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 $C_1$ and $C_2$, relaxation moduli $E_1(0)$ and $E_2(0)$, relaxation time $\tau_1$ and $\tau_2$ 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 (Mn) 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
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].

The molecular weight and inherent viscosity of the synthesis are given in Table I. The Mn and Mw/Mn were determined by Waters gel-permeation chromatograph, the solvent was 4,4'-dimethyl formamide (DMF) containing 0.05 mol l⁻¹ LiCl. The column was 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, σλ was plotted versus ε, where λ is the principal extension ratio, which equals ε + 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]

\[
\sigma = RT \frac{ve}{V} (\lambda - \lambda^{-2})
\]

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