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Mechanical behaviour of block copolymers of polyurethane with poly (4,4′-diphenylsulphone terephthalamide)

MING-FUNG LIN, HUEI-HSIUNG WANG, KAI-RHEN SHIAO
Graduate School of Textile Engineering, Feng Chia University, Taichung. 40724, Taiwan, R.O.C.

Two poly (tetramethylene glycols) (PTMG), molecular weight of 650 and 2000, with 4,4′-diphenylmethane diisocyanate (MDI) and poly(4, 4′-diphenylsulphone terephthalamide) (PSA) prepolymer were polycondensated. Four different molar ratios of PTMG, MDI and PSA prepolymer were synthesized to form eight PU-PSA block copolymers. The mechanical properties including stress–strain and stress–relaxation measurements of each copolymer were discussed. The determined values of Young's modulus E, Mooney–Rivlin relation elastic parameters $C1$ and $C2$, relaxation moduli $E1(0)$ and $E2(0)$, relaxation time $\tau1$ and $\tau2$ were used to estimate the effect of hard segment and soft segment domains on the mechanical behaviour of copolymers. It was found that PU-PSA block copolymers apparently displayed elastic properties, especially using the molecular weight 2000 of PTMG which exhibited more elastic behaviour.

1. Introduction

Polyurethane may be described as linear block copolymers composed of relatively immobile regions, short urea or urethane segments connected to flexible and long polyester or polyether chains. The soft segments provide the flexible character of polyurethane, while the degree of molecular association with the hard segments results in pseudocrosslinks that provide restraining forces which result in the elastomeric properties of polyurethane. Due to the polar nature of the urethane or urea groups in the hard segments, these polymers possess considerable hydrogen bonding capabilities for both intra- and intersegment interaction [1–4]. As hydrogen bonding and other secondary attractive forces contribute much to the mechanical properties of polyurethanes, their mechanical behaviour strongly depends on temperature. With increasing temperature, rapid degradation of the mechanical properties took place, which is caused by breaking of hydrogen and other secondary bonds.

The deformational behavior of polyurethanes are also influenced by viscoelastic properties, whose contribution depends on the chemical structure and morphology of polyurethanes. Stress–relaxation measurement is a particularly good static method for the research of viscoelasticity. It enables the investigation of the processes of breaking and rebuilding polyurethane networks as well as changes occurring in supermolecular structure.

The purpose of the present study was to examine the effect of different molecular weights and of changing their molar ratios on the tensile and stress-relaxation properties of PU-PSA block copolymers.

2. Experimental

2.1. Materials

Poly(tetramethylene glycols) (PTMG 650, 2000) were kindly provided by Evermore Chemical Industry Co. 4,4′-Diphenylmethane diisocyanate (MDI) was supplied by San Fang Chemical Industry Co. Both 4,4′-diaminodiphenyl sulphone (DDS) and terephthaloyl dichloride (TPC) were purchased from Merck Co., and used as received. *N*-Methyl-2-pyrrolidone (NMP) and 4,4′-dimethyl acetamide were first distilled over CaH_2 at 92–94 °C/14 mmHg and then stored in the molecular sieves. Lithium chloride (LiCl) was dried under vacuum at 160 °C for 5 h.

2.2. Preparation of PSA prepolymer

Low molecular weight of amine-terminated PSA prepolymer was first prepared by low-temperature polycondensation of 10.2 g (50 mmol) TPC with 24.8 g (100 mmol) DDS. The inherent viscosity of PSA prepolymer in 98% concentrated sulphuric acid was 0.04 dl g^{-1} at 30 °C. The average molecular weight ($\bar{M}n$) was about 600 which was measured by gel-permeation chromatography. The reaction scheme is shown in Fig. 1 [5–8].

2.3. Synthesis of PU-PSA block copolymers

The preparation of the various PU-PSA block copolymers was carried out by solution polymerization in DMAc. Samples were prepared by a standard two-step reaction. The five-necked flask, equipped with

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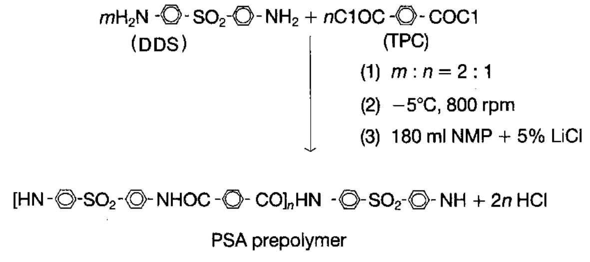

Figure 1 The reaction scheme of PSA prepolymer synthesis.

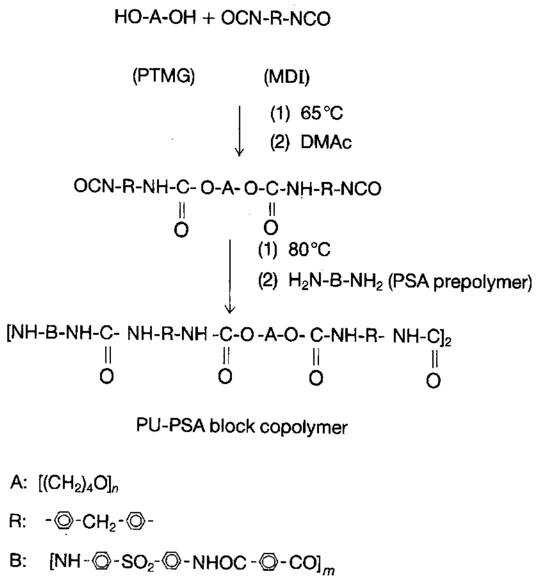

Figure 2 The reaction scheme of PU-PSA block copolymer synthesis.

TABLE I Components and molecular weight of PU-PSA block copolymers

Code	Main components	Molar ratio	$\bar{M}n \times 10^{-4}$	$\bar{M}w/\bar{M}n$
A1	650[a]:MDI:PSA	1:2:1	3.66	1.54
A2	650:MDI:PSA	1:3:2	3.69	1.54
A3	650:MDI:PSA	1:4:3	3.70	1.56
A4	650:MDI:PSA	1:5:4	3.82	1.59
B1	2000:MDI:PSA	1:2:1	4.12	1.51
B2	2000:MDI:PSA	1:3:2	4.08	1.60
B3	2000:MDI:PSA	1:4:3	4.16	1.48
B4	2000:MDI:PSA	1:5:4	4.23	1.55

[a] The molecular weight of PTMG.

a mechanical stirrer, thermometer, condenser, drying tube, and inert gas inlet, is purged by nitrogen for 30 min at 65 °C. 5 g (20 mmol) of MDI was dissolved in 30 ml DMAc and then 10 mmol of PTMG in 15 ml of DMAc was slowly added to the solution with vigorous stirring over a period of 1 h. The temperature was further raised to 70 °C. The reaction time was varied according to the molecular weight of PTMG. The molecular weight of 650 or 2000 and reaction time of 20 or 60 minutes was used respectively. Finally, 6 g (10 mmol) of PSA prepolymer in 30 ml of DMAc was added slowly and heated to 80 °C. After reaction for 2 h, the solution was slightly cooled and kept stirred for 90 min. The reaction scheme is shown in Fig. 2 [9, 10].

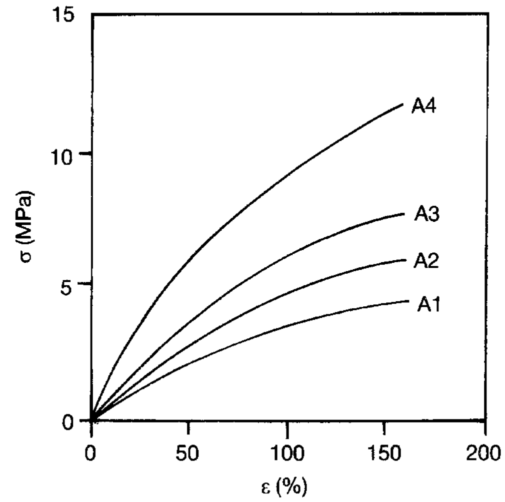

Figure 3 Stress–strain dependence for samples A1 to A4. Temperature 60 °C.

The molecular weight and inherent viscosity of the synthesis are given in Table I. The $\bar{M}n$ and $\bar{M}w/\bar{M}n$ were determined by Waters gel-permeation chromatograph, the solvent was 4,4′-dimethyl formamide (DMF) containing 0.05 mol^{-1} LiCl. The column was μ. BONDAGEL E-Linear which was calibrated at a flow rate of 1 ml min^{-1}.

3. Results and discussion

3.1. Analysis of stress–strain behaviour

For all PU-PSA block copolymers, the stress (σ)–strain(ε) curves were not linear. Fig. 3 shows the typical stress-strain curves of these copolymers (A series samples). In order to obtain Young's modulus E, $\sigma\lambda$ was plotted versus ε, where λ is the principal extension ratio, which equals $\varepsilon + 1$, yielding good linear relationships as seen in Fig. 4. Young's moduli E were calculated from the slopes of these plots. The moduli, E, increased with increasing amount of hard segments. All the E values at a temperature of 60 °C were higher than those measured at 80 °C. From the chemical structure, PU-PSA block copolymers possess a high degree of hydrogen bonding [11–13], like those of polyurethanes. When the temperature is raised about 50 °C, hydrogen bonds dissociate easily with other secondary ones [14, 15]. As the temperature increases, those secondary bonds disappear, causing the drop in values. B series samples had the same behaviour as A series ones. In order to describe clearly the extension behaviour of PU-PSA block copolymers, the theory of rubber elasticity was used. The equation was expressed as follows [16]

$$\sigma = RT\frac{ve}{V}(\lambda - \lambda^{-2}) \qquad (1)$$

where R is the gas constant, T is absolute temperature, and ve/V is the elastically effective crosslinking

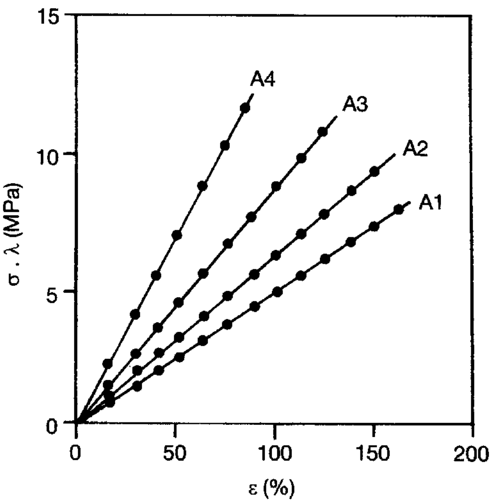

Figure 4 Stress–strain dependence in terms of σ. λ versus ε for samples A1 to A4. Temperature 60 °C.

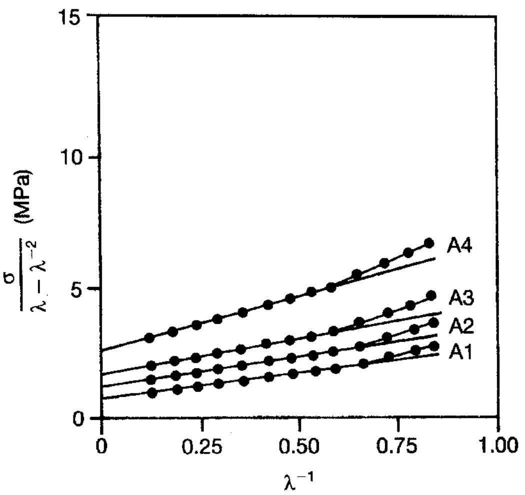

Figure 6 Mooney–Rivlin plots for samples A1 to A4. Temperature 60 °C.

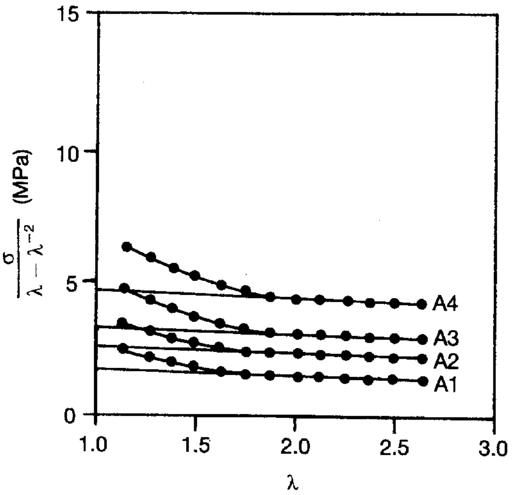

Figure 5 Stress–strain dependence in terms of $\sigma/(\lambda - \lambda^{-2})$ versus λ for samples A1 to A4. Temperature 60 °C.

density. According to the theoretical equation, $\sigma/(\lambda - \lambda^{-2})$ was plotted versus λ, and a straight line approximately parallel to the λ axis was obtained, though the plots began with a rapid nonlinear decrease in values of $\sigma/(\lambda - \lambda^{-2})$. When increased, the plots become linear with slight slopes as seen in Fig. 5. The shear modulus G^*, which equals $RT\ ve/V$, was obtained from the linear part of these plots extrapolated to $\lambda = 1$. For most rubber-like polymers including PU-PSA block copolymers, the E^* values are equal to $3G^*$ [17]. From Table II it was found that the E^* moduli were in good agreement with the E values; the former were a few percent smaller than the latter. It is indicated that PU-PSA block copolymers tend towards rubber-like elastic behaviour. Mooney–Rivlin plots, $\sigma/(\lambda - \lambda^{-2})$ versus λ^{-1}, were done from the extension stress-strain measurements to calculate the values of the elastic parameters $C1$ and $C2$ of the Mooney–Rivlin equation [18]

$$\sigma = (C1 + C2\lambda^{-1})(\lambda - \lambda^{-2}) \qquad (2)$$

All PU-PSA block copolymers yielded good Mooney–Rivlin plots, A series of samples are shown in Fig. 6, which became a straight line as λ^{-1} increased. It was indicated that these copolymers' elastic properties predominated. Both $C1$ and $C2$ increased with increasing hard segment concentration. The results are shown in Table III.

Equations 1 and 2 were combined to form the well-known expression $G = C1 + C2$, and hence $E = 3(C1 + C2)$. From Table III it was found that the values of $3(C1 + C2)$ were about 15% larger than the E values. The copolymers did not show any apparent dependence of $C2/C1$ ratio on the amount of hard segment. The $C2/C1$ ratio is often taken as important variable characterizing departures from ideal elasticity

TABLE II Stress-strain properties of PU-PSA block copolymers measured at 60 °C and 80 °C

Code	60 °C			80 °C		
	E(MPa)	E^*(MPa)	$3(C1 + C2)$(MPa)	E(MPa)	E^*(MPa)	$3(C1 + C2)$(MPa)
A1	5.66	5.52	6.54	5.44	5.04	6.33
A2	7.84	7.59	9.24	7.26	7.02	8.46
A3	9.50	9.38	11.64	9.10	8.64	10.50
A4	14.86	14.41	18.09	14.48	14.13	16.53
B1	4.62	4.53	5.58	4.05	4.29	5.25
B2	6.66	6.36	7.62	6.28	6.12	7.14
B3	8.30	8.05	9.42	8.02	7.89	9.06
B4	12.82	12.75	14.88	12.52	12.27	14.37

TABLE III Mooney–Rivlin elastic parameters of PU-PSA block copolymers measured at 60 °C and 80 °C

Code	60 °C			80 °C		
	C1(MPa)	C2(MPa)	C2/C1	C1(MPa)	C2(MPa)	C2/C1
A1	0.93	1.25	1.34	0.82	1.19	1.45
A2	1.27	1.81	1.43	1.09	1.73	1.59
A3	1.43	2.45	1.71	1.26	2.24	1.78
A4	2.51	3.52	1.40	2.29	3.22	1.41
B1	0.84	1.02	1.21	0.78	0.97	1.24
B2	0.91	1.63	1.79	0.86	1.52	1.76
B3	1.13	2.01	1.78	1.08	1.94	1.80
B4	1.92	3.04	1.58	1.82	2.97	1.63

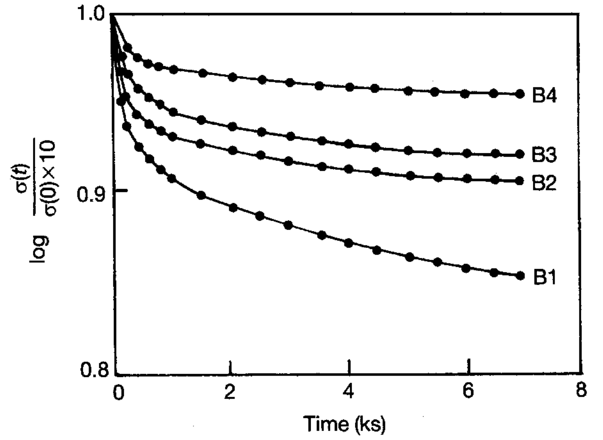

Figure 7 Stress–relaxation in terms of log ($\sigma(t)/\sigma(0) \times 10$) versus time for B1–B4 copolymers.

[19, 20], as well as a relative measure of intermolecular interaction. When the molecular weight 2000 PTMG was used, these copolymers (B series samples) exhibited more elastic behaviour.

3.2. Analysis of stress–relaxation behaviour

Tobolsky, *et al.* [22, 23] had already successfully researched the stress-relaxation behaviour of various elastomers. In this case, the stress-relaxation behaviour of PU-PSA block copolymers was investigated at a temperature of 60 °C. The relaxation moduli $E(t)$ were calculated using the following equation

$$E(t) = \sigma(t)\varepsilon^{-1} \quad (3)$$

where $f(t)$ is the tensile force at the time t, related to the initial cross-sectional area, and ε is the deformation. The isothermal stress-relaxation observed in various elastomers held at constant extension has usually been fitted to a simple Maxwell model, the behaviour of which is described by the following equation [24]

$$\sigma(t) = \sigma(0)\exp(-t/\tau) \quad (4)$$

or

$$E(t) = E(0)\exp(-t/\tau) \quad (5)$$

where $\sigma(0)$ is the tensile force measured initially at time t and $E(0)$ is the corresponding relaxation modulus and τ is the measured relaxation time constant. According to Equation 4, the plots of the form log $\sigma(t)/\sigma(0)$ versus time should be linear by logical analysis. However, a pronounced nonlinearity is apparent in all the plots, like the ones shown in Fig. 7 for B1–B4 copolymers, indicating that a simple Maxwell model does not adequately describe the relaxation behaviour of these copolymers and suggesting that the stress–relaxation data might better conform to a multi-Maxwell model expressed by the following equation [25]

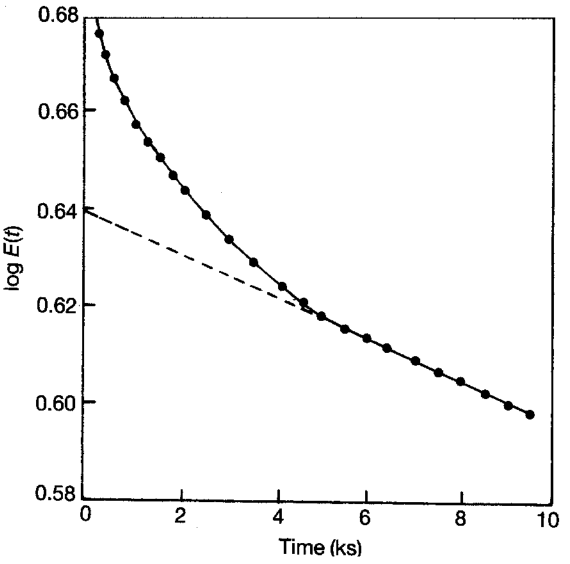

Figure 8 Dependence of log $E(t)$ versus time for B1 copolymer. Temperature 60 °C.

$$E(t) = \sum_{i=1}^{m} Ei(0)\exp(-t/\tau i) \quad (6)$$

in which the observed decrease of modulus results from the degradation processes, each acting as a Maxwell element characterized by its own component $Ei(0)$ in the relaxation modulus $E(t)$, and its own τi, termed the relaxation time. The concept of a multi-Maxwell model seems reasonable in view of the ever present possibility of inadvertently forming allophanate and biuret linkages in fabricating these copolymers. The simultaneous cleavage of these various type of linkages would probably contribute to the observed stress–relaxation behaviour.

The stress-relaxation parameters obtained for these copolymers were fitted to Equation (6) by means of a unique graphical analytical procedure which is illustrated in Fig. 8 for the data obtained at 60 °C for copolymer B1. Here, the straight line part of the plot of log $E(t)$ versus time is extrapolated to zero time. The straight line represents the contribution to the modulus relaxation of the slowest Maxwellian process, i.e., the one with the longest relaxation $\tau 1$. The intercept $E1(0)$ is established by the structural elements involved in the procedure. The value of $\tau 1$ is obtained from the slope of the line.

The plot of $\log[E(t) - E1(0)\exp(-t/\tau 1)]$ versus time also approaches a straight line as shown in Fig. 9. The values of $E2(0)$ and $\tau 2$ of the next relaxation process are calculated from the intercept and slope of this extrapolated line.

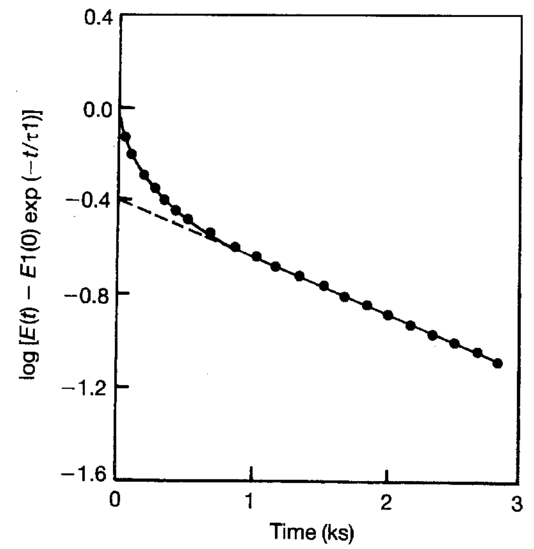

Figure 9 Dependence of log $[E(t) - E1(0)\exp(-t/\tau1)]$ versus time for B1 copolymer. Temperature 60 °C.

TABLE IV Stress-relaxation parameters of block copolymers at 60 °C

Code	$\tau g(ks)$	$\tau 1(ks)$	$\tau 2(ks)$	$E1(0)$(MPa)	$E2(0)$(MPa)
A1	10.6	63.0	1.40	5.25	0.479
A2	18.3	124.2	1.74	7.41	0.501
A3	38.2	310.6	1.67	9.06	0.552
A4	50.7	621.1	1.76	14.10	0.692
B1	22.9	98.8	1.61	4.37	0.398
B2	38.1	173.9	1.81	6.24	0.437
B3	52.6	395.3	1.79	7.94	0.516
B4	73.5	724.6	1.80	12.60	0.603

The data on these copolymers studied generally, conform to a three-component model. The stress-relaxation parameters derived for the two main components of the copolymer modulus relaxation curves are given in Table IV. The values for overall relaxation time τ_g were estimated from plots of $E(t)$ versus time. These represent the time required for the relaxation modulus to relax to 36.8% (1/e) of its initial values. Since the stress–relaxation properties of these copolymers examined do not conform to the elemental Maxwell model, the value of τ_g can only be considered as a convenient empirical parameter, characterizing The mechanical stability of the system. For all copolymers, in which hard segment content increases, an apparent increase in the relaxation parameters $E1(0)$ and $\tau 1$ of the slowest process, as well as the overall relaxation time τ_g can be observed. The relaxation time $\tau 2$ of the fast process is not influenced by hard segment amount and the parameter E2(0) increases slightly with an increase in the variables. The improvement in the stress-relaxation properties of copolymers B1–B4 was due to increased elasticity of soft segment domains. In the soft domains of these copolymers, the possibility of formation of ordered structure is smaller.

4. Conclusions

The mechanical properties of PU-PSA block copolymers were influenced strongly by temperature. From the stress–strain measurements it was evident that these copolymers yielded good Mooney–Rivlin plots. The values of $3(C1 + C2)$ were about 15% larger than the ones of E and E^*. PU-PSA block copolymers apparently displayed elastic properties, especially using the molecular weight 2000 of PTMG which exhibited more elastic behaviour. From the stress relaxation measurements results it was found that these copolymers did not fit a simple Maxwell model and might better conform to a multi-Maxwell model.

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