

EFFECT OF CHAIN EXTENDERS ON THE STRUCTURE AND PROPERTIES OF POLYURETHANES

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Abstract

The objective of this work was to determine the influence of different chain extenders (CEs) on the structures and properties of polyurethanes (PUs) materials. CEs increase phase separation in thermoplastic and thermoset PUs with significantly impact the density of hydrogen bonds (X_b). In general, the higher the miscibility of CEs with hard and soft domains, the lower tendency to phase separation and the appearance of a single glass transition temperature (T_g). In addition, the miscibility of CEs and side groups tend to form polymers with no long-range order. The results shown in this work can contribute to obtaining polyurethane materials with tunable structures.

Keywords: PUs, TPUs, chain extender

Introduction

Segmented polyurethane materials are copolymers formed by thermodynamically incompatible segments a soft segment (SS), usually derived from a macrodiol, and a hard segment (HS) formed by a diisocyanate and a low-molecular diol (chain-extender). PUs exhibit versatile physical properties due to microphase separation due to the thermodynamic immiscibility existing between HS and SS. These materials can be thermoplastic (TPU) or thermoset (PU). In both types of copolymers, the morphology of polyurethane varies widely, depending on the monomer characteristics. In general, HS comprises polymer chains formed from diisocyanate and chain extender (CEs). When synthesized with aromatic diisocyanates (TDI and MDI, and others), these are usually more rigid than aliphatic ones such as HDI. Hard blocks can also be crystalline and thus communicate primarily in the mechanical properties of polyurethane. PU crystallization of soft segments is hindered in the polyurethane with high hard segment content, while the higher symmetry of hard segments the easier crystallization of hard segments. For this reason, the symmetry of the rigid segment plays a fundamental role in many properties of polyurethanes. They are having effects on mechanical properties, diffusion, adhesiveness, and operating range [1-4].

The CEs functionality, structure, and amount can increase chemical crosslinking and thus restrict physical crosslinking, such as macromolecular chain movement in the soft block, due to hydrogen bonds. Therefore, the properties of PUs are strongly dependent on intra- and interchain interactions, such as hydrogen bonds between polar chain groups, mainly NH nitrogen (proton donors) and C=O carbonyl (electron donors) groups present in the urethane group and polyols. Chain extenders can alter the compatibility between the SS and HS segments, resulting in the formation of polymers with high transparency. As phase separation is dependent on the density of hydrogen bonds, there is a correlation of this property both in TPUs and in PUs from renewable sources [1-4].

This work aims to present results related to the effect that chain extenders have on the morphology, hydrogen bonding density, and thermal properties of polyurethanes from renewable

sources and TPUs obtained by reactive extrusion. It is intended to use thermodynamic approaches to elucidate the nature of the phase separation of copolymers. Given future applications such as getting parts with extreme transparency and the use of renewable sources, it is fundamental to evaluate these properties due to their impact on the final characteristics of the polymers obtained.

Experimental

PU synthesis

The following raw materials were used in the polyurethane synthesis: Soy oil polyol was obtained from soybean oil by a procedure used in our research group [5]. PUs with different CEs were synthesized without any catalyst by one-step bulk polymerization with approximately 39 wt.% hard domains. First, the MDI was heated at 45°C for 5min. Then the soybean oil polyol (SOP), MDI, and CE were mixed for approximately 40s, under slow stirring, to prevent bubbles formation, 1.1:1.0 OH:NCO molar ratio. Here, PUs with butane-1,4-diol (BDO), ethane-1,2-diol (MEG), and (2-hydroxypropoxy)propane-2-ol (DPG) used as CEs were prepared in the same way. After homogenization, the samples were placed in a Teflon-coated petri dish in an oven at 60°C for 96 h.

TPU synthesis

A blend 75/25 m%/m% of the two polyols (Elapol 3020A/Elapol 5010A; 2000/1000 g.mol⁻¹, respectively) was previously prepared in a stainless steel reactor of 5L at 80°C. This blend was kept under stirring for 15 min. before starting the reactive extrusion. According to previous studies of our research group, this polyol composition has been optimized to maximize mechanical properties. All TPUs were synthesized with 50 m% of rigid phase and 50 m% flexible phase at a 1.05/1 NCO/OH functional groups ratio. TPUs containing different BDO/DPG ratios (100/0, 75/25, 50/50, 25/75, and 0/100 m%/m%) were prepared. The pre-polymer and chain extenders (BDO, DPG, and their mixtures) were dosed to obtain a constant production rate of approximately 2 kg.h⁻¹ of TPU in a LTE 16-48 twin-screw extruder (LabTech Engineering Company Ltd., Thailand) with a length-to-diameter ratio (L/D) of 48. Processing temperatures ranged from 160-220°C, and the screw speed used was 250 rpm. The screw profile was optimized for TPU production.

Characterizations

All materials were characterized by ATR-FTIR (Perkin-Elmer Spectrum 400 spectrometer instrument) in attenuated total reflection (ATR; diamond crystal at 45°) mode. The samples were scanned 32 times, in the range from 4000 to 450 cm⁻¹ at 2 cm⁻¹ resolution. The hydrogen bonding degree and the hard domain amount dispersed in the soft phase were computed by mathematical deconvolution of the signal according to the literature [3,5].

SAXS experiments were performed on the SAXS1 beamline of the Brazilian Synchrotron Light Laboratory (LNLS), the samples-detector (Pilatus 300 k) distance was maintained at 836 mm. The generated scattering wave vectors (q) ranged from 0.13 to 2.5 nm⁻¹ at room temperature. The wavelength of the incident X-ray beam (λ) was 0.155 nm. Samples with 3 mm in diameter and 1 mm thick were used. A silver behenate (AgBeH) standard was used for calibrating the diffracting angle.

The thermal transitions of the polyols and TPUs were determined by differential scanning calorimetry (DSC, Netzsch DSC 204 Phoenix) under nitrogen atmosphere (50 mL.min⁻¹). Samples of 9-10 mg were used.

Results and Discussion

In all polyurethane samples, bands up to 1307 cm⁻¹, 1500 cm⁻¹ and 1520 cm⁻¹ are attributed to stretching modes of CN, CH₂-CH₃, and NH₂. Also observed, the band at 3318 cm⁻¹ is assigned to the free NH stretching vibration of the urethane groups and the benzene ring domain in MDI (band up to 1600 cm⁻¹) [3,4].

The hydrogen bond amount and distribution contribute to the phase separation degree in PU materials [2,3]. The main band contributing to the inter-urethane hydrogen bond formation shows up in the carbonyl region ($1600\text{--}1800\text{ cm}^{-1}$). These bands have been found helpful for the relative amount determination of hydrogen bonds in polyols. Figure 1(a) shows the region between $1600\text{--}1800$ of PUs produced with soybean oil using different chain extenders. The greater intensity of the band close to 1685 cm^{-1} is related to greater phase separation. Figure 1 (b) illustrates an example of a mathematical deconvolution procedure applied in this work, as described in the literature. Through this procedure, it is possible to quantify the specific contributions of each region and quantify the relative fraction of hydrogen bonding (X_b), amount of rigid segment dispersed in the flexible (W_h), and phase fraction that is mixed (MP). When using CEs, it is noted that the hydrogen bond fraction increases. Due to the formation of domains that can organize themselves. PU tends to have a lower hydrogen bond fraction and a lower weight fraction of hard segment dispersed soft segment when not used. Regarding the type of extender, it is noted that extenders with side groups ($-\text{CH}_3$) or with isomers form smaller X_b due to minor steric hindrance. X_b for TPU with BDO changed from 0.76 to 0.66 for DPG.

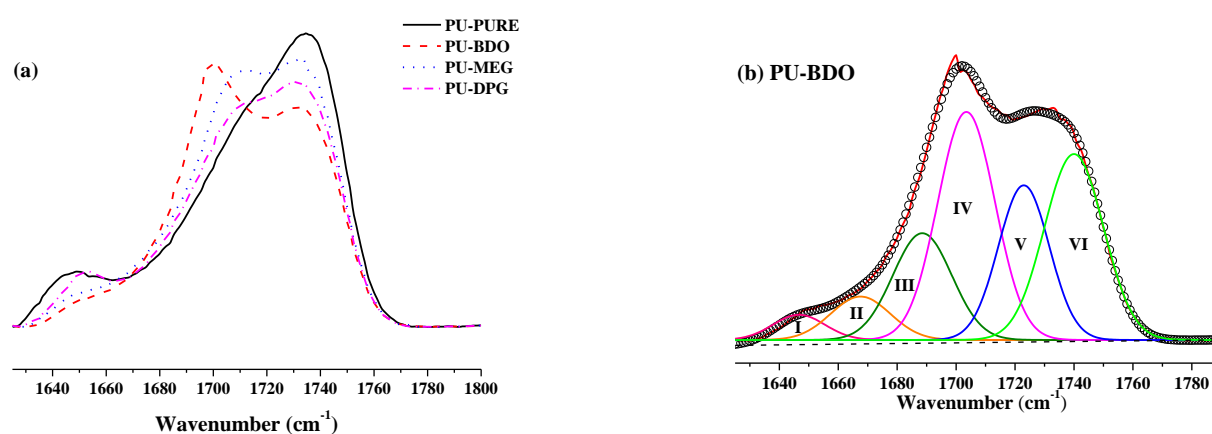


Figure 1 – (a) ATR-FTIR carbonyl absorbance regions and (b) example of deconvolution spectra for PU-BDO

Similar observations are made on both PUs and TPUs [2,3]. Using Fox's equation to predict the relative quantities of the rigid and flexible segments, $1/T_{gs} = (1 - W_{h,Fox})/T_{gs^0} + W_{h,Fox}/T_{gH^0}$, where, T_{gH^0} is the hard domain glass transition, thus for MDI/BDO, $T_{gH^0} = 110\text{ }^{\circ}\text{C}$, MDI/MEG $T_{gH^0} = 139\text{ }^{\circ}\text{C}$ and MDI/DPG $T_{gH^0} = 108\text{ }^{\circ}\text{C}$. The T_{gs^0} is the temperature corresponding to the soft domain glass transition, with the soft segment $T_{gs^0} = -80\text{ }^{\circ}\text{C}$. Note that, the W_h presents values similar to those found by FTIR (0.2–0.35).

Chain extenders that tend to increase the miscibility between the rigid and flexible segment by promoting a smaller solubility parameter difference between the rigid (δ_H) and flexible (δ_S) segments usually result in a reduction in the transition temperature difference vitreous between the segments. This difference can be compared by analyzing the Bagley graph [6] (Fig. 2(a)) and comparing the difference between the MDI parameters and the chain extenders. This comparison can be made simply by the distance to the solubility parameter that is in the center, in this case, MDI. Regarding the glass transitions, it is noted that when there is a reduction in the compatibility parameter (χ_N) in copolymers $(AB)_n$, as is the case with TPUs, the flexible and rigid domains tend to increase

their free energy of mixing and result in an increase the glass transition of the flexible phase and reduce that of the rigid segment to tend to observe a single T_g (Fig. 2(b)).

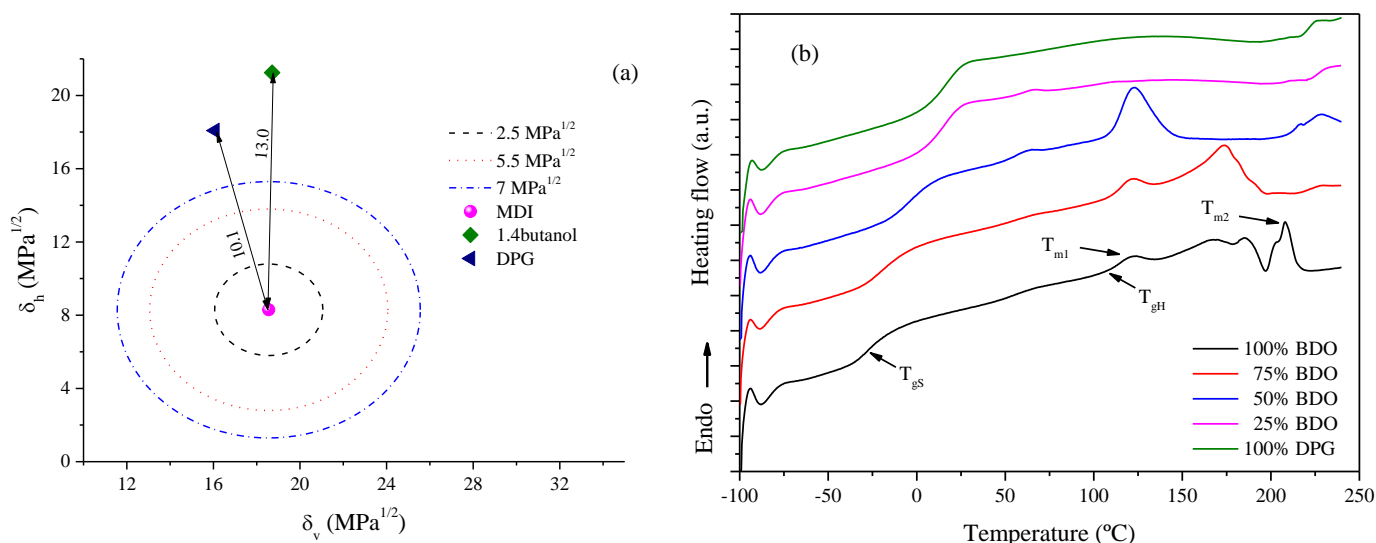


Figure 2 – (a) Bagley plots for MDI, BDO, and DPG obtained using group contribution method and (b) DSC thermographs for TPU with different DPG amount (data recording at 10°C.min⁻¹ from the second heating cycle)

CEs play a fundamental role in the formation of crystalline morphology in polyurethanes regarding morphology domain and sizes. For the soy PUs, the domain size, dispersion, and formation of organized phases were evaluated by WAXD and SAXS. The WAXD and SAXS were merged to elucidate the structure levels in PUs. The Lorentz correction profiles $I(q)q^2$ vs. q of the demerged SAXS-WAXD data are plotted on a relative scale and shown in Figure 3 (a). The PUs showed correlation peaks ($q_{1max} \sim 0.6 \text{ nm}^{-1}$, $q_{2max} \sim 5.5 \text{ nm}^{-1}$, and $q_{3max} \sim 14.5 \text{ nm}^{-1}$) that are characteristic of phase-separated domains and interchain distances. It has also been noted that PUs with BDO and MEG extenders have a narrower peak, which is a smaller polydispersion characteristic. In contrast, DPG is broader because it is an isomer.

Another important point is that CEs such as DPG can induce the formation of TPUs with virtually no long-range order formation (Fig. 2(b)). By comparing the q_0/q_{max} ratio, we can get an idea about the domain dispersion between the BDO and DPG extenders. The formation of non-regular structures has two reasons: the higher compatibility between rigid and flexible segments and spatial factors.

The control of the morphology of PUs has a fundamental role in the final properties of these polymers. In TPU formulations with DPG, the amount of chain extender is around 14% in the formulation, but it profoundly modifies these polymers' morphological and thermal characteristics. Concerning PUs from renewable sources, both dispersion and hydrogen bonds are affected by chain extenders. This type of investigation allows us to obtain materials with tuned properties both in PUs from renewable sources and in petrochemical sources.

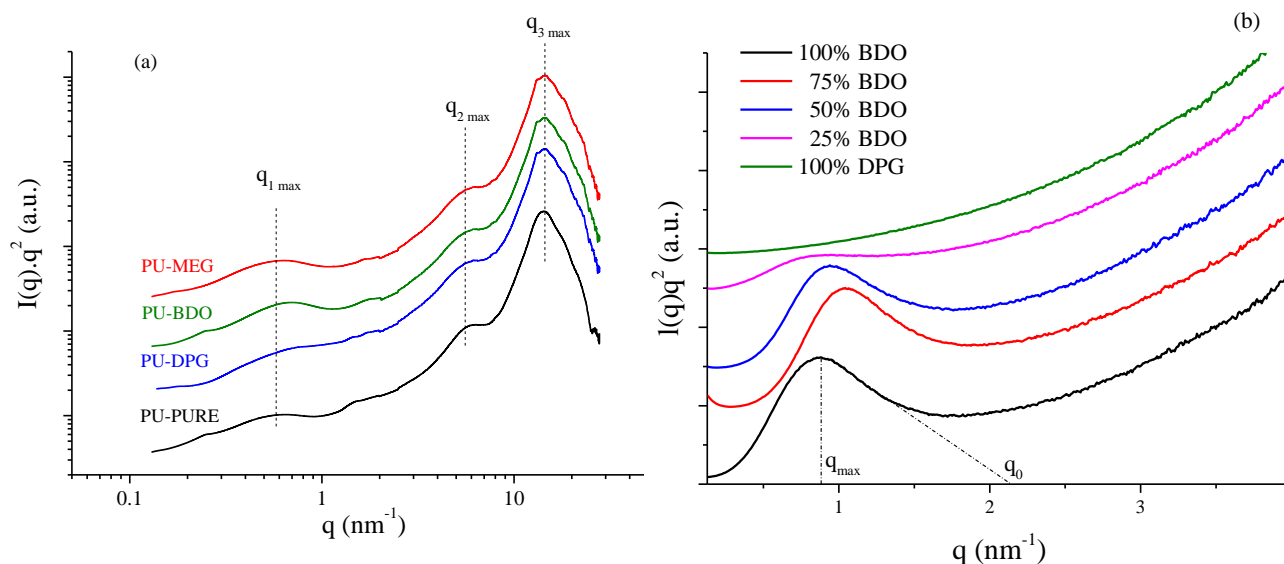


Figure 3 – (a) SAXS-WAXD profiles for soy PUs and (b) SAXS profiles for TPU with different DPG amount

Conclusions

Chain extenders play a key role in the structure and properties of polyurethanes. Overall, there is an increase in the density of hydrogen bonds, which will lead to increases in properties such as mechanics. ECs as isomers can contribute to the reduction of rigid segment regularity. The higher miscibility of the blocks substantially alters the glass transitions of the copolymers. These results serve as the basis for understanding the relationship between the structure and properties of polyurethanes.

Acknowledgements

The author thank the Brazilian Synchrotron Light Laboratory for use your installation (SAX1 beamline) and National Council for Scientific and Technological Development (CNPq) (grant number 306086/2018-2).

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