Transition behaviour of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks

I. Hermant, M. Damyanidu and G. C. Meyer*

Ecole d'Application des Hauts Polymères, Louis Pasteur University, F-67000 Strasbourg,

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The transition behaviour of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks (PUR/PAc IPN's) was studied by means of differential scanning calorimetry (d.s.c.), dynamic mechanical spectroscopy (d.m.s.) and thermally stimulated depolarization (t.s.d.). Instead of a sharp discontinuity in heat capacity, as for the individual networks, a very broad change is observed by calorimetry and some intermediate changes in heat capacity appear too. D.m.s. yields only two peaks which show a marked inward shift, with an important damping and broadening, as compared to the individual networks. Some preliminary results obtained by t.s.d. confirm these findings. It can be concluded that PUR/PAc IPN's are phase separated, but that the mutual miscibility of both components is enhanced by the special mode of combining them, namely interpenetration. When the second component is not crosslinked, phases appear to be less entangled. Previous results on physical and mechanical properties corroborate these conclusions.

Keywords Polymers; interpenetrating networks; polyurethane; polyacrylic resin; transition behaviour

INTRODUCTION

Like other polymeric blends, interpenetrating polymer networks (IPN's) undergo phase separation. The advantage over other methods of combining polymers is that once both crosslink reactions are completed, no further demixing can occur, thanks to the high degree of physical entanglement of the components[1]. Several authors have investigated the morphology of the IPN's and of related materials by means of methods which give information about the transition behaviour, like dynamic mechanical spectroscopy (d.m.s.) or calorimetry (d.s.c.). Sometimes electron microscopy allows the visualization of the phase arrangement. Such studies are essential when structure–property relationships have to be established. Thus, Sperling[2] has prepared IPN's based on poly(ethyl acrylate) (PEA) as the first network combined with a crosslinked poly(MMA-co-S) random copolymer. In the latter, he varied the MMA content from 0% to 100%. He has shown that when the IPN contains only acrylic polymers (%S = 0), the dispersion of the phases is very high, contrary to what happens when PEA is associated with PS. In this case, he has found two transitions, whereas only one broadened transition was observed for the PEA/PMMA IPN. Sperling ascribed this difference to the better compatibility of the two acrylic polymers, as compared to the PEA/PS couple. By measuring the optical transmission of polymer blends, Kanig and Neff[3] have demonstrated that crosslinking of at least one component yields materials with a higher transparancy, an observation that they have explained by the finer phase dispersion. Kim[4] has come to the same conclusion by comparing linear blends and the corresponding semi-IPN's and full IPN's. Allen and coworkers[5] have examined the morphology and the relaxation processes in composites formed by the interstitial polymerization of vinyl polymers in polyurethane elastomers and concluded that both phases are still separated, though some interaction exists, which they locate at the domain boundaries.

In our laboratory, polyurethane–poly(methyl methacrylate) IPN's (PUR/PAc IPN's) have been studied for several years. First, the chemical aspect of the synthesis has been investigated thoroughly, namely the occurrence of unwanted side reactions or of intersystem grafting, and the kinetics of network formation[6]. Then, the effect of various compositional parameters on synthesis was examined, and several physical characteristics of the IPN's were given[7]. More recently, some mechanical properties have been described[8]. All these investigations have emphasized the role of the crosslink degree of each network, mainly of the one formed first (PUR). They have also shown that interpenetration and phase continuity exist in such IPN's.

In this paper, we report the transition behaviour of PUR/PAc IPN's with various crosslink degrees and compositions, by means of d.m.s. and d.s.c. Some preliminary results obtained by using thermally stimulated depolarization (t.s.d.) are given for comparison matters; a complete t.s.d. study will be reported later. We have shown that the previous conclusions are corroborated by the results of the present investigation of the transition behaviour.

EXPERIMENTAL

Materials and synthesis

All the reagents used are listed in *Table 1*. When necessary, functional and other analyses were carried out

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* To whom enquiries should be addressed

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Table 1 Materials

Materials	Description	Source	Code
Polyol	Poly(oxypropylene)glycol; $\bar{M}_n$ 2000; 1.05 OH kg^{-1}; density : 1.0 g ml^{-1}; viscosity : 370 cps	P.C.U.K. (P 1020)	POPG
Polyisocyanate	Trimethylol-1,1,1 propane/toluene diisocyanate adduct, containing 25 weight % of ethyl acetate; 3.1 NCO kg^{-1}; density : 1.17 g ml^{-1}	Bayer (L 75)	L 75
PUR catalyst	Stannous octoate : 28.5% tin; density : 1.25 g ml^{-1}	Goldschmidt (KOSMOS 29)	OcSn
Acrylic monomer	Methylmethacrylate : stab. : hydroquinone 50 ppm	Fluka	MMA
Acrylic crosslinker	Trimethylol-1,1,1 propane trimethacrylate; stab. : methylhydroquinone 100 ppm; density : 1.06 g ml^{-1}	Degussa (TRIM)	TRIM
Initiator	Azo-bisisobutyronitrile	Merck	AIBN

to check the indications given by the manufacturers. Water traces were eliminated, whereas the methacrylic monomers were not freed from the inhibitor molecules. More details, and the determination of the compositional parameters, are given in previous papers[6,7]. A standard synthesis proceeds as follows: the calculated amounts of the various reagents are mixed and stirred thoroughly in a dry nitrogen atmosphere for a few minutes. The blend is poured into a glass mould. The PUR network is formed first at room temperature, in 15–20 min and without noticeable exothermy. Thirty minutes after the complete mixing of the reagents (taken as the origin of reaction times), the mould is transferred into a heating oven at 56°C where the radical copolymerization of the PAc phase is initiated. A forced air circulation in the oven allows an effective temperature regulation within ±2°C. After one hour, the temperature is raised to 75°C for a further two hours. Then, the IPN is annealed: 75°C for overnight and 3 h at 120°C.

If not otherwise indicated, the standard values, for a given PUR content, are: $K = \mathrm{NCO/OH} = 1.07$; TRIM $= 5\%$; AIBN $= 1\%$. In the semi-1 IPN's mentioned hereafter, the acrylic component is not crosslinked (%TRIM $= 0$).

Dynamic mechanical spectroscopy

A Rheometrics spectrometer (RMS 605) was used to measure the shear modulus and the loss tangent in a temperature range from −70° to +130°C and at various frequencies (0.1 to 10 rad s^{-1}). Samples were either bars (60 × 12 × 3 mm) or discs (diameter 25 mm). It happens that the viscosity of some test samples decreases too largely at higher temperatures, so that a larger strain must be applied in order to obtain a measurable and accurate signal. Depending on the material, the strain varied from 0.05% to 2%, after it had been verified that the torque value was not affected by this change. Temperature sweep: 5°C. The temperature at which the loss tangent is maximum was taken as the transition temperature T_g. The accuracy is satisfactory; for instance, the tan δ vs. temperature curves of two successive runs superpose completely. Finally, the different curves are given without the experimental points (1 point each 5°, from −70°C) so as not to surcharge the figures.

D.s.c. measurements

The glass transition temperatures were determined with a Perkin-Elmer DSC-1B calorimeter, in standard aluminium pans. Preceding the first measurement, the pan containing the polymer was annealed for 10 min at 147°C and then brought back to the starting temperature at a rate of 4°C min^{-1}. As T_g depends strongly on the rate of heating, we operated at various heating speeds ($v = 4$, 8, 16 and 32°C min^{-1}). For each heating rate, three measurements were carried out, the deviation being less than 1°C between the three values. The same sample was used for all determinations; the cooling rate was always kept at 4°C min^{-1}. The transition temperatures obtained at the different speeds were plotted as a function of v and can be placed on a straight line. The zero-rate extrapolated value was taken as T_g for the sample[9] with an accuracy of ±2°C; indium (melting point (m.p.) 156.6°C) and n-octane (m.p. −56.5°C) were used to calibrate the apparatus.

Thermally stimulated depolarization

T.s.d. measurements are done by applying a d.c. electric field at high temperature, quenching to −190°C and heating while the current is recorded under short circuit conditions. One observes various peaks due in part at least to dipole disorientation. As only a few preliminary results will be reported for comparison matters, a detailed description of the t.s.d. method is not given here, but may be found elsewhere[10].

RESULTS AND DISCUSSION

Dynamic mechanical spectroscopy

In the following Figures and Tables, G', the storage modulus and $\tan\delta = G''/G'$ (G'': loss modulus) are reported as a function of the temperature. As higher frequencies tend to level the transition peaks (for tan δ), all the experiments were carried out at the relatively low frequency of 0.1 rad s^{-1}. The influence of the degrees of crosslinking ($K = \mathrm{NCO/OH}$, % TRIM) and of the elastomer content (% PUR), on the transition behaviour is discussed and compared with that of the individual networks.

Influence of $K = \mathrm{NCO/OH}$: this parameter governs the degree of crosslinking of the PUR network. *Figure 1* shows the tan δ vs. temperature curves for various values of K. Decreasing K shifts the PUR peak towards lower temperatures. For $K = 0.77$, the maximum is even below the T_g of the homo-PUR (−40°C), and corresponds to a more or less loose network containing free or pendent polyether glycol chains. At the same time, the upper transition coincides with the T_g of the pure PAc network. Thus, in IPN's where the PUR network is incompletely formed, both components seem to be more independent from each other. Conversely, the inward shift of the upper transition when the PUR network becomes more completely formed (increasing K values), indicates the impor-

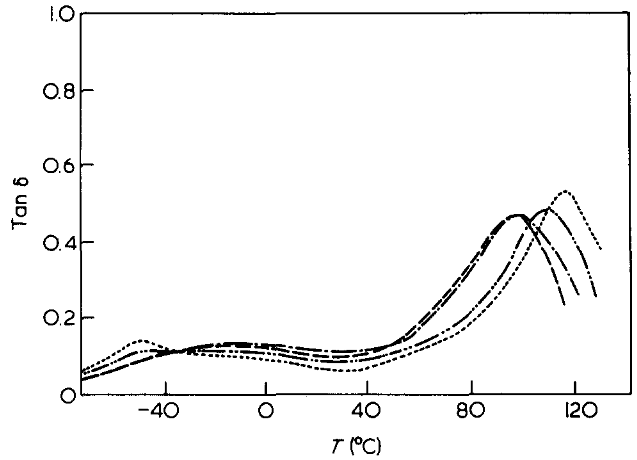

Figure 1 Variation of the loss tangent, tanδ, with temperature, for IPN's with various values of K=NCO/OH: (-·-) 1.28; (——) 1.07; (-··-) 0.89; (···) 0.77. 34% PUR; 5% TRIM

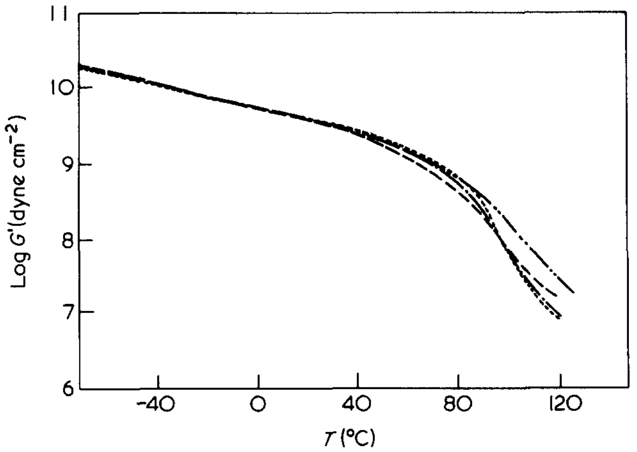

Figure 2 Variation of the storage modulus, G', with temperature, for IPN's with various acrylic crosslinker contents. % TRIM: (···) 0; (-·-) 3; (——) 5; (-··-) 7.5. 34% PUR; K = NCO/OH = 1.07

Table 2 Some viscoelastic properties of IPN's with various amounts of acrylic crosslinker

% TRIM	tanδ max*	T(tanδ max)* (°C)	tanδ max**	T(tanδ max)** (°C)	G'_{20} (MPa)	$\tan\delta_{20}$
0	0.14	−23	0.73	100	431	0.09
1	0.14	−10	0.63	94	421	0.10
3	0.14	−10	0.65	99	414	0.11
5	0.14	−10	0.53	100	393	0.11
7.5	0.14	−10	0.47	109	389	0.12

PUR content of the IPN's: 34%; K = NCO/OH = 1.07
* Relating to lower transition
** Relating to upper transition

tant influence of the soft phase on the rigid component. It appears that through the PUR network, a high degree of entanglement of the second phase is actually realized in this case. The $G'=f(t)$ curves are not reported: they resemble the curves in *Figure 2* concerning the influence of the acrylic crosslinker and do not show the classical discontinuity existing for incompatible polymers. However, for $K=0.77$, such a discontinuity exists, showing again the increase in phase dispersion obtained by a PUR network of good 'quality'.

Influence of variable acrylic crosslinker contents: IPN's with an increasingly crosslinked PAc phase were prepared (0 to 7.5% TRIM). The results appear in *Table 2* and in *Figures 2* and *3*, for IPN's containing 34% PUR. Up to room temperature, the dynamic mechanical properties do not vary; this is due to the fact that the material is far below its glass transition temperature, so that its properties are not affected by crosslinking. When the test temperature approaches the upper T_g, the heat resistance becomes higher when the per cent of TRIM increases. Though such a result may be expected in the crosslinking of homopolymers, it was not sure that in a system like the present one, all the crosslinking reactions would actually take place[7]. The loss tangent curves (*Figure 3*) show that crosslinking induces some peak damping, so that the loss tangent value is not only a function of the composition of the IPN. Applied to the soft component, the pronounced damping of the lower transition may therefore be also the indication of a high degree of crosslinking of the PUR network. Nielsen has reported similar effects of crosslinking on the peak damping[11]. Concerning their position on the temperature scale, all loss peaks are shifted downwards, as compared to the PAc network. However, the difference in temperature for the IPN's containing 0% and 7.5% TRIM is not important (10°C).

Influence of the PUR content: in *Figure 4*, G' is plotted against temperature for IPN's with various PUR contents. The individual networks each exhibit one sharp transition. As expected, the curves relating to the IPN's are between the ones of the individual networks; their upper transition becomes less marked as the elastomer per cent is increased, whereas the lower transition is very weak for the IPN with 50% PUR and disappears for the lower PUR contents. The loss tangent curves (*Figure 5* and *Table 3*) show the peaks corresponding to the pure PUR and the pure PAc phases, at −40°C and 122°C respectively. Furthermore, a slight maximum, corresponding to the β-relaxation of PMMA, appears around 1°C. The loss curves of the IPN's are completely different. They present two maxima: the upper one is rather pronounced and corresponds to the acrylic phase in the IPN. The lower transition is a plateau and its maximum cannot be set very accurately. It is also more damped than the acrylic transition peaks. For both transitions, the tan δ value decreases with the amount of the corresponding network in the IPN: damping is therefore a function of composition, though other parameters, like the crosslink degree play a role too. The curves show also an important broadening of the peaks, together with a shift towards lower temperatures, mainly for the upper transition. Both

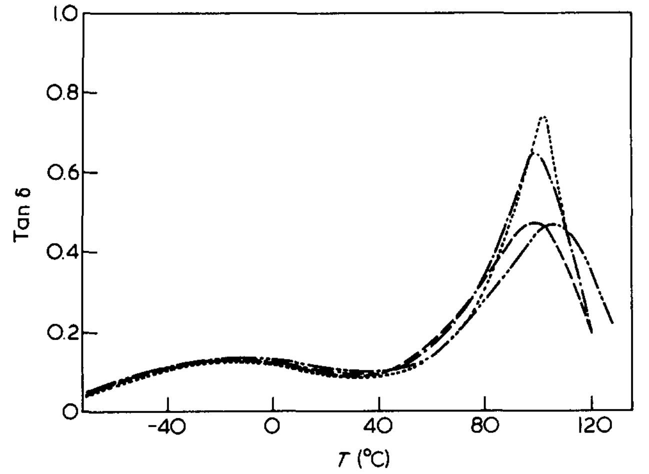

Figure 3 Variation of the loss tangent, tanδ, with temperature, for IPN's with various acrylic crosslinker contents. Symbols as for *Figure 2*. 34% PUR; K = NCO/OH = 1.07

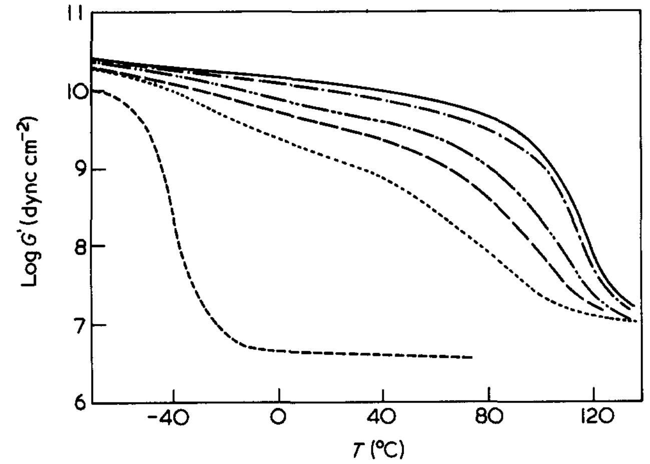

Figure 4 Variation of the storage modulus, *G'*, with temperature, for IPN's with various PUR contents. PUR/PAc: (——) 0/100; (–·–) 15/85; (–··–) 25/75; (– – –) 34/66; (···) 50/50; (---) 100/0. 5% TRIM; K=NCO/OH=1.07

transition peaks come closer to each other when the PUR content increases. Unfortunately, the shapes of the loss curves of the PAc network and of the IPN's are quite similar. Thus, the lower transition, which corresponds to the β-relaxation for the pure PMMA, may be attributed to the same process in the IPN's, instead of corresponding to the transition of the PUR. However, in this case, the α-relaxation of the soft phase would have completely disappeared, which cannot be explained easily. Perhaps hydrogen bonding[6,12] between both components could induce high phase miscibility, resulting in the observed plateau. But on the other hand, with increasing PUR content, the maximum of the lower transition shifts downwards. It becomes thus more and more separated from the proper β-relaxation of the acrylic phase; correspondingly, the loss tangent values increase. Being always higher as the tan δ of PMMA, they are obviously related to the PUR. The same happens when the factor K decreases (*Figure 1*): tan δ decreases in the temperature zone around 1°C, but increases at the same time at lower temperatures. This observation is one more reason for ascribing the lower transition to the PUR network, even if some hydrogen bonding intervenes in the relaxation process. What is mainly demonstrated by the comparison of the loss curves of the individual networks and the various IPN's is that an enhanced miscibility and a better phase dispersion have been obtained by combining both components as IPN's.

Behaviour of semi-1 IPN's with various PUR contents: it is interesting to compare PUR/PAc semi-1 IPN's, where the hard phase is not crosslinked, to the corresponding full IPN's (5% TRIM), for various PUR contents. As a matter of fact, a discontinuity in the transition values appears (see for example *Table 2*), and it seems that even small crosslinker amounts change considerably the relaxation behaviour of the material. All the corresponding results are listed in *Table 3*. The lower T_g, corresponding to the PUR phase, is shifted upwards by about 20°C with regard to the pure network, but contrary to the full IPN's, its position does not change with the composition: the PAc network seems to restrict the mobility of the PUR more than the linear PMMA, and here the interpenetration effect is obvious. The value of the upper T_g varies with the PUR content, but less than in the full IPN's (20° against 40°C), indicating that the hard phase, when it is linear is less affected by the PUR network. Whereas the lower tan δ values are identical, the upper ones reflect at least in part the effect of crosslinking, which damps more severely the loss peaks[11]. The measurement of the width at mid-height of the loss peaks gives also an indication about the miscibility of the two components, as in incompatible blends, the peaks are always sharper[13]. *Table 4* shows that the broadening is more important for the IPN's, which represent a higher degree of entanglement of both phases than the semi-IPN's. Finally, it should be mentioned that other marked differences exist between full and semi-IPN's. So, the kinetics of formation, the transparency and the mechanical properties are considerably affected by the degree of crosslinking of the second phase[8,14]. Allen *et al.*[5] also observed well defined PUR loss peaks in similar PUR/PMMA semi-1 IPN's.

D.s.c. measurements

The change in heat capacity at the transition zone is

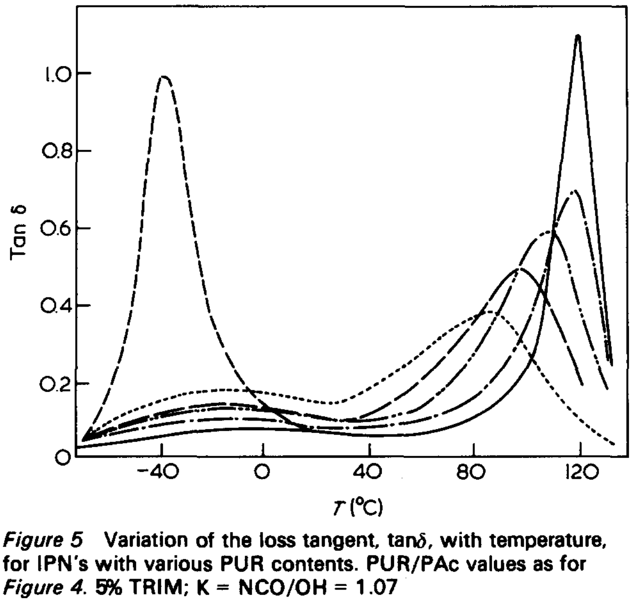

Figure 5 Variation of the loss tangent, tanδ, with temperature, for IPN's with various PUR contents. PUR/PAc values as for *Figure 4*. 5% TRIM; K = NCO/OH = 1.07

Table 3 Lower and upper transitions and loss tangent for IPN's and semi-1 IPN's with various PUR contents

Sample	Lower T_g (°C) and $\tan\delta$				Upper T_g (°C) and $\tan\delta$			
PUR/PAc	IPN		semi-IPN		IPN		semi-IPN	
0/100	1[a]	0.08[a]	–	–	122	1.1	–	–
15/85	0	0.09	–20	0.1	117	0.69	110	0.91
25/75	– 7	0.12	–20	0.12	108	0.55	110	0.95
34/66	–10	0.14	–23	0.14	100	0.53	100	0.73
40/60	–15	0.15	–20	0.15	98	0.43	103	0.30
50/50	–15	0.19	–20	0.18	79	0.37	90	0.48
100/0	–40	1.05	–40	1.05	–	–	–	–

$\omega = 0.1$ rad s^{-1}
IPN's are crosslinked with 5% TRIM
[a] β peak of PMMA

Table 4 Width at mid-height for the upper loss tangent peaks of IPN's and semi-IPN's with various PUR contents

Sample	15/85	25/75	34/66	40/60	50/50
IPN	42.5	53	54	72.5	76
Semi-IPN	24	31.5	36	34.5	55

Results in degree Celsius

Table 5 Transition temperatures for IPN's and related samples by d.s.c.

Sample	Lower transition (°C)	Upper transition (°C)
PMMA crosslinked (5% TRIM)	–	111
PUR (K = 1.07)	–62	–
Physical blend	–61	111
IPN	–64	38 to 48
	–27 to –24	77 to 86
		~120

Physical blends and IPN's contain 34% PUR

satisfactorily high for the individual networks, so that the corresponding temperature may be determined easily. This is not the case for the IPN's, where the transition zone extends over a quite large temperature range and the discontinuity of the base line is very difficult to observe. In order to check if the too small change was not due to a lack of sensitivity of the apparatus, physical blends with the same PUR content as in IPN's (34%) were prepared and tested in identical experimental conditions. As it appears from *Table 5*, the physical blends show two transition temperatures corresponding to those of the individual networks. This observation confirms that in an IPN, the phases exist in a different, more dispersed state than in the blend. Thus, there is a true interpenetration effect. From the very slight variations in the d.s.c. curves of the IPN's, it was possible to detect a transition zone, but the accuracy is low. It seems that some new transitions exist in the IPN's as compared to the individual networks: around –27° to –24°C in the lower range, and two transitions (38° to 48°C, and 77° to 86°C) in the upper temperature range. Though these transitions cannot yet be ascribed to a particular phase arrangement, the temperature shift is important and indicates partial interpenetration. A similar behaviour has been reported by Klempner *et al.* and attributed to the physical interlocking of the two polymer chains[15].

Thermally stimulated depolarization

T.s.d. results will be fully reported in a forthcoming paper, but it seemed interesting to compare them to those obtained by d.m.s. and d.s.c. This method reveals more transitions than the two other ones (*Table 6*), but all of them do not correspond to glass transitions. For pure PMMA, the peak at –40°C is the β relaxation peak, another peak appears at 120°/130°C, a temperature which is a little higher than for linear PMMA (115°C)[16]. The PUR network shows also a peak at –40°C: it is, however, markedly more important than the β relaxation of PMMA. Two more groups of peaks appear at –25°/–10°C and 40°/50°C: as yet, they have not been assigned to a particular chain motion. The IPN containing 34% PUR has two transitions in the lower temperature range, at –46° and –35°C; it is difficult to state whether the first belongs to a less complete PUR network or not. Two more transition zones appear near 13°/21°C and 45°/55°C. Finally, the peaks around 130°/140°C coincide with the ones obtained for the PAc network.

Comparison of the results obtained by the three methods

In *Table 6* are listed the different transitions observed for the individual networks and for a 34/66 IPN ($K = 1.07$; TRIM = 5%), by using d.s.c., d.m.s. and t.s.d. It cannot be expected to find the same values by all these methods, as more or less peaks appear and as the transitions may be shifted on the temperature scale[17]. For example, for the β peak of PMMA, the temperatures are –40°C (t.s.c.) and +1°C (d.m.s.). Considering now the IPN's, two peaks are always found by mechanical spectroscopy, but in fact, they consist of very broad transition zones. T.s.d. yields more and sharper peaks, however it may be assumed that they are contained in the transition zones of d.m.s. spectra. D.s.c. too gives heat capacity changes extending over a large temperature scale. The three methods confirm more or less a lower and an upper transition. The intermediate peaks are more difficult to interpret in the present state of this work: the maximum at –10°C (d.m.s.) roughly corresponds to –27°C (d.s.c.) and perhaps to the peaks shifted at 13° and 21°C as compared to –25° and –10°C (t.s.d.) for the PUR network. These transitions can therefore be ascribed to this phase, as well as the ones near 40°/50°C. Further studies are necessary to elucidate completely the experimental results.

Table 6 Comparison of the transitions given by d.s.c., d.m.s. and t.s.d. experiments

Sample	Method	Transition (°C)					
PUR (K = 1.07)	d.s.c.	−62					
	d.m.s.	−40					
	t.s.d.	−40	−25; −10		40; 50		
PMMA (cross. 5% TRIM)	d.s.c.						111
	d.m.s.			1			122
	t.s.d.	−40					120; 130
IPN(34% PUR)	d.s.c.	−64	−27		38/48	77/86	~120
	d.m.s.		−10				100
	t.s.d.	−46; −35		13; 21	45; 55		130; 140

D.s.c.: differential scanning calorimetry; d.m.s.: dynamic mechanical spectroscopy; t.s.d.: thermally stimulated depolarization

(t_1; t_2): two peaks or one peak with shoulder

(t_1/t_2): transition from t_1 to t_2 (lack of accuracy)

CONCLUSION

To conclude, we should like to show how the present results are corroborated by previous findings on PUR/PAc IPN's. The study of the transition behaviour has established that phase separation exists, but that the mutual miscibility of PUR and PAc is increased by combining them as interpenetrated networks. The important parameters are the quality of the PUR network, through the value of K, and the degree of crosslinking of the PAc phase. So far, changing the composition of the IPN's has not yielded any unexpected behaviour.

These conclusions are confirmed by our previous studies on the physical characteristics and on some mechanical properties of PUR/PAc IPN's. At a given composition, an uncompletely formed PUR network leads to less transparency, lower ultimate elongation and higher impact strength for the IPN. The pendent and the free polyether glycol chains, which are clearly shown by a new peak in the loss curves for $K<1$, are responsible for these changes. The degree of crosslinking of the second network, governed by the TRIM %, induces changes in the properties of the IPN's: the swelling degree and the ultimate elongation decrease with increasing crosslink density. The importance of crosslinking the second phase appears fully by the comparison between the IPN's and the corresponding semi-1-IPN's[14]: even a low crosslink degree (1% TRIM) yields materials with properties different to those where the second component remains linear. The effect of crosslinking the hard phase on the properties establishes also that the PAc network must be continuous through the PUR matrix, at least to some extent.

Presently, morphological studies are being carried out, which should complete all these conclusions and allow us to establish a relationship between the structure and the properties of PUR/PAc IPN's.

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