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Effect of soft/hard segments in poly (tetramethylene glycol)-Polyurethane for water barrier film

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ABSTRACT

A series of thermoplastic polyurethanes (TPUs) with the same molecular weight but different soft/hard ratios were synthesized by in-situ condensation polymerization using poly (tetramethylene glycol) (PTMG) as the polyol and methylene diphenyl diisocyanate (MDI) as the isocyanate. The weight fractions of the hard segments were varied from 0.0 to 0.4. The structures of the TPU series were analyzed by Fourier transform infrared spectroscopy and gel permeation chromatography. The changes in the thermal and optical properties due to the hard segment crystallinity were also measured by differential scanning calorimetry and UV–vis spectroscopy. Increasing the hard content promoted phase separation and served as absorption blocks in the TPU. The water vapor permeability of the TPU films with different soft/hard ratios ranged from 223.63 to 116.26 g/m^2 day.

1. Introduction

The moisture barrier treatment of a number of industrial end-products has been of considerable importance because of the difficulty of ensuring long-time reliability in electronic or bio-devices. Without a barrier film, they can be broken or corroded easily through the permeability of moisture. The development of a new barrier film that can resist moisture has attracted considerable interest in the past few years. Among other materials, polymeric materials are outstanding candidates owing to their great performance, such as high processability and high flexibility. Several materials can be used to impart water-resistant ability, such as carbon materials based on the polymer matrix [1–3].

Hydrophobic TPUs are prepared by a combination of hydrophobic poly (tetramethylene glycol) (PTMG) and 1, 4-butanediol (1,4-BD) as polyols, and methylene diphenyl diisocyanate (MDI) as the isocyanate component to optimize the moisture barrier properties without the loss of other physical properties. PTMG-blocked urethanes have been used frequently for encapsulation applications [4–10]. TPU composed of MDI and PTMG satisfies the lax requirements as a moisture-barrier due to mechanical degradation by penetrating liquids over long periods [11,12]. To analyze and overcome the drawback of standard PTMG-blocked TPU in barrier-film applications, the soft/hard segments dependence of the property-structure relationships in the TPU should be evaluated in terms of the mechanical and thermal properties at the same molecular weight (MW). The incorporation of PTMG/1, 4-BD as soft/hard blocks to produce a TPU copolymer might impart interesting bulk and surface properties because of the characteristics of the soft/hard segments.

In this study, a series of PTMG-PU were synthesized and the content ratios of the hard segment to chain extender to the soft segment based on 1,4-BD and PTMG were controlled to achieve the required mechanical and physical properties of the prepared PTMG-TPUs. The effects of soft/hard ratios on the moisture-barrier property, which leads to the reinforcing encapsulation performance of PTMG-TPU were also examined.

2. Experimental section

2.1. Materials

Poly (tetramethyleneglycol) (PTMG, M_n = 1000 g/mol, Sigma-Aldrich), 4,4′-methylene bis(phenylisocyanate) (MDI, Junsei), and 1,4-butanediol (1,4-BD, Junsei) were dried over 20 h in a vacuum prior to use. Dimethylformamide (DMF, Duksan Chemical) was used as the solvent to prepare PTMG-TPU. De-ionized water as a purifying agent was used to rinse any residual reactants.

2.2. Preparation of PTMG-TPU with the different soft/hard segment ratios

Scheme 1 presents the synthetic procedure of TPU comprised of soft and hard domains. The PTMG-TPUs were successfully prepared through a two-stage synthetic process of NCO-terminated prepolymer and chain

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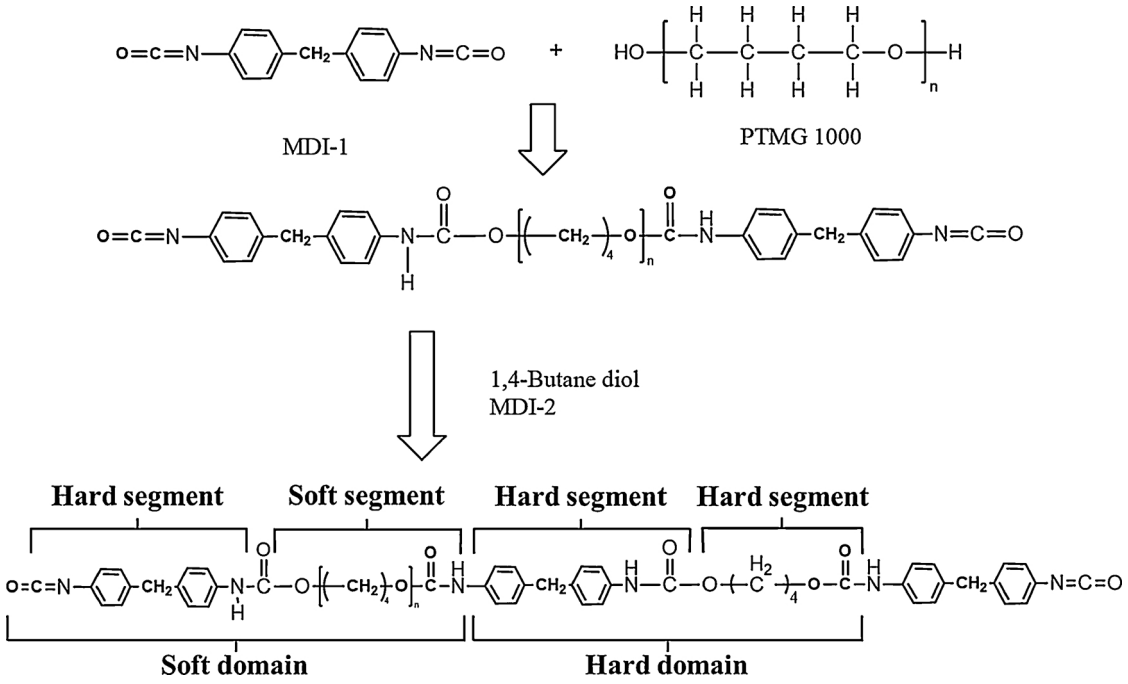

Scheme 1. Hard and soft segments in a linear PU.

Table 1
Composition of the PUs.

Sample Code	Reactants (g)			
	MDI	PTMG	1,4-BD	MDI-2
PU 10/0	10.2582	39.7418	–	–
PU 9/1	9.2574	35.7426	1.3238	3.6761
PU 8/2	8.2566	31.7434	2.6477	7.3523
PU 7/3	7.2558	27.7442	3.9716	11.0284
PU 6/4	6.2549	23.7450	5.2954	14.7046

extender with 1,4-BD. First, NCO-terminated prepolymer was prepared at 60 °C by reacting with 27.9 g (0.1 mol) PTMG and 178.1 g (0.6 mol) MDI-1 in a 250 mL four-necked reactor equipped with a mechanical stirrer, condenser, temperature controlled oil bath, and nitrogen purge. After 3 h, two solutions, one containing 11.1 g of 1,4-BD and the other containing 10.1 g of MDI-2, both in 5 mL DMF, were poured sequentially in the reaction mixture. The reaction was performed consistently by mechanical stirring at 60 °C under a nitrogen atmosphere. After verification by GPC, each satisfactory molecular weight PTMG-TPU with soft/hard ratios ranging from 10/0 to 6/4, was achieved with a similar molecular weight. Table 1 lists the individual reactant components of the synthesized PTMG-PUs.

2.3. Characterization

The molecular structures of the synthesized PTMG-TPU were verified by a Fourier-transform infrared (FT-IR, CARY-640, Agilent) spectroscopy. The light-transmittance of PTMG-TPU films with different soft/hard ratios was evaluated using a Jasco V630 UV–vis spectrophotometer, with wavelengths ranging from 200 to 1100 nm. The glass transition temperatures (T_g) and melting temperatures (T_m) of the resulting PTMG-TPUs were measured by differential scanning calorimetry (DSC, DSC-Q20, TA instruments) under both heating and cooling scans at a rate of 10 °C/min between −80 and 250 °C. Five tests for the tensile strength were carried out using a universal testing machine (UTM, LRX PLUS, LLOYD INSTRUMENT) at a cross head speed of 500 mm/min. The water vapor transmission rates (WVTRs) of the dried PTMG-TPU films were determined using an AQUATRAN Model 2 (MOCON Inc.) as a function of time under 37 °C/100% relative humidity (RH).

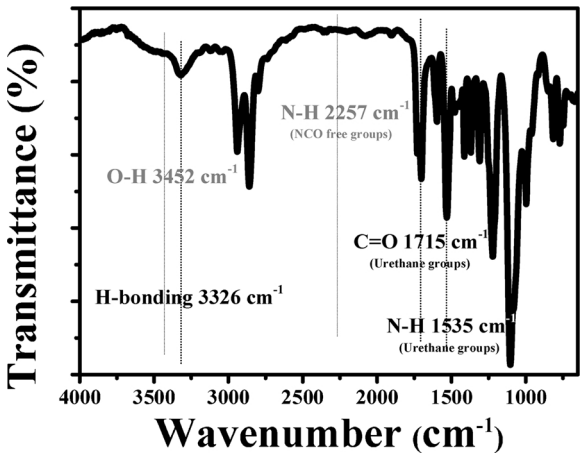

Fig. 1. FT-IR spectrum of a PTMG-TPU synthesized through a two-stage synthetic process.

3. Results and discussion

Fig. 1 presents the FT-IR spectrum of PTMG-TPU synthesized after the two-stage synthetic process. The formation of the urethane groups was confirmed by the detection of a C=O stretching and N−H bending bands at 1715 cm^{-1} and 1535 cm^{-1}, respectively, in the resulting PTMG-TPU. The non-presence of 3452 cm^{-1} OH groups and 2257 cm^{-1} NCO free groups suggests that all the NCO-terminated pre-polymers reacted with the hydroxyl groups of the polyol. The N−H primarily hydrogen-bonding peak at 3326 cm^{-1} was detectable only as a very small shoulder. These results show that the hard domains occur in the interior of PTMG-TPU.

The effects of the soft/hard ratios on the characteristics and mechanical properties of a PTMG-TPU series with a similar molecular weight of $\overline{M_n} = 4 \times 10^4$ were analyzed. Fig. 2 presents the GPC curves of the synthesized PTMG-TPU series for comparison. A series of