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Morphologies and mechanical properties of polyblends of polyurethane with poly(4,4′-diphenylsulphone terephthalamide)

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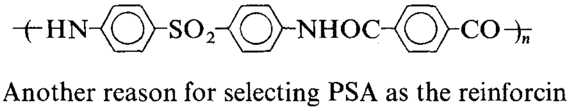
Two polyurethane (PU) elastomers were blended physically with various ratios of poly(4,4′-diphenylsulphone terephthalamide) (PSA) to form eight PU/PSA polyblends in order to modify their mechanical properties. The stress–strain and stress–relaxation behaviour of PU/PSA polyblends were studied. The measured values of Young's modulus, E, Mooney–Rivlin elastic parameters, C_1 and C_2, relaxation moduli, $E(10\ \mathrm{s})$ and $E(100\ \mathrm{s})$, as well as relaxation speed, V_r, were used to estimate the effect of semi-rigid PSA molecules on the mechanical behaviour of polyblends. It was found that PU/PSA polyblends still displayed good elastic properties, although PU/PSA polyblends had a dispersed phase structure. At lower of PSA contents (below 10 wt% PSA), PU/PSA polyblends showed improved stress–relaxation properties.

1. Introduction

Polymer blends had received much attention in recent years due to the possibility of obtaining compounds with novel and/or different properties through proper marriage of the properties of the respective monocomponents. They are important in at least two major areas of application. First, a rigid phase can be added to a rubber to increase its strength and decrease its tendency to flow or to undergo permanent deformation under a load [1–3]. Second, a rubbery phase can be added to a brittle polymer to increase the toughness and elongation at breakpoint of a brittle polymer [4–7]. Polymer blends are a major topic in the research and development laboratories of the large plastics manufacturers. PU-based polyblends generally have a thermoplastic hard component, such as ABS and PVC [8, 9], added to them to increase their tensile strength, initial modulus, and also impact strength and dimensional stability. According to Howe [10], ABS resin might be used as a second component to reduce the costs of PU without deteriorating its original properties. Thermofil Inc. have consequently manufactured a PU/ABS polyblend, which could be used for making goods such as take-ups for cinematographic projectors. These blends have a very good resistance to abrasion [11].

In this study, a wholly aromatic PSA was selected as a reinforcement part for PU for strengthening the mechanical and thermal properties of PU, owing to its excellent solubility [12, 13] and thermal stability [14]. The chemical structure of PSA is



Another reason for selecting PSA as the reinforcing element was that it could readily form a strong intermolecular hydrogen bond with PU and therefore a good molecular compatibility could be expected.

2. Sample preparation and experiments

2.1. Materials

Polytetramethylene glycol (PTMG 1000 and 2000), 4,4′-diphenylmethane diisocyanate (MDI), 4,4′-diaminodiphenyl sulphone (DDS) and terephthaloyl dichloride (TPC) were used as-received. *N*-Methyl-2-pyrrolidone (NMP) and 4.4′-dimethylacetamide (DMAc) were distilled over CaH_2 at 93–94 °C/14 mm Hg and then stored in molecular sieves. Lithium chloride (LiCl) was dried under vacuum at 160 °C for 5 h.

2.2. Synthesis of polyurethanes

Polyurethanes were prepared by the following procedures. In a 250 ml five-necked flask equipped with a droping funnel, a nitrogen gas inlet, a mechanical stirrer and a thermometer, 12.5 g (50 mmol) 4,4′-diphenylmethane diisocyanate (MDI) was dissolved in 30 ml dimethyl acetamide (DMAc) and then heated to 65 °C. Then 25 mmol polytetramethylene glycol (PTMG) in 15 ml DMAc was slowly added to the solution with vigorous stirring over a period of 30 min. The temperature was further raised to 70 °C. The reaction time was varied according to the molecular weight of PTMG. For a molecular weight of 1000 or 2000, a reaction time of 40 or 60 min was used, respectively. Finally 2.25 g (25 mmol) 1,4-butanediol(BD) in 5 ml DMAc was added slowly and allowed to react at 80 °C for 45 min. The solution was slightly cooled and continually stirred for 90 min. The polyurethanes were thus obtained [15].

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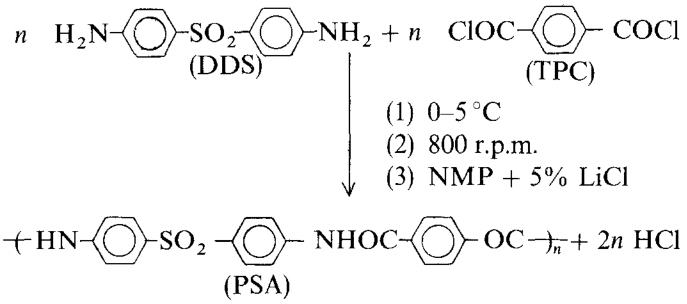
2.3. Synthesis of poly(4,4′-diphenylsulphone terephthalamide) (PSA)

PSA polymer was prepared by low-temperature polymerization of 24.8 g (100 mmol) 4,4′-diaminodiphenyl sulphone (DDS) with 20.3 g (100 mmol) terephthaloyl dichloride (TPC) in 200 ml *N*-methyl-2-pyrrolidone (NMP) containing 5% LiCl, at a stirring rate of 800 r.p.m. as shown below [13]



The molecular weight and logarithmic viscosity number of these polymers are given in Table I. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by Waters gel-permeation chromatography (GPC). The polymer solution was first quenched in distilled water and dried in a vacuum oven for 2 days at 50–60 °C. The solid polymer was then dissolved in dimethylformamide (DMF) containing 0.05 mol^{-1} LiBr to make a 0.54% solution. The function of LiBr was to prevent the aggregation of polymers by increasing polymer/solvent interaction. The column set (μ. Bondagel E-Linear) was calibrated with a monodisperse polystyrene standard at a flow rate of 1 ml min^{-1}.

2.4. Preparation of polyblends of PU with PSA

Two polyurethane elastomers (PU-1000-BD and PU-2000-BD) were blended physically with various ratios (5%, 10%, 15% and 20%) of PSA to form eight PU/PSA polyblends. The mixture was dissolved in DMAc and stirred vigorously. Then the solutions were cast on a glass plate and dried under vacuum at 80 °C for 16 h to prepare the films. The compositions of the PU/PSA polyblends are shown in Table II.

2.5. Measurements

Infrared spectra of PU and PSA were obtained using an Hitachi Model 260-50 Type, over the range 250–4000 cm^{-1}. These samples were in the form of a film about 10 μm thick. A scanning electron microscope, Cambridge Steroscan-600, was also used to examine the morphological structure of samples which were sputter-coated with gold to prevent their oxidation. The density of the samples was measured at 25 °C by a density gradient method using toluene–carbon tetrachloride mixtures.

Extension stress–strain measurements were performed on the Instron 1122 Type. Strips of samples of approximate dimensions 50 mm × 50 mm × 2 mm were continuously extended at a low constant crosshead speed of 5 mm min^{-1} up to an elongation of about 200%. The increasing value of the tensile forces was recorded on the moving chart. The measurements were carried out at 60 and 80 °C.

Stress–relaxation experiments were also performed on the Instron 1122 Type. Samples of approximate dimensions 50 mm × 50 mm × 2 mm were rapidly extended at a crosshead speed of 500 mm min^{-1} to an elongation of 40%. The strain was maintained constant throughout the experiment. The changing value of the tensile force was recorded on a moving chart. The stress–relaxation behaviour was investigated at a temperature of 60 °C. The relaxation moduli, $E(t)$, were calculated using

$$E(t) = f(t)\varepsilon^{-1} \qquad (1)$$

where $f(t)$ is the stress at time t, related to the initial cross-sectional area, and ε is the deformation.

3. Results and discussion

3.1. Analysis of infrared spectra

Infrared spectra were obtained using the thin film technique. The transmission infrared spectra of polymers are shown in Fig. 1. The infrared spectrum of

TABLE I The molecular weight and logarithmic viscosity of polymers

Polymer	Molecular weight by GPC			
	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	η_{inh}
PU-1000-BD[a]	3.48	5.33	1.53	0.40[b]
PU-2000-BD	3.08	5.13	1.67	0.38[b]
PSA	7.31	14.41	1.97	0.60[c]

[a] Polyurethane: molar ratio, PTMG/MDI/1,4-BD = 1/2/1.
[b] Conditions: solvent (DMAc), temperature (25°C).
[c] Conditions: solvent (98% conc. H_2SO_4, temperature 30°C).

TABLE II The compositions of PU/PSA polyblends

Code	Polyblends	PSA (wt %)
A1	PU-1000-BD/PSA	0
A2	PU-1000-BD/PSA	5
A3	PU-1000-BD/PSA	10
A4	PU-1000-BD/PSA	15
A5	PU-1000-BD/PSA	20
B1	PU-2000-BD/PSA	0
B2	PU-2000-BD/PSA	5
B3	PU-2000-BD/PSA	10
B4	PU-2000-BD/PSA	15
B5	PU-2000-BD/PSA	20

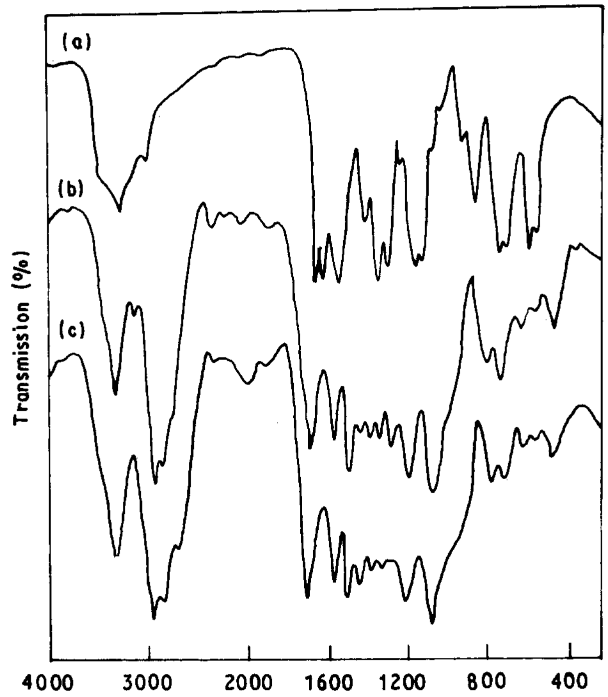


Figure 1 Infrared spectra of polymers: (a) PSA; (b) PU-1000-BD; (c) PU-2000-BD.

PSA is characterized at 3400 cm^{-1} (–NH– stretching vibration), 1680 cm^{-1} (C=O), 1610 and 1540 cm^{-1} (C–C), 1340 cm^{-1} (–SO$_2$–), whereas the characteristic infrared spectra of polyurethanes are shown at 3400 cm^{-1} (–NH– stretching vibration), 1700 cm^{-1} (C=O), 2940 cm^{-1} (–CH– stretching vibration), and 1560 cm^{-1} (–NH– deformation) absorptions.

3.2. Morphological observation by SEM, and the densities

The scanning electron microscope was used to visualize the microstructure of polyblends. It is seen in Fig. 2 that although pure PU-1000-BD (A1 sample; 0 wt % PSA) appeared to have a uniform surface structure, their blends showed a grain size which increased with increasing amounts of PSA added (Fig. 2b). The grain particles were considered to be the aggregation of PSA molecules. With a content of 20 wt % PSA, the blend (A5 sample) exhibited larger size grains from 3–5 µm diameter (Fig. 2c). Similarly, the morphology of other polyblends was also found to behave in the same way.

The densities of the polyblends are given in Fig. 3 and Table III, respectively. In Fig. 3, the densities of the blends were found to increase initially and then decrease as the proportion of PSA was increased. This is due to the competitive effect of the compactness of semi-rigid PSA and its structural aggregation. At lower amounts of PSA (below 10 wt % PSA), the aggregation of PSA was small. Owing to the increase in the intermolecular hydrogen bonding between semi-rigid PSA and the hard butyl segment (the short (MDI-BD) polyurethane segment), densities increased. Moreover, in the blends with higher amounts of PSA (more than 10 wt % PSA), the aggregation of PSA molecules became more pronounced and exhibited a clear phase-segregation structure (as seen in Fig. 2c) to make a weak adhesive interface between PSA and PU, which resulted in lower densities.

3.3. Discussion of stress–strain and stress–relaxation behaviour

For all PU/PSA polyblends, the stress (f)–strain (ε) plots were not linear. Fig. 4 shows the typical stress–strain curves of the blends (A series samples). In order to obtain the Young's moduli, $E, f\lambda$ was plotted versus ε, where λ is the principal extension ratio, which equals $\varepsilon + 1$, yielding good linear relationships as seen in Fig. 5. The Young's moduli, E, were calculated from the slopes of these plots. The moduli, E, increased with increasing amount of semi-rigid PSA molecules. All the E values at 60 °C were higher than those measured at 80 °C. From the chemical structure it is known that PU/PSA polyblends possess a high degree of hydrogen bonding. When the temperature was increased by about 50 °C, hydrogen bonding dissociated readily with other secondary bonds [16–20]. As the temperature increased, those secondary bonds disappeared, causing the drop in values. B series samples exhibited the same behaviour as A series ones.

In order to describe clearly the extension behaviour of PU/PSA polyblends, the theory of rubber elasticity was used. The equation was expressed as [21]

$$f = G^*(\lambda - \lambda^{-2}) \qquad (2)$$

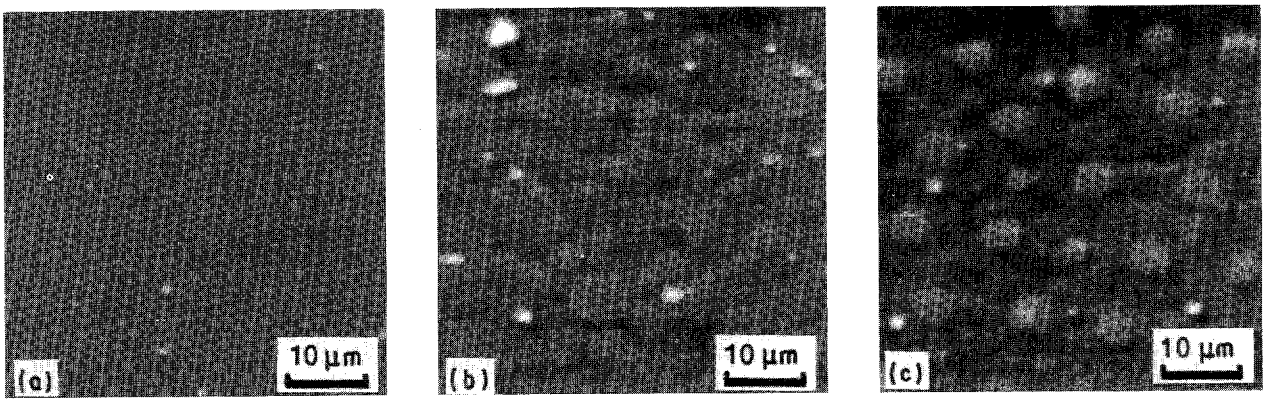


Figure 2 SEM observations of PU-1000-BD/PSA series polyblends containing various amounts of PSA: (a) A1 (0 wt % PSA); (b) A3 (10 wt % PSA); (c) A5 (20 wt % PSA).

TABLE III Densities of polyblends

Polymer	PSA (wt %)					
	0	5	10	15	20	100
PU-1000-BD/PSA	1.082	1.098	1.127	1.124	1.094	–
PU-2000-BD/PSA	1.041	1.051	1.067	1.045	1.040	–
PSA	–	–	–	–	–	1.282

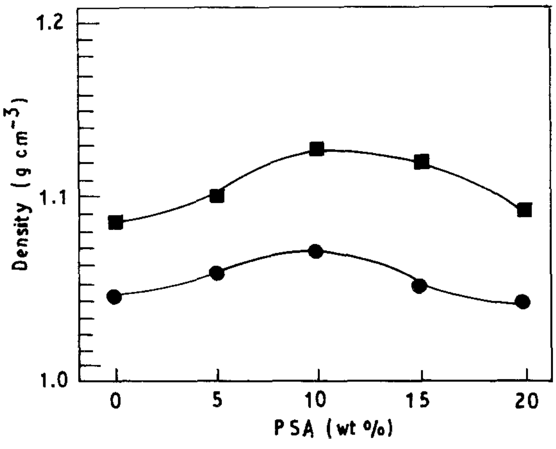


Figure 3 Densities of PU/PSA polyblends: (■) PU-1000-BD/PSA series; (●) PU-2000-BD/PSA series.

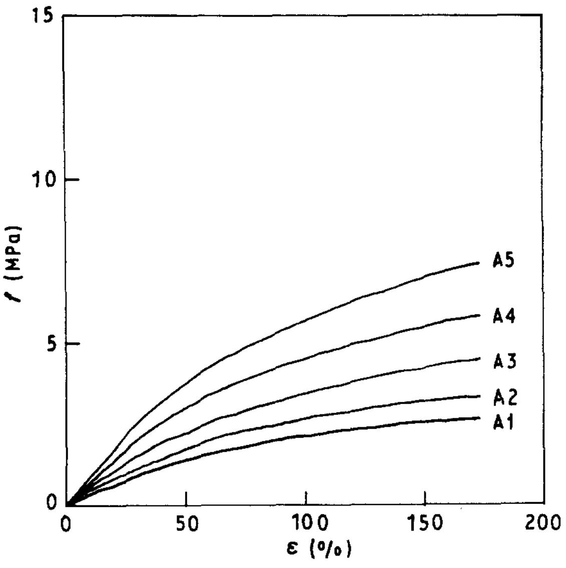


Figure 4 Stress–strain dependence for Samples A1–A5 at 60 °C.

where G^* is the shear modulus. According to the theoretical equation $f/(\lambda - \lambda^{-2})$ was plotted versus λ, and a straight line approximately parallel to the λ axis was obtained. Although the plots began with a rapid non-linear decrease in values of $f/(\lambda - \lambda^{-2})$, when λ increased, the plots became linear with slight slopes as seen in Fig. 6. The shear moduli, G^*, were obtained from the linear part of these plots extrapolated to $\lambda = 1$ and then converted to E^* values using the expression $E = 3G$ [21]. From Table IV it can be seen that E^* values are in good agreement with the values of E, the former being a few per cent smaller than the latter. It is indicated that PU/PSA polyblends were behaving in a rubber-like elastic manner.

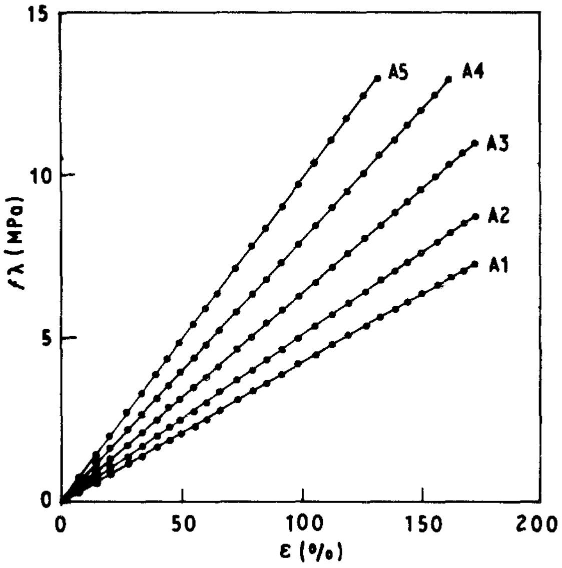


Figure 5 Stress–strain dependence in terms of $f\lambda$ versus ε for Samples A1–A5 at 60 °C.

Mooney–Rivlin plots were done from the extension stress–strain measurements to calculate the values of the elastic parameters C_1 and C_2 of the Mooney–Rivlin equation [22]

$$f = (C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \qquad (3)$$

All PU/PSA polyblends yielded good Mooney–Rivlin plots. A series of samples is shown in Fig. 7, in which straight lines are obtained as λ^{-1} increases. This indicates that the elastic properties of the blends predominated. Both C_1 and C_2 increased with increasing semi-rigid PSA molecule concentration. The results are shown in Table V.

Equations 2 and 3 may be combined to form the well-known expression $G = C_1 + C_2$, and hence $E = 3(C_1 + C_2)$. From Table VI was found that the values of $3(C_1 + C_2)$ were about 20% larger than the E values. The ratio C_2/C_1 is often taken as an important variable characterizing departures from ideal elasticity [23], as well as a relative measure of intermolecular interaction. The C_2/C_1 ratio hardly increased with increasing semi-rigid PSA segment concentration.

To evaluate the influence of the amount of semi-rigid PSA segments and the molecular weight of PTMG on the stress–relaxation properties of polyblends, the 10 and 100 s moduli, $E(10\text{ s})$ and $E(100\text{ s})$, were estimated and the values of $V_r = [E(10\text{ s}) - E(100\text{ s})]/E(10\text{ s})$, which can be taken as a qualitative measure of the relaxation speed, were calculated for the blends at 60 °C. The results obtained are listed in Table VI. With lower amounts of PSA molecules

TABLE IV The mechanical properties of PU/PSA polyblends measured at 60 and 80 °C

Code	60 °C			80 °C		
	E (MPa)	E^* (MPa)	$3(C_1 + C_2)$ (MPa)	E (MPa)	E^* (MPa)	$3(C_1 + C_2)$ (MPa)
A1	4.19	4.09	5.22	3.82	3.75	4.79
A2	5.10	4.95	6.39	4.66	4.53	5.88
A3	6.32	6.21	8.04	5.96	5.86	7.51
A4	8.02	7.83	10.17	7.20	7.02	9.20
A5	9.98	9.81	12.62	9.17	9.06	12.03
B1	3.64	3.57	4.47	3.21	3.18	3.99
B2	4.48	4.41	5.58	4.06	3.93	5.10
B3	5.34	5.30	6.84	4.99	4.86	6.33
B4	6.88	6.75	8.79	6.14	6.03	7.83
B5	8.76	8.61	11.10	7.87	7.74	10.05

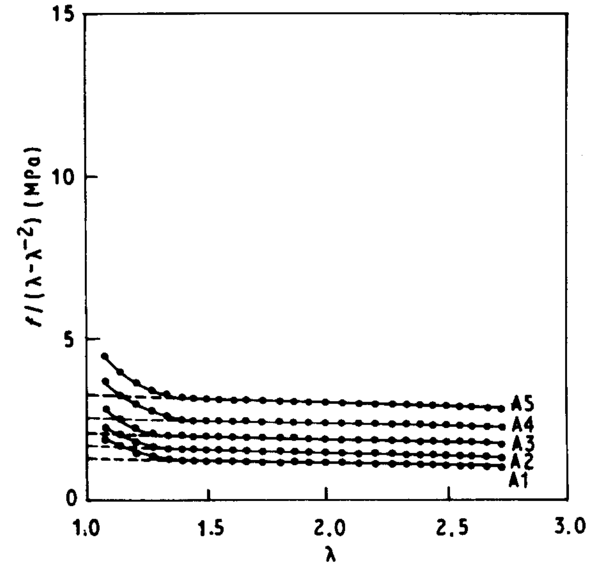


Figure 6 Stress–strain dependence in terms of $f/(\lambda - \lambda^{-2})$ versus λ for Samples A1–A5 at 60 °C.

TABLE V Mooney–Rivlin elastic parameters of PU/PSA polyblends measured at 60 and 80 °C

Code	60 °C			80 °C		
	C_1 (MPa)	C_2 (MPa)	$\frac{C_2}{C_1}$	C_1 (MPa)	C_2 (MPa)	$\frac{C_2}{C_1}$
A1	0.76	0.98	1.30	0.68	0.92	1.34
A2	0.89	1.24	1.39	0.81	1.15	1.42
A3	1.11	1.57	1.42	1.01	1.49	1.48
A4	1.41	1.98	1.40	1.25	1.82	1.46
A5	1.75	2.45	1.40	1.63	2.37	1.45
B1	0.66	0.83	1.26	0.58	0.75	1.29
B2	0.86	1.06	1.33	0.72	0.98	1.36
B3	0.96	1.32	1.38	0.88	1.23	1.40
B4	1.23	1.70	1.38	1.10	1.51	1.37
B5	1.56	2.14	1.37	1.42	1.93	1.36

TABLE VI Stress–relaxation properties of PU/PSA polyblends measured at 60 °C

Code	E(10 s) (MPa)	E(100 s) (MPa)	V_r[a]
A1	5.16	4.14	0.198
A2	5.94	4.97	0.163
A3	7.25	6.31	0.130
A4	7.89	6.81	0.137
A5	10.38	8.85	0.149
B1	4.51	3.64	0.193
B2	5.33	4.50	0.156
B3	6.24	5.46	0.125
B4	7.57	6.59	0.129
B5	9.37	8.08	0.138

[a] $V_r = [E(10\text{ s}) - E(100\text{ s})]/E(10\text{ s})$.

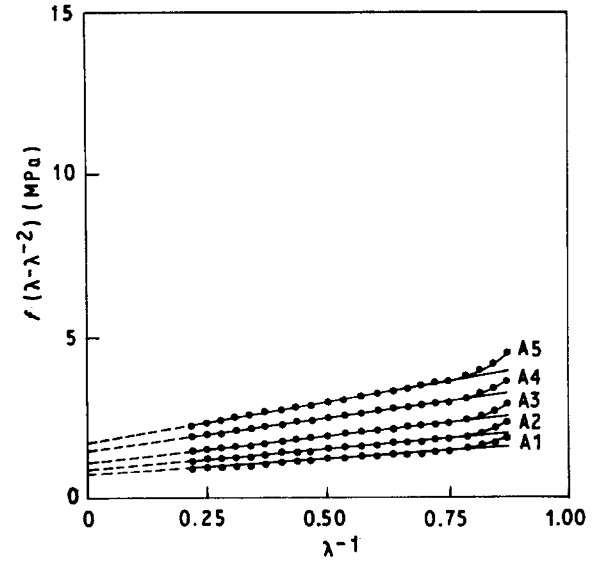


Figure 7 Mooney–Rivlin plots for Samples A1–A5 at 60 °C.

(below 10 wt % PSA), the moduli E(10 s) and E(100 s) apparently increased with increasing amount of semi-rigid PSA segments, and the relative relaxation speed, V_r, decreased. The drop in V_r values was supposedly caused by the influence of the semi-rigid PSA segment content on the disappearance of viscoelastic properties, and especially with a molecular weight of 2000, PTMG exhibited a more elastic behaviour. However, with higher amounts of PSA (more than 10 wt % PSA), PU/PSA polyblends exhibited a pronounced two-phase structure producing a weak adhesive work of the interface, and the V_r values increased. The phenomenon agrees with previous results of the densities and morphological observations by SEM.

5. Conclusions

The mechanical properties of PU/PSA polyblends were found to be influenced strongly by the temperature. From the stress–strain measurements it was evident that the blends yielded good Mooney–Rivlin plots. The values of $3(C_1 + C_2)$ were about 20% larger than those of E and E^*. At lower contents of PSA (below 10 wt % PSA), PU/PSA polyblends still displayed good elastic properties, although PU/PSA polyblends exhibited a dispersed phase structure.

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