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Title: Structure/Property Behavior of a Segmented Poly (ester urethane) Containing Different Hard Segment Contents

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STRUCTURE/PROPERTY BEHAVIOR OF A SEGMENTED POLY(ESTER URETHANE) CONTAINING DIFFERENT HARD SEGMENT CONTENTS

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Abstract

A series of poly(ester urethanes) containing different hard segment contents were synthesized to provide information on the development of hard domain structure. In contrast to previous studies, this work focuses on segmented poly(ester urethanes) containing low hard segment contents. By incrementally increasing the hard segment content, we monitored the development of the hard domain structure using thermal analysis and x-ray diffraction. Rapid quenching of the samples from the melt shows that the hard and soft segments are miscible for all compositions at elevated temperatures. If the Tg of the mixed phase is greater than ambient temperature, the structure is trapped in a metastable mixed phase. Heating the materials above the Tg causes demixing and the Tg of the soft domain decreases. If the mixed phase Tg is below ambient conditions, the hard domains spontaneously phase separate. The alternating copolymer of poly(butylene adipate) (Mn=1K) soft segment and methylene diisocyanate (MDI) (19% hard segment) shows high poly(butylene adipate) crystallinity. The addition of very small amounts of butanediol chain extender greatly inhibits soft segment crystallization. For hard segment compositions greater than 45%, hard domains crystallize.

STRUCTURE/PROPERTY BEHAVIOR OF A SEGMENTED POLY(ESTER URETHANE) CONTAINING DIFFERENT HARD SEGMENT CONTENTS

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Introduction

Thermoplastic polyurethanes derive their elastomeric properties from the thermodynamic incompatibility of low T_g soft segments from covalently attached hard segments. [1-3] The phase separation of the hard segments into domains greatly increases the modulus and strength of the elastomer by creating an effective cross-linked network. For low hard segment compositions, the flexible soft segments form the continuous rubbery matrix while the rigid aromatic hard segments form domains that behave as multifunctional cross-links. Methylene diisocyanate (MDI) and toluene diisocyanate (TDI) are the most commercially important isocyanates. The isocyanates are usually chain extended with butanediol and reacted with hydroxyl terminated soft segments to form the segmented polyurethanes. The purpose of the chain extender is to increase hard segment length which results in increasing the thermodynamic driving force for phase separation, thereby, improving the mechanical properties. Heating the segmented polyurethane, disrupts the hard domains and the elastomer becomes processible. Upon cooling to ambient temperatures, the hard segments phase separate reforming the network structure.

There have been many studies on the effects of chemical structure and annealing on the morphology of segmented polyurethanes,[3-13] While the general aspects of phase separation in segmented polyurethanes are known, details of the morphology and phase behavior of these complex materials is far from understood. The size, shape, distribution, orientation, and interfacial domain structure influence the properties of these materials. The effect of hard segment content, polymerization conditions, thermal history, environmental degradation, soft segment composition and molecular weight, all have an impact on the resulting morphology. This paper will investigate phase separation by utilizing soft and hard segment crystallinity as a probe for domain formation. In contrast to previous studies, this work will focus on segmented poly(ester urethanes) containing low hard segment content. By incrementally increasing the hard segment content, we will characterize the development of the hard domain structure.

Experimental

Materials. Poly(ester urethanes) (PESU) containing different wt. % hard segment were synthesized in a single-step, solution-polymerization procedure. The MDI and butanediol (BDO) were obtained from Aldrich Chemical Co. The dimethyl formamide (DMF) was obtained from Fisher Chemical Company, and the poly(butylene adipate) oligomer Rucoflex® S101 was obtained from Ruco Chemical Company. The poly(butylene adipate) oligomer had an average molecular weight of 1040 AMU. Prior to use the BDO and DMF were dried over calcium hydride overnight and then vacuum distilled. The MDI was recrystallized from hexane, and the Rucoflex® was dried in a 70°C convection oven prior to polymerization. BDO and Rucoflex® were heated in DMF solution at 100°C under inert atmosphere while the MDI in DMF was added. The resulting mixture was heated to 120°C (using an oil bath) for about 3 hours; afterwards the solution was viscous. The mixture was cooled to 55°C and *n*-propanol was added to endcap any unreacted isocyanate. The polymer was then precipitated by pouring into water and agitating, followed by washing with water and methanol. The polymer was dried overnight in an oven at 60°C. The samples were compression molded at 20°C greater than their Tm and were rapidly cooled to room temperature. The samples were stored in the dark at least two weeks prior to testing.

Gel Permeation Chromatography. Molecular weights were determined in dimethylformamide by Gel Permeation Chromatography (GPC). The GPC consisted of an Alliance® 2690 pump equipped with a 2410 differential refractometer and utilized Shodex® 806, 804 and 802.5 GPC Columns. The flow rate was 1.0 mL/min. The molecular weights were calculated relative to poly(ethylene oxide) standards.[14]

Differential Scanning Calorimetry. Thermal Properties were measured on a TA Instruments 2920 Modulated Differential Scanning Calorimeter (MDSC). For samples with less than 85% hard segment content, (ca. 15 mg) were cooled to -120 °C and then scanned at a rate of 20 °C/min to 240°C; while samples with higher HS contents were heated to 260 °C. Rapid quenching was performed by removing the sample at the final DSC temperature and placing it against a refrigerated metal block.

Wide Angle X-ray Diffraction. Crystalline structure was determined using wide-angle x-ray diffraction (WAXD). Cu Kα x-rays were scanned in reflection at 2θ from 3 to 50 in steps of 0.050 at a rate of 1°/min.

Results and Discussion

The effect of hard segment composition on the thermal properties of rapidly quenched PESU are shown in Figure 1. Rapid quenching of PESUs containing between 19 and 23% hard segments show only a Tg upon rescanning. Heating samples with hard segment contents greater than 23% above their Tg, causes an exothermic reorganization process which is attributed to development of a phase separated structure. Continued heating causes an endothermic process which is related to disruption of the structure. Both the exothermic and endothermic processes increase in temperature and magnitude with increasing hard segment content. For hard segment compositions greater than 45%, the endothermic process can be attributed with hard segment melting.

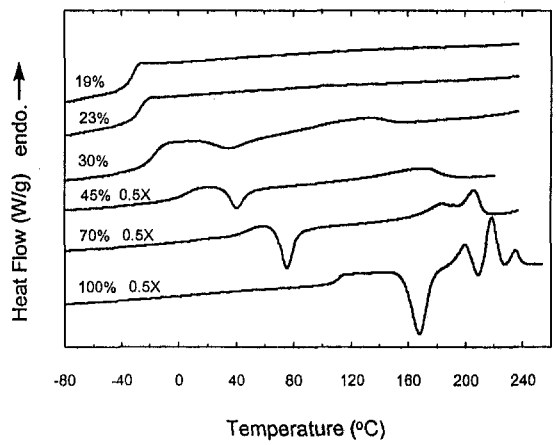

Figure 1. Effect of hard segment content on DSC scans of rapidly cooled poly(ester urethanes).

The effect of room temperature annealing on the thermal properties of PESU containing various hard segment compositions is shown in Figure 2. The unreacted PBA oligomer (0% HS) has a Tg of -69°C and multiple melting endotherms are observed. The multiple melting peaks are due to the distribution of molecular weights in the oligomer. The highest melting endotherm has a peak at 50°C which is less than the reported equilibrium melting point of 61°C for high molecular weight poly(butylene adipate).[15] The reduction of the melting point may due to the exclusion of the end-groups from the crystallite structure or formation of the metastable β crystal form that melts at 49°C.[16] Reaction of poly(butylene adipate) oligomer with MDI produces a polyurethane with an alternating soft segment MDI composition. The absence of chain extender gives the alternating copolymer a HS content of 19 wt %. The incorporation of the MDI increases the Tg to -29°C and inhibits crystallization of the shorter oligomer species. Even with 19% HS, the alternating copolymer still displays significant soft segment crystallinity.

The addition of the butanediol causes chain extension of the MDI segments which cause them to be less soluble in the polymer. The endotherm is significantly reduced by the addition of small quantities of butanediol chain

extender. In addition, the small amounts of chain extender reduces the Tg to -34°C and produces a new endotherm between 40 and 80°C. The insolubility of the chain extended MDI segments in the polyester phase is the driving force for phase separation. The decrease in Tg is due to exclusion of the hard segments from the soft matrix. Increasing the hard segment content has little effect on the soft domain Tg until the hard domains begin to form the continuous phase around 50% hard segment content. Also there is little change in endotherm associated with the hard domain disruption. Above 23% HS, a shoulder develops on the hard domain endotherm and increases in magnitude and temperature with increasing hard segment content. Between 45 and 57% HS, the samples begin to show a endotherm associated with melting of the crystalline hard domains.

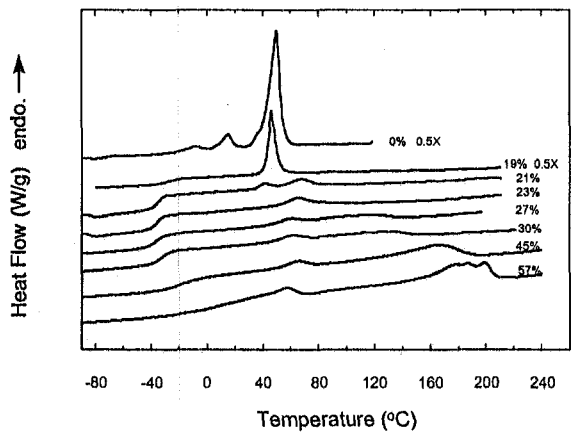

Figure 2. DSC scans of room temperature annealed poly(ester urethanes) containing various hard segment contents.

Wide Angle X-ray Diffraction (WAXD) was utilized to identify the crystalline structure of the PESU. The WAXD profiles of the PESU's containing different HS concentrations are shown in Figure 3. The poly(butylene adipate) oligomer show intense diffraction peaks at 21.1, 22.2, and 24.2 2θ. The peak spacing is not affected when the poly(butylene adipate) oligomer is copolymerized with MDI, though the increase in the amorphous halo shows a lower degree of crystallization. No poly(butylene adipate) crystallization was observed using WAXD for HS greater than 19%. The discrepancy in the crystallization between the DSC and WAXD data for the 19% HS may be due to the small degree of crystallinity being masked by the amorphous halo in the WAXD. At high HS compositions, the development of HS diffraction peaks are observed and are due to crystallization of the hard segments.

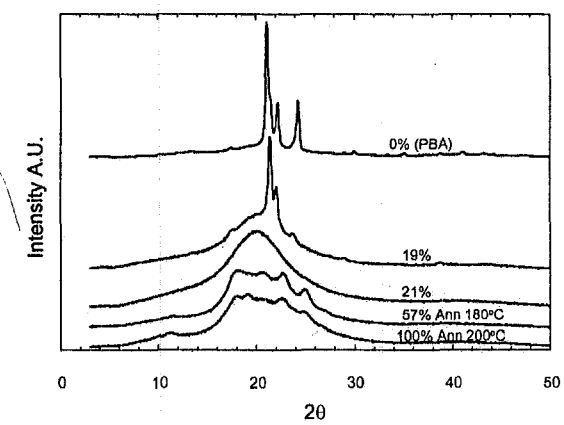

Figure 3. WAXD of PESU containing various hard segment contents.

Conclusions

A series of poly(ester urethanes) containing various concentrations of hard segments have been synthesized. Thermal analysis and x-ray diffraction results show that the small amounts of chain extender dramatically alter the morphology of these materials. The morphology is governed by the relative ability of the soft and hard segments to form domains. Rapid cooling from the melt shows that the hard and soft segments are miscible at elevated temperatures for all hard segment compositions. If the Tg of the mixed phase is greater than ambient temperature, the structure is trapped in a metastable state. Heating the materials above the Tg causes demixing and the Tg of the soft domain decreases. If the mixed phase Tg is below ambient conditions, the hard domains spontaneously phase separate. In absence of chain extender, alternating copolymers of the soft segment and MDI contain 19% hard segment and display large amounts of soft segment crystallinity. The addition of very small amounts of butanediol chain extender greatly inhibits soft segment crystallization. For hard segment compositions greater than 19%, an endotherm between 40 and 90°C was observed. This endotherm is attributed to localized disruption of the hard domains. The breadth of the endotherm increases to higher temperatures with increasing hard segment content. For hard segment concentrations greater than 45%, the hard domains crystallize.

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