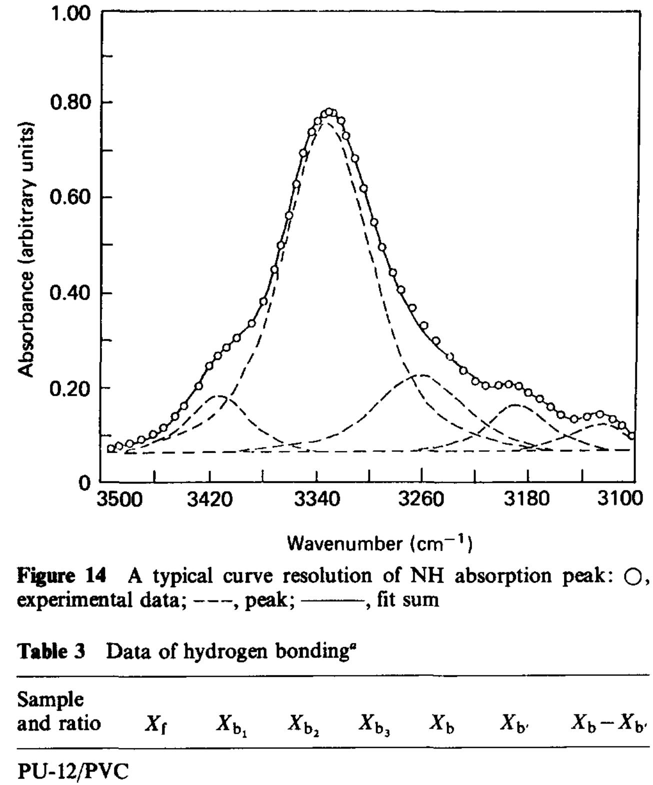


Figure 14 A typical curve resolution of NH absorption peak: ○, experimental data; – – –, peak; ———, fit sum

Table 3 Data of hydrogen bonding[a]

Sample and ratio	X_f	X_{b_1}	X_{b_2}	X_{b_3}	X_b	$X_{b'}$	$X_b - X_{b'}$
PU-12/PVC							
100/0	0.085	0.850	0.055	0.005	0.910	0.30	0.610
80/20	0.090	0.820	0.060	0.030	0.910	0.29	0.620
50/50	0.245	0.675	0.065	0.015	0.755	0.17	0.585
35/65	0.230	0.585	0.135	0.050	0.770	0.13	0.640
20/80	0.280	0.565	0.105	0.050	0.720	0.02	0.700
PU-22/PVC							
100/0	0.055	0.865	0.075	0.005	0.945	0.29	0.655
80/20	0.060	0.800	0.080	0.060	0.940	0.29	0.650
50/50	0.100	0.745	0.095	0.060	0.900	0.36	0.540
35/65	0.175	0.660	0.090	0.075	0.825	0.22	0.605
PU-32/PVC							
100/0	0.110	0.620	0.210	0.060	0.890	0.64	0.250
80/20	0.125	0.570	0.245	0.060	0.875	0.65	0.225
50/50	0.175	0.470	0.265	0.090	0.825	0.57	0.255
35/65	0.240	0.440	0.235	0.085	0.760	0.56	0.200
20/80	0.405	0.285	0.240	0.070	0.595	0.44	0.155
PU-42/PVC							
100/0	0.110	0.650	0.175	0.065	0.890	0.61	0.280
80/20	0.150	0.635	0.170	0.045	0.850	0.59	0.260
50/50	0.155	0.605	0.195	0.045	0.845	0.60	0.245
35/65	0.195	0.595	0.180	0.030	0.805	0.59	0.215
20/80	0.320	0.450	0.200	0.030	0.680	0.58	0.100

[a] X_f content of free NH; $X_b = X_{b_1} + X_{b_2} + X_{b_3}$; $X_{b'}$ content of bonded urethane carbonyl

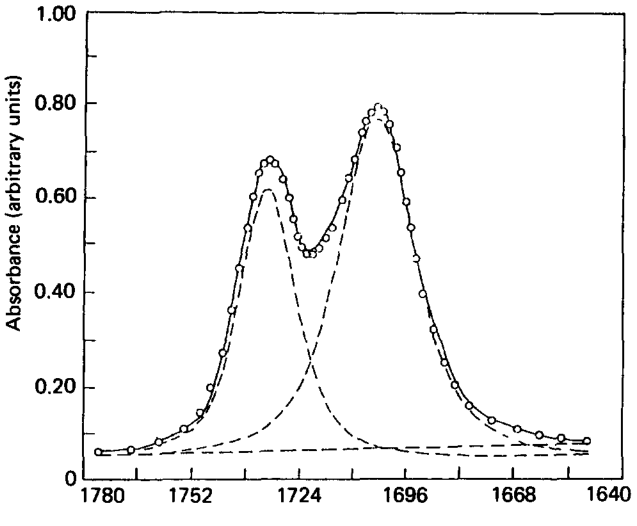


Figure 14 A typical curve resolution of carbonyl absorption for polyether polyurethane blends: ○, experimental data; ---, peak; ———, fit sum

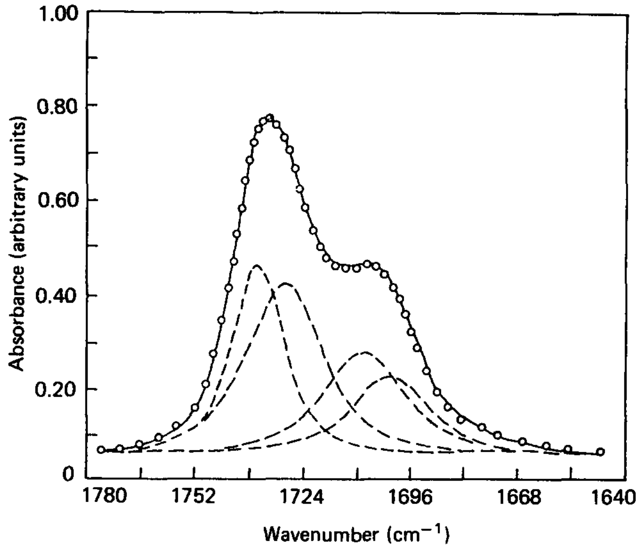


Figure 16 A typical curve resolution of carbonyl absorption for polyester polyurethane blends: ○, experimental data; ---, peak; ———, fit sum

by assuming that the ratio of relative absorptivity of the bonded group to that of the free one is 1.0[18,28]. These data are also listed in *Table 3*. The $X_{b'}$ values of polyether polyurethanes are almost twice as large as those for polyester polyurethanes, and the latter exhibit an obvious decrease with PVC content of the blends. As there are equal molar contents for NH and carbonyl groups in the hard segments, so the difference $X_b - X_{b'}$ gives the amount of NH groups that are bonded with acceptor atoms in the soft segments, i.e. the ether oxygen and the carbonyl oxygen for polyether and polyester polyurethanes respectively. The values of $X_b - X_{b'}$, given in *Table 3*, remain almost unchanged for polyester polyurethanes during blending with PVC, while a tendency to decrease can be observed for polyether polyurethanes. The frequency shifts of the carbonyl bands are given in *Figures 17–20*.

DISCUSSION

The single narrow glass transition observed in dynamic mechanical and d.s.c. measurements indicates that PVC molecules are very compatible with the PCL segments of PU-12 of any composition in the solution-cast specimens. This is quite reasonable, as PVC and PCL homopolymers are well known to be compatible as a blend[29]. The existence of two T_g values for blends of PVC and polyether polyurethanes means phase separation in the non-crystalline regions. The PU-42/PVC blends should be considered as completely incompatible, because the exact T_g values of the constituents were always observed for the blends. However, there is a limited partial mixing between the PVC molecules and the PTMO segments in PU-32/PVC blends evidenced by the deviation of their lower T_g value from that of the PTMO polyurethane to higher temperatures. The observed slight increase of the T_g peak width after blending may imply some kind of heterogeneity in the PVC–PTMA segment phase of the PU-22/PVC specimens. The compatibility of PVC and MDI based polyurethanes has been studied by different authors[1,2,5–8]. Although polyurethanes of polyether and polyester soft segments have been used in these studies, the molecular weight and content of soft segments and the composition and conditions of blending were not the same. One cannot get direct comparison of the compatibility of PVC with different soft segments from those reports. The results given in this paper indicate clearly that the compatibility of the soft segments used

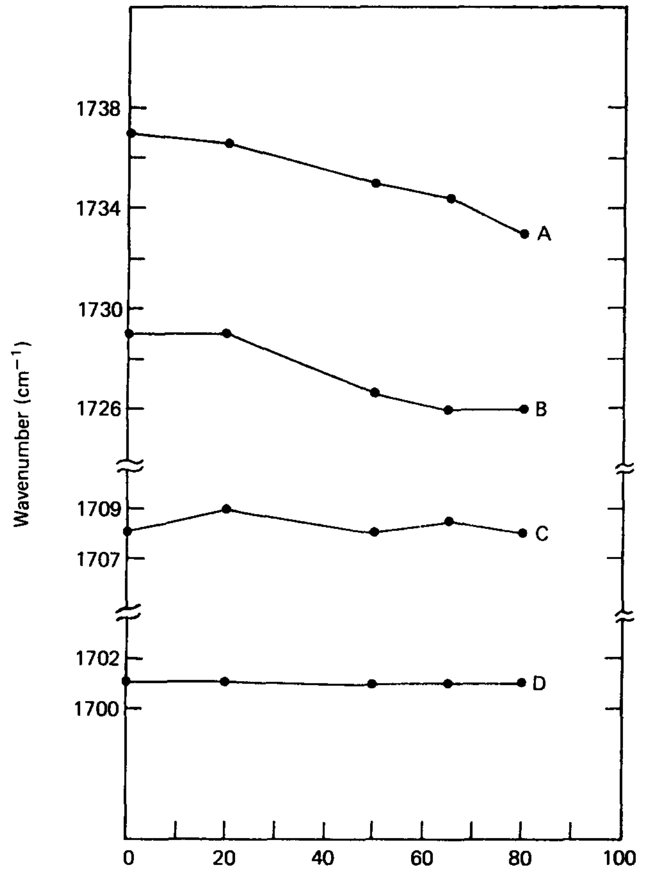


Figure 17 The shift of the carbonyl bands with PVC content for PU-12/PVC blends: A, free C=O of soft segment; B, free C=O of hard segment; C, bonded C=O of soft segment; D, bonded C=O of hard segment. (Results were obtained after curve resolution)

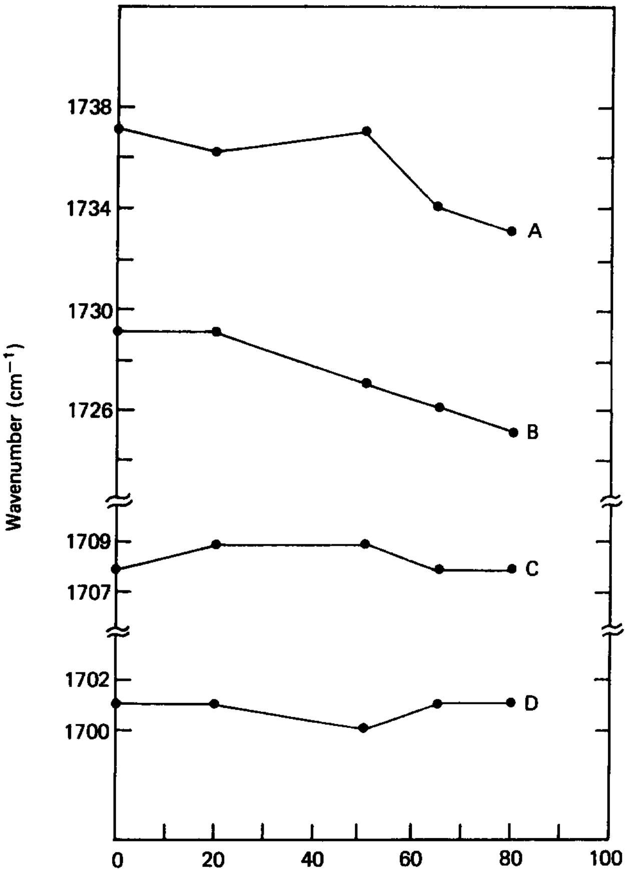


Figure 18 The shift of the carbonyl bands with PVC content for PU-22/PVC blends: A, free C=O of soft segment; B, free C=O of hard segment; C, bonded C=O of soft segment; D, bonded C=O of hard segment. (Results were obtained after curve resolution)

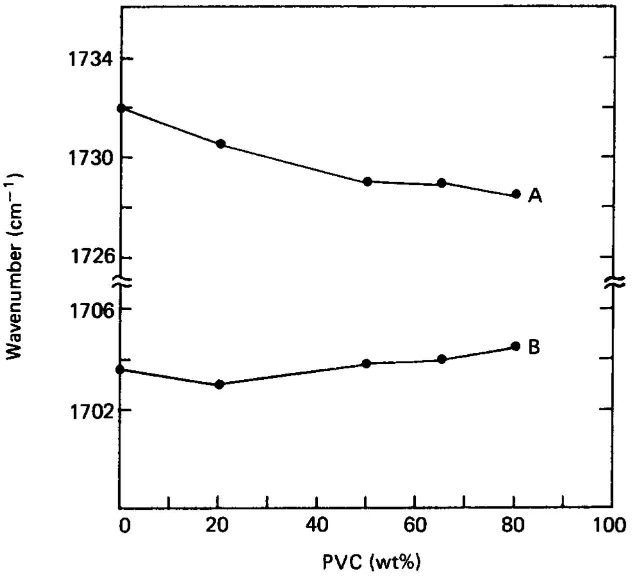


Figure 19 The shift of the carbonyl bands with PVC content for PU-32/PVC blends: A, free C=O of hard segment; B, bonded C=O of hard segment. (Results were obtained after curve resolution)

with PVC molecules decreases in the following order in solution-cast specimens:

$$\mathrm{PCL} > \mathrm{PTMA} \gg \mathrm{PTMO} > \mathrm{PPO}$$

The results also exhibit the possibility of changing the morphology and properties of PU/PVC blends by proper selection of the structure of the soft segment in the polyurethanes.

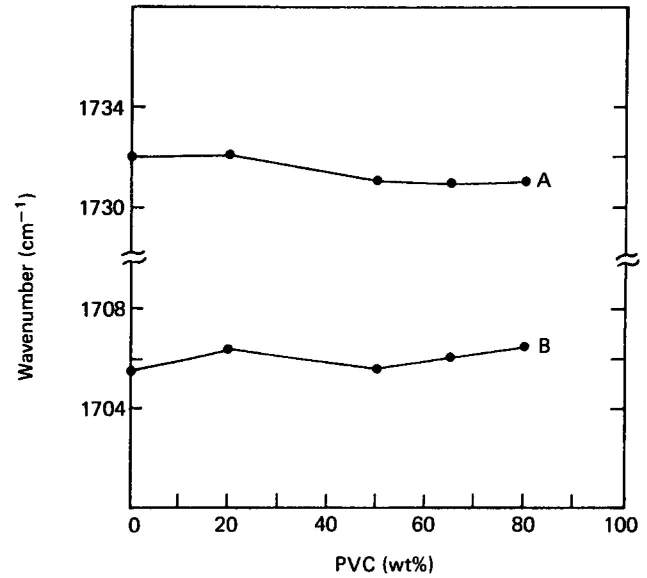


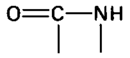
Figure 20 The shift of the carbonyl bands with PVC content for PU-42/PVC blends: A, free C=O of hard segment; B, bonded C=O of hard segment. (Results were obtained after curve resolution)

Information about the compatibility of PVC and soft segments is necessary to understand the morphology and properties of these samples, but is far from sufficient for a multicomponent system like the PU/PVC blends discussed here. Segmented polyurethanes are composed of hard and soft segments, which may segregate to form microphase separated domain structure. Besides, there is usually some mixing of hard and soft segments, the amount and degree of which are dependent upon their structure and the processing conditions and will have an important influence on the properties of the polyurethanes. So it is of great interest to find out the mixing situation of hard and soft segments in the polyurethanes as well as in their blends with PVC.

One convenient technique that can be used for quantitatively analysing the mixing of hard and soft segments is to study their hydrogen-bonding effect by means of infra-red spectroscopy, which is based on the idea that the morphology determines the distribution of hydrogen-bonding interaction of NH groups among the various acceptors in the hard and soft segments. Detailed studies have been made for MDI- and TDI-based polyurethanes with PTMO and polybutadiene soft segments[5,18,22,28,30].

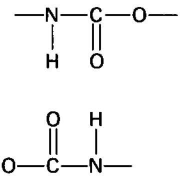
The data listed in *Table 3* show that the NH groups of the polyurethanes are almost completely (~90%) hydrogen-bonded. For polyurethanes with polyether soft segments most of the NH groups are bonded with the carbonyl groups of the hard segments. These results are consistent with those of Srichatrapimuk and Cooper for MDI polyurethanes[18]. The molar ratio of the ether oxygen to NH for the two polyether polyurethanes is about 4, so only 7% of the ether oxygens are bonded with NH groups. The behaviour of polyester polyurethanes is different from that of the polyether ones. Only a small fraction of the NH groups are bonded with carbonyl groups of the hard segments, but more than 60% of the NH contribute to the hydrogen-bonding interaction with soft segments. The fraction of ester carbonyls that are bonded with NH groups is as high as 27% calculated by taking into account the molar ratio between the ester carbonyl and NH groups in the polyurethane molecules. These results indicate a better mixing of hard and soft segments in ester polyurethanes than in the ether ones. In the latter cases most of the hard segments must be segregated into domains, and only very few of them may be individually dispersed in the soft-segment matrix, if the possibility of hydrogen bonding between the soft and hard segments at the boundary of the domains is considered.

The splitting of the hydrogen-bonded NH stretching band has been mentioned in some studies of polyurethanes. It used to be accepted that the peak position of the bonded NH band will depend mainly on whether the NH group exists in the *cis* or *trans* form. Bands at 3320, 3270 and 3185 cm^{-1} have been assigned respectively to bonded NH and to *trans* and *cis* NH groups in the



$$\mathrm{O{=}C{-}NH}$$

structure for MDI-based polyurethanes[18]. A similar assignment has been made for bands at 3320, 3200 and 3130 cm^{-1} by Brunette *et al.* for TDI-based polyurethanes[22]. Darmon and Sutherland[23] have suggested that the 3175 cm^{-1} absorption may arise from a 'double *cis*-bonded' structure as shown below:



$$-\underset{H}{N}-\underset{O}{C}-O-$$
$$-O-\overset{O}{C}-\overset{H}{N}-$$

Recently Christenson *et al.*[25] concluded from their studies on model MDI/butanediol polyurethanes that the splitting of the bonded NH band is related to different acceptors with which the NH groups are hydrogen-bonded, and the bands at 3325 and 3260 cm^{-1} were assigned to NH groups bonded with carbonyl and ether oxygens respectively.

The data of X_{b_1}, X_{b_2} and X_{b_3} show clearly the difference between polyester and polyether polyurethanes. The predominant part of bonded NH contributes the band $(NH)_2$ for PU-12 and PU-22 polyurethanes with polyester soft segments, while about one-third of the bonded NH is related to band $(NH)_3$ for polyether polyurethanes PU-32 and PU-42. However these results cannot be used to discriminate the different assignments of the hydrogen-bonded NH bands. Although the polyether polyurethanes are expected to have more NH groups bonded with ether oxygen than the polyester ones, they may also have more *cis* form –CONH– groups owing to better segregation of hard and soft segments[15].

The influence of PVC on the mixing of hard and soft segments in the blends finds its reflection in the dependence of X_b on the PVC content. The amount of bonded NH decreases with increasing PVC content, especially when the PVC content is larger than 50%. Although the tendency is similar for all the PU/PVC blends, the mechanism of the phenomenon seems different for the ester and ether polyurethanes.

The value of $X_{b'}$, the content of bonded carbonyl in hard segments, decreases obviously due to blending with PVC for PU-12/PVC blends, while the fraction of hydrogen bonding between hard and soft segments remains almost unaffected. The small $X_{b'}$ value for specimens of high PVC content implies that most of the hard segments are separated from each other and dispersed in the PVC/soft-segment matrix. In contrast, for PU-42/PVC blends $X_{b'}$ remains constant with increasing PVC content, but a parallel decrease of X_b and $X_b - X_{b'}$ with blending can be observed. As the same T_g values of PU-42 and PVC were detected for their blends of any ratio, it should be assumed that there is no mixing between the PVC molecules and the PPO segments, and the unmixing situation of hard and soft segments is not changed due to the existence of the PVC component. So the decrease of X_b and $X_b - X_{b'}$ with PVC content may imply that the hard-segment domains are partially isolated from the PPO soft-segment domains by the PVC phase, which results in the loss of some hydrogen bonding between the hard- and soft-segment domains. Blends with polyurethanes of PCL and PPO segments are two extreme examples. PU-22/PVC and PU-32/PVC blends are similar to PU-12/PVC and PU-42/PVC blends respectively, but no so typical as the latter described before.

The interaction between PVC molecules and the hard segments is relatively difficult to study, and usually they are considered to be incompatible. Wang and Cooper have found that it is possible to discuss the interaction between the α-hydrogen of PVC and the free carbonyl of the urethane hard segments according to the shift of the free carbonyl bands[5]. *Figures 17–20* show significant band shifting, up to 3–4 cm^{-1}, for free carbonyl of hard segments in blends with PCL, PTMA and PTMO polyurethanes compared to blends with PPO polyurethanes. These results are consistent with those in ref. 5 for PTMO–PU/PVC specimens prepared by solution casting in different solvents.

Models describing the characteristic morphological features of the two kinds of polyurethanes and their blends with PVC are shown in *Figures 21* and *22*. Hard-segment domains exist in both ether and ester polyurethanes, but in the latter more hard segments are dispersed in the soft-segment matrix. For blends with polyester polyurethanes the PVC molecules may disperse in the soft-segment phase with little influence on the microphase separation and mixing of the hard and soft segments at low PVC concentrations (*Figure 21b*). When the content of PVC is high in the blends, the hard segments will be dispersed in the diluted soft-segment matrix without segregation (*Figure 21c*). In the case of blends with poor compatibility between PVC molecules and the polyether soft segments, PVC molecules segregate and form an individual phase. At low PVC content the influence of the isolated PVC domains is negligible. However in blends of high PVC content PVC forms a continuous phase and some PVC regions may penetrate into the soft-segment-rich polyurethane regions or may be embedded among the soft- and hard-segment domains (*Figure 22c*). Wang and Cooper[5] have given morphological models for compatible and incompatible blends based on their studies of PVC and PTMO polyurethane blends. Their models are similar to ours for blends of low PVC contents given in *Figure 21b* and *22b*.

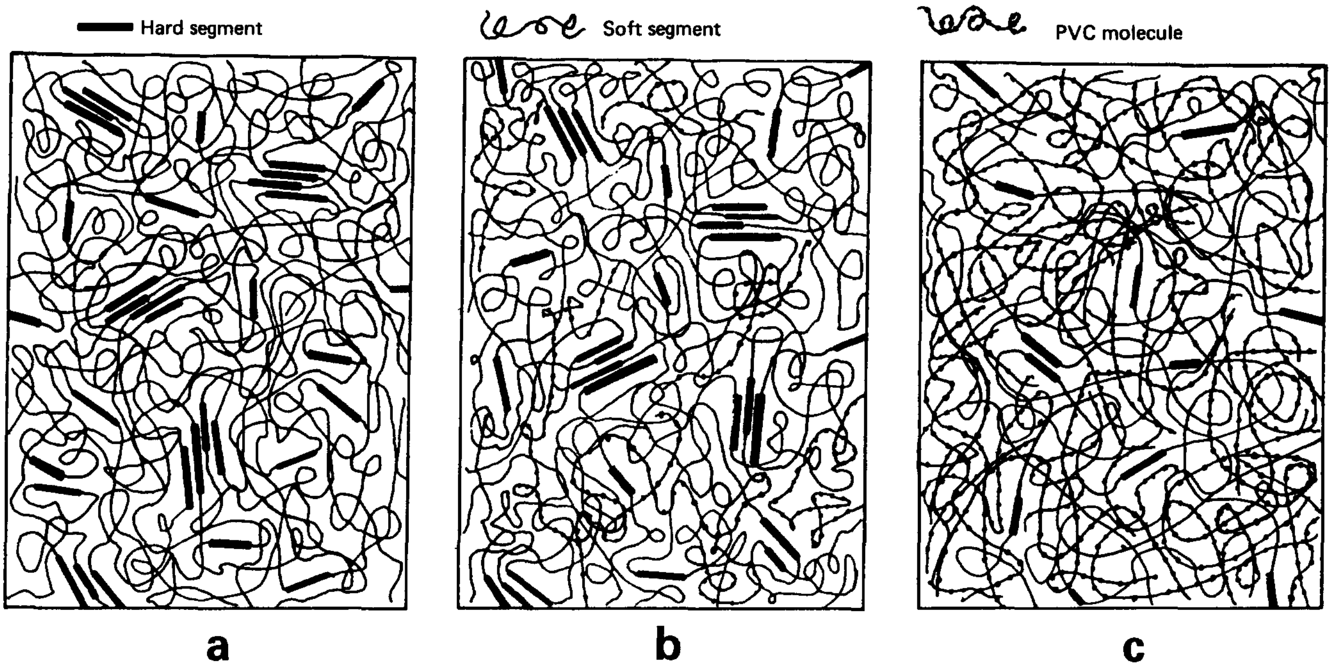


Figure 21 Morphological models for PU-12 and its blends with PVC: (a) PU-12; (b) blends of low PVC content; (c) blends of high PVC content

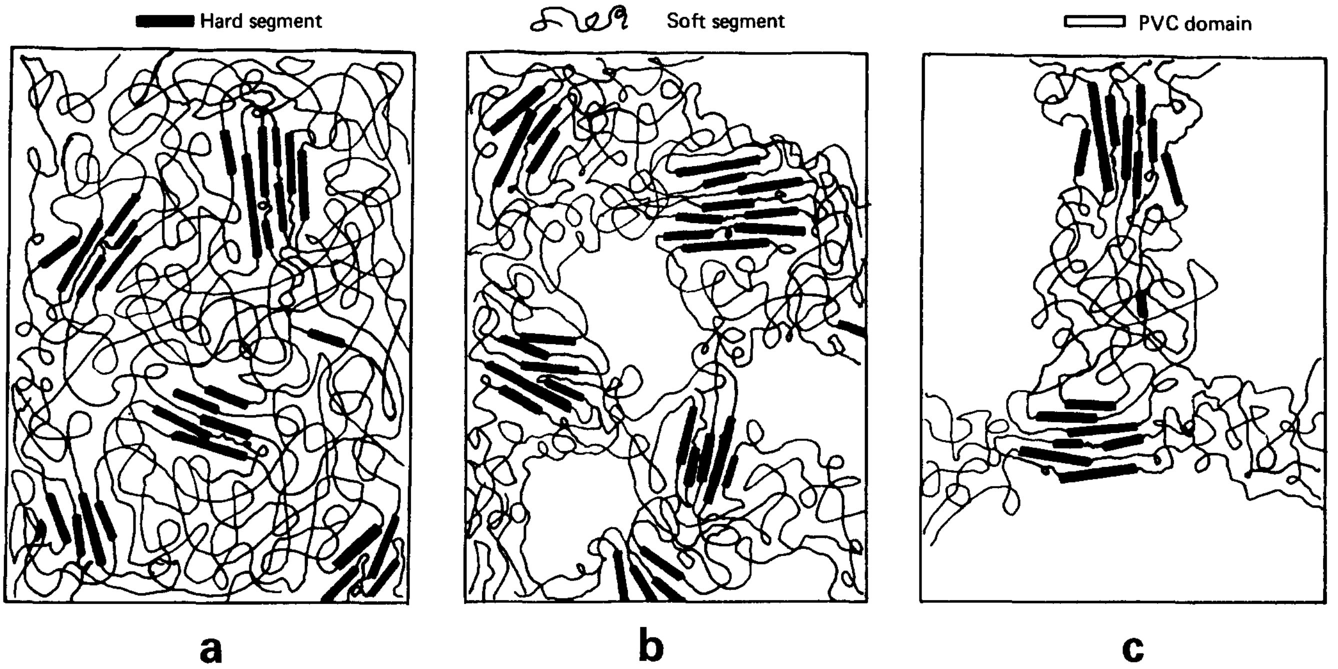


Figure 22 Morphological models for PU-42 and its blends with PVC: (a) PU-42; (b) blends of low PVC content; (c) blends of high PVC content. □, PVC domain (only for b and c)

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REFERENCES

1 Piglowski, J. and Laskawski, W. *Angew. Makromol. Chem.* 1979, **82**, 157
2 Piglowski, J., Skowronski, T. and Masiulanis, B. *Angew. 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. *Angew. Makromol. Chem.* 1984, **12**, 49
8 Mao, R. S., Thesis, Department of Applied Chemistry, University of Science and Technology of China, 1985
10 Ferguson, J., Hourston, D. J., Meredith, R. and Patsavoudis, D. *Eur. Polym. J.* 1972, **8**, 369
11 Ng, H. N., Allegrezza, A. E., Seymour, R. W. and Cooper, S. L. *Polymer* 1973, **14**, 255
12 Seefried, Jr, C. G., Koleske, J. V. and Critchfield, F. E. *J. Appl. Polym. Sci.* 1975, **19**, 2493, 2503
13 Nishi, T. and Kwei, T. K. *J. Appl. Polym. Sci.* 1976, **20**, 1331
14 Huh, D. S. and Cooper, S. L. *Polym. Eng. Sci.* 1981, **11**, 369
15 Xiao, F. F., Zhang, X., Hu, S. R., Ma, D. Z., Luo, X. L. and Xu, M. *J. Polym. Sci.* (*China*) to be published
16 Malac, J., Altmann, V. and Zelinger, J. *J. Appl. Polym. Sci.* 1970, **14**, 161

17 Seymour, R. W. and Cooper, S. L. *Macromolecules* 1973, **6**, 48

18 Srichatrapimuk, V. W. and Cooper, S. L. *J. Macromol. Sci.* 1978, **B15**, 267

19 Kwei, T. K. *J. Appl. Polym. Sci.* 1982, **27**, 289

20 Anton, A. *J. Appl. Polym. Sci.* 1968, **12**, 2117

21 Bessler, E. and Bier, G. *Makromol. Chem.* 1969, **122**, 30

22 Brunette, C. M., Hsu, S. L., MacKnight, W. J. and Schneider, N. S. *Polym. Eng. Sci.* 1981, **21**, 163

23 Bellamy, L. J., 'The Infrared Spectra of Complex Molecules', Chapman and Hall, London, 1975

24 Coleman, M. M., Skrovanek, D. J., Hu, J. and Painter, P. C. *Polym. Prepr.* 1987, **28**(1), 19

25 Christenson, C. P., Harthcock, M. A., Meadows, M. D., Spell, H. L., Howard, W. L., Creswick, M. W., Guerra, R. E. and Tunner, R. B. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1401

26 Tanaka, T., Yokoyama, T. and Yamaguchi, Y. *J. Polym. Sci.* (*A-1*) 1968, **6**, 2137

27 MacKnight, W. J. and Yang, M. *J. Polym. Sci.* (*C*) 1973, **42**, 817

28 Seymour, R. W., Estes, G. M. and Cooper, S. L. *Macromolecules* 1970, **3**, 579

29 Krause, S., 'Polymer Blends', (Eds. D. R. Paul and S. Newman), Academic Press, New York, Vol. 1, 1978

30 Paik Sung, C. S. and Schneider, N. S. *Macromolecules* 1977, **10**, 452