Effect of intersegmental interactions on the morphology of segmented polyurethanes with mixed soft segments: A coarse-grained simulation study

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ABSTRACT

Segmented thermoplastic polyurethanes, polyureas and polyurethaneureas (TPU) based on a given hard segment and two chemically different soft segments display interesting microphase morphologies and thermal, mechanical and surface properties. In these systems the final TPU morphology is mainly controlled by the structure, amount and molecular weight of the soft segment oligomers and the nature and extent of specific intermolecular interactions between the mixed soft segments themselves and with the urethane hard segments. These interactions lead to variable compatibilities between the soft and hard segments resulting in interesting TPU morphologies. The proper choice of the two chemically different soft blocks provides more flexibility in controlling the extent of microphase separation, size and shape of the microphase domains and offers new possibilities for controlling the properties of TPUs. In this study coarse grained computer simulations were carried out to better understand the nature of intermolecular interactions and to elucidate the equilibrium microphase morphologies of TPUs with two different soft segments at 300 K. Model TPU systems investigated are comprised of poly(tetramethylene oxide) (PTMO) or poly(hexylethyl carbonate) (PHEC) and polydimethylsiloxane (PDMS) or poly-isobutylene (PIB) soft segments with molecular weights in the range of 500–2500 g/mol. Hard segments consisted, in all cases, of diphenylmethane diisocyanate (MDI) based urethane repeat units and ranged from 25 to 50% by weight. Through coarse grained Dissipative Particle Dynamics (DPD) simulations it was demonstrated that by varying the composition and the chain lengths of the soft and hard blocks, quite different morphologies from homogeneous (or mixed) to gradient and to completely microphase separated structures were attainable. As expected, fairly hydrophobic soft blocks such as PIB and PDMS favored strong microphase separation when compared with relatively hydrophilic PHEC and PTMO segments. For comparison, morphologies of the TPUs based on single soft segments (PTMO, PHEC, PDMS and PEO) with varying molecular weights and hard segment contents were also simulated.

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1. Introduction

Segmented polyurethanes, polyureas and polyurethaneureas (TPU) are a technologically important class of thermoplastic elastomers, which are composed of alternating hard and soft segments along a linear polymer backbone. While the soft segments (SS) have glass transition temperatures well below room temperature and provide flexibility, urethane hard segments (HS) behave as reinforcing nano-sized physical crosslinks and provide increased tensile strength and mechanical integrity to the TPUs. Based on their backbone compositions, hard and soft segment types and contents, TPUs may display a broad range of properties from soft elastomers to rigid plastics and find various applications ranging from molded/cast materials, coatings, membranes to applications in medical devices and implants [1–6].

TPUs with hard segment contents in the range of 20–40% by weight, generally display microphase separated morphologies, where the HS microdomains are relatively dispersed in a

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continuous SS matrix [7,8]. It has been clearly demonstrated that a large number of factors, which include SS structure, symmetry and molecular weight, HS structure, symmetry, molecular weight and content, synthetic method and sample preparation technique used, play critical roles in affecting the degree of microphase separation and TPU morphologies obtained [1,3]. Another important factor is the difference between the solubility parameters or polarity of the hard and soft segments, which strongly influences the degree of miscibility between the two phases [3]. For example, poly-dimethylsiloxane (PDMS) based segmented polyurethanes and polyureas have been shown to display excellent microphase separation due to major differences between the solubility parameters of PDMS (15.6 $(J/cm^3)^{1/2}$), urethane (25.4 $(J/cm^3)^{1/2}$) and urea (34.2 $(J/cm^3)^{1/2}$) hard segments [9–11]. However, in some cases, especially when the HS content of the PDMS based TPUs are increased, tensile properties, especially the elongation at break and the ultimate tensile strength values show a substantial decrease [11]. This has been mainly attributed to the presence of a very sharp interface leading to poor interfacial adhesion between PDMS and the urethane or urea microphases, which results in poor stress transfer and premature failure [11–13]. Interestingly, when a second soft segment with higher solubility parameter, such as poly(ethylene oxide) (PEO) [14,15], poly(propylene oxide) (PPO) [12,15,16], poly(tetramethylene oxide) (PTMO) [15,17,18] or aliphatic polyester [19] or polycarbonate [18,20,21] is also chemically incorporated into the same PDMS-urea polymer backbone, a dramatic increase in the tensile properties is observed [12,14]. This is explained by the interaction of PEO, PPO, polyester or polycarbonate with the urethane or urea HS through weak hydrogen bonding [22] and thus leading to the formation of a gradient interphase between PDMS and the HS, which results in better stress transfer [12,14]. Very similar behavior was observed in polyisobutylene (PIB) (16.4 $(J/cm^3)^{1/2}$) based polyureas. When PIB-urea copolymers based on PIB SS with M_n = 1500, 4000 and 11,000 g/mol were modified by the chemical incorporation of 10 and 20% by weight of PTMO oligomer (M_n = 1000 g/mol), dramatic improvements in the ultimate tensile strengths and elongation at break values were obtained [21,23,24].

In this study Dissipative Particle Dynamics (DPD) method, which is a coarse grained simulation technique was employed at the nano scale to gain insight into the microphase separation and determine the equilibrium morphologies of polyurethanes containing mixed soft segments, which is schematically shown in Fig. 1, at 300 K.

In these investigations PDMS and PIB based TPUs were modified by the chemical incorporation of PTMO and poly(hexylethyl carbonate) (PHEC). The urethane hard segment structure utilized in simulations is provided in Fig. 2, which can be obtained by the reaction of MDI with bisphenol F. The simulation studies are based on "model" systems, as a result it is assumed that the soft segment oligomers, urethane hard segments and the TPUs investigated all have uniform molecular weights and no molecular weight distribution. The strong dependence of the shape and the nature of the TPU nanostructures formed on; (i) the soft segment structures, (ii) hard and soft segment molecular weights, (iii) TPU compositions, and (iv) the extent of inter and intra-segmental interactions and hydrogen bonding, are explored in detail.

2. Computational methods

2.1. Calculation of mixing energies between segments

Flory Huggins interaction parameters (χ) between the interacting polymer segmented chains were calculated and used to obtain input parameters for the DPD simulations [25–27]. The χ (chi) parameter is a measure of the interactions or the miscibility of two chains or segments in the present report; smaller χ parameter values indicate stronger favorable interaction between two components or better miscibility or mixing. It can be calculated by using the values of the mixing energies (ΔE_{mix}), which provide the interaction energy between urethane hard segments (U) and various soft segments such as; U-PHEC, U-PTMO, U-PDMS and U-PIB and also the energy of soft–soft segment interactions such as PHEC-PDMS, PHEC-PIB, PTMO-PDMS, PTMO-PIB. Mixing energies are calculated from molecular dynamics (MD) simulations by using the cohesive energy densities of the blends of the oligomers and also that of the pure components as shown in Fig. 3. Model systems or unit cells used in the calculation of the mixing energies for pure PDMS and pure PHEC consisted of four chains of each oligomer with a segment molecular weight of 1000 g/mol. For PDMS/PHEC blends 4 oligomer of each type, with a molecular weight of 1000 g/mol were used. It is important to note that there may be slight deviations in the results obtained when the chains are chemically linked to form a copolymer as compared to blends. Nevertheless, the simulations provided in this study for various TPU copolymers and terpolymers still provide very good estimate of the energetics of the systems, although parameters are calculated using blends.

E_{coh} is the cohesive energy obtained from the difference of the total non-bonded (nb) energies of the system in the isolated chain state ($E_{isolated}$) and in the amorphous periodic state ($E_{periodic}$) in MD simulations as shown in Eq. (1). In periodic MD simulations amorphous periodic state indicates a unit cell or the cubical simulation box, which gives the bulk structure when replicated in all dimensions to form an infinite lattice-like structure.

$$E_{coh} = E_{isolated}^{nb} - E_{periodic}^{nb} \tag{1}$$

E_{coh}/V represents the cohesive energy density (CED), where (V) is the amorphous cell volume and (φ) is volume fraction of the constituting segments in the system. The square root of CED gives the Hildebrand solubility parameter (δ), a critical factor in predicting the miscibility of different segments with each other. ΔE_{mix} is calculated by Eq (2).

$$\Delta E_{mix} = \varphi_i \left(\frac{E_{coh}}{V}\right)_i + \varphi_j \left(\frac{E_{coh}}{V}\right)_j - \left(\frac{E_{coh}}{V}\right)_{ij} \tag{2}$$

To calculate the mixing energies between blocks, 50 different amorphous cells were constructed by using the Amorphous Cell module of Materials Studio 6.1 Software [28]. These cells were composed of four chains of two different segments and eight chains of their blends under periodic boundary conditions. This method creates many (at least 50) disordered polymer conformations with
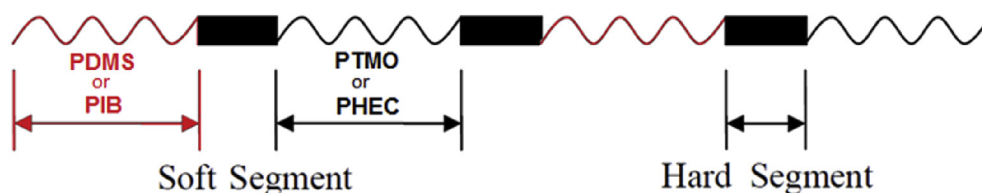

Fig. 1. Schematic description of the structure of segmented TPUs prepared using two different soft segments.