

Structure Property Relationships of Flexible Polyurethane Foams

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Abstract

This study examined several features of flexible polyurethane foams from a structure-property perspective. A major part of this dissertation addresses the issue of connectivity of the urea phase and its influence on mechanical and viscoelastic properties of flexible polyurethane foams and their plaque counterparts. Lithium salts (LiCl and LiBr) were used as additives to systematically alter the phase separation behavior, and hence the connectivity of the urea phase at different scale lengths. *Macro* connectivity, or the association of the large scale urea rich aggregates typically observed in flexible polyurethane foams was assessed using SAXS, TEM, and AFM. These techniques showed that including a lithium salt in the foam formulation suppressed the formation of the urea aggregates and thus led to a loss in the *macro* level connectivity of the urea phase. WAXS and FTIR were used to demonstrate that addition of LiCl or LiBr systematically disrupted the local ordering of the hard segments within the microdomains, i.e., it led to a reduction of *micro* level connectivity or the regularity in segmental packing of the urea phase. Based on these observations, the interaction of the lithium salt was thought to predominantly occur with the urea hard segments, and this hypothesis was confirmed using quantum mechanical calculations. Another feature of this research investigated model trisegmented polyurethanes based on monofunctional polyols, or “monols”, with water-extended toluene diisocyanate (TDI) based hard segments. The formulations of the monol materials were maintained similar to those of flexible polyurethane foams with the exceptions that the conventional polyol was substituted by an oligomeric monofunctional polyether of ca. 1000 g/mol molecular weight. Plaques formed from these model systems were shown to be solid materials even at their relatively low molecular weights of 3000 g/mol and less. AFM phase images, for the first time, revealed the ability of the hard segments to self-assemble and form lath-like percolated structures, resulting in solid plaques, even though the overall volume of the

system was known to be dominated by the two terminal liquid-like polyether segments. In another aspect of this research, foams were investigated in which the ratios of the 2,4 and 2,6 TDI isomers were varied. The three commercially available TDI mixtures, i.e., 65:35 2,4/2,6 TDI, 80:20 2,4/2,6 TDI, and 100:0 2,4/2,6 TDI were used. These foams were shown to display marked differences in their cellular structure (SEM), urea aggregation behavior (TEM), and in the hydrogen bonding characteristics of the hard segments (FTIR). Finally, the nanoscale morphology of a series of 'model' segmented polyurethane elastomers, based on 1,4-butanediol extended piperazine based hard segments and poly(tetramethylene oxide) soft segments, was also investigated using AFM. The monodisperse hard segments of these 'model' polyurethanes contained precisely either one, two, three, or four repeating units. Not only did AFM image the microphase separated morphology of these polyurethanes, but it also revealed that the hard domains preferentially oriented with their long axis along the radial direction of the spherulites which they formed.

This dissertation is dedicated to my parents

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