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Alteration of polyurea hard domain morphology by diethanol amine (DEOA) in molded flexible polyurethane foams

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Abstract

In this study, the morphology of polyurea hard domains in flexible polyurethane molded foams was investigated to evaluate the influence of diethanol amine (DEOA), a commercially utilized cross-linking agent. Tapping Mode AFM was utilized to reveal that DEOA dramatically alters the morphology of the solid state. Without DEOA, the solid state phase separation leads to the formation of lamellae-like polyurea domains ca. 50–100 nm long by 5 nm wide, and these lamellae frequently aggregate to form larger precipitates ca. 30–50 nm in diameter. These larger aggregations appear to be evenly distributed in the material. However, when DEOA is added to the formulation, the hard domains become smaller and more geometrically isotropic, ca. 5 nm in diameter. Furthermore, in the DEOA containing material, the hard domains do not appear to form the larger 50 nm aggregates but instead remain distributed at ca. 10 nm apart. The addition of DEOA thus reduced the observed level of hard domain interconnectivity, an effect which is suggested to explain in part the corresponding reduction in modulus (i.e. stiffness) that is commonly observed when DEOA is added to such foam formulations. The morphological alterations observed using AFM were also found to correlate well with the DEOA induced changes in the small angle X-ray scattering profiles of these samples.

Keywords: Polyurethane; Foam; Hard domain

1. Introduction

As flexible polyurethane foams have been introduced for many new applications, it has proven more economical in some cases to produce foams by casting the reactive mixture into molds of the desired form rather than by the traditional slabstock method. As discussed elsewhere, this production technique eliminates much time and waste in trimming, and it widens the range of obtainable properties [1]. To take advantage of these possible benefits and to meet the demands of processing with molds, many changes have been made in the formulations of flexible polyurethane foams [1,2].

These formulations are optimized to obtain the lowest mold residence times possible while still achieving the desired performance in tests such as compressive load bearing and resiliency. Among these alterations is the addition of cross-linking agents for improved stability of the cellular structure. Increasing the rate of covalent cross-linking allows other changes to be made to the formulation which reduce the time that the foam requires to achieve enough dimensional stability for it to be removed from the mold. These changes are enumerated in a recent publication by the authors [3]. As formulations are altered with a view toward macroscopic mechanical performance, the optimization generally focuses much attention on the cellular structure of the foam with measurements such as airflow, cell count, and apparent density.

Despite this emphasis on millimeter scale morphology, structure occurs at many scale lengths in flexible foams, and it is important to consider how they convolute together to yield the properties exhibited in macroscopic mechanical tests. This convolution was clearly demonstrated by two recent studies from this laboratory on the influence of a commercially used cross-linking agent, diethanol amine (DEOA). In one study [4], DEOA was shown to increase the compressive load bearing (i.e. stiffness) as a result of increasing the amount of closed cells in the foam. This constricted the air from flowing through the cellular matrix resulting in an apparently stiffer foam bun. In a subsequent work [3], the variation of airflow was removed by controlling the millimeter scale structure, and it was shown that DEOA actually reduces the compressive load bearing (i.e.

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stiffness) by nearly half as a result of the DEOA altering the structure and distribution of the polyurea hard domains (ca. 10 nm structure). Taken together, these two studies help to underline the fact that every level of structure in a flexible foam contributes significantly to its properties.

The complex morphology of the solid state arises from the microphase separation that occurs during the production of the foam. Flexible polyurethane foams are based on two well-known reactions. The “blow” reaction sequence typically involves the reaction of water with toluene diisocyanate to yield an amine, carbon dioxide and heat. The evolved gas and the reaction exotherm help to expand the fluid into a cellular structure, and the amine undergoes reaction with another isocyanate group to yield a urea linkage. Toluene diisocyante is typically used in an 80/20 blend of the 2,4 and 2,6 isomers, but other isomeric blends and other isocyanates are sometimes utilized. Generally, the blow reaction initiates first and proceeds at a faster rate yielding an essentially linear polyurea “hard” segment of four to six repeat units.

The second major reaction occurs between the isocyanate groups and the hydroxyl functionalities of the polyether polyol, and it generates a urethane linkage. Because the polyol usually has a functionality between 2 and 3, this process leads to a three-dimensional covalent network. At some point, the concentration of hard segments being generated by the blow reaction will surpass a system-dependent solubility limit leading to a microphase separation of the urea-based hard segments, which produces precipitates of the polyurea. Each of these precipitates or “hard domains” is a pseudo- or physical cross-linking point that is instead dependent upon strong intermolecular interactions (i.e. hydrogen bonding) for its cohesive strength. These strong interactions cause the hard domains to internally organize in a specific way, sometimes termed “para-crystalline” ordering, and variation of their size and concentration has been shown to have profound influence on the overall properties of the foam. In slabstock foams with ca. 29 wt.% hard segment material in the formulation, recent work from our own laboratory has shown that this ordering can lead to the formation of lamellae-like hard domains ca. 10 nm wide by 50–300 nm long [5].

An additional structure is also frequently observed in slabstock foam systems. At high water feed concentration with a stoichiometrically higher feed of isocyanate, the urea precipitates can aggregate further to form what have been termed “urea balls” or urea-rich aggregates [1,6]. These larger aggregates (ca. 200–500 nm in diameter) are frequently observed in conventional slabstock flexible foam formulations of high water concentration; however, these structures are not typically observed in molded or high-resiliency (HR) foams of the same water feed concentration [1,2,7]. This difference results from the chemistry of the typical components (most significantly the polyol component) used in each. Other recent work has suggested that the polyurea balls in slabstock systems are actually aggregations of lamellae-like hard domains [5]. The typical slabstock formulation used for that study, having four parts water per hundred polyol and an isocyanate index of 105, suggested that even at relatively low volume percent (estimated to be 24 vol.% hard segment material) the development of geometrically anisotropic hard domains may lead to significant amounts of connectivity and dramatically alter the properties of the solid state [5,8].

A large amount of interconnectivity between the hard domains may lead to a much higher modulus (i.e. stiffness) than a polymer with a dispersed hard domain morphology would attain. Moreover, alterations in that interconnectivity might be observed as a significant softening. It was shown in the earlier study [3] that DEOA substantially softens the foam by disrupting the “para-crystalline” ordering of the hard domains [9]. This disruption occurs as the DEOA changes the hard segment structure precluding the development of local ordering. However, it is unclear whether the softening occurred solely due to the changes in the packing of the hard segments within the hard domains (ca. 10 nm structure), or whether these alterations of the hard segment composition altered the larger scale morphology (ca. 50–500 nm) that might lead to interconnectivity. Since the properties of these foams depend so strongly upon the morphology of the solid-state, and since DEOA is so widely utilized commercially, this work seeks to further elucidate the influence which that component has upon hard domain morphology.

2. Experimental

2.1. Materials

Two foam samples of flexible water-blown polyurethane foams were made with varying DEOA concentrations by workers using a Hi-Tech RCM 30 foam machine at Dow Chemical in Freeport, TX. This operation consists of two hydraulic pistons to dispense the liquid components to the mixing head. The formulation components described below were prepared in two storage tanks, A and B. The A side consisted of the isocyanate. The B side consisted of the polyols, water, surfactants, and catalysts. An aluminum mold having dimensions of 15 in. × 15 in. × 4.5 in. was used and the mold was at 65°C when the reactive mixture was injected.

These foams were based on 72.25 parts of an experimental ethylene oxide endcapped polyether polyol produced by Dow Chemical which was based on a glycerine/sucrose mixed initiator and had a functionality ca. 2.4 and a molecular weight of 5000. The foams were also based on 27.75 parts of Voranol® 4703 (Dow Chemical), a 5000 molecular weight polyether triol. No copolymer polyol (a common reinforcing filler for molded foams) was used for these formulations. One foam was made with 1.275 DEOA parts per hundred polyol (pphp), and one was made without

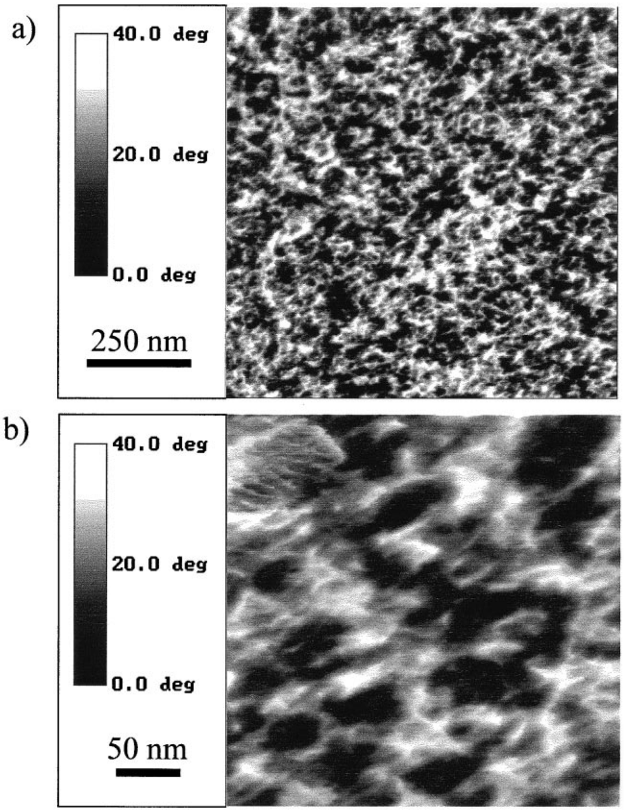

Fig. 1. AFM phase images of a molded foam without diethanol amine at: (a) low magnification; and (b) high magnification.

any DEOA. Total water in each foam was 3.82 pphp. Three catalysts were used: 0.22 pphp of Dabco® 33LV (Air Products and Chemicals) which is 33% triethylene diamine in dipropylene glycol; 0.08 pphp of Dabco® BL11 (Air Products and Chemicals) which is 70% bis(*N*,*N* dimethylaminoethyl) ether in dipropylene glycol; and 0.6 pphp of Niax® A4 (Union Carbide) which is a catalyst blend primarily promoting the gelation reaction but tends to increase the blow reaction rate as well. Two surfactants were utilized for the foam with DEOA to obtain the desired cell structure: 0.5 pphp of DC5043 and 0.5 pphp of DC5169. The foam without DEOA required further stabilization and the surfactant blend was: 0.43 DC5043 pphp, 0.43 DC5169 pphp, and 0.15 BF2370 pphp. The 80/20 2,4/2,6 isomeric blend of toluene diisocyanate was used at a stoichiometric feed rate. Therefore, to maintain stoichiometry, the TDI was decreased in proportion to the decrease of DEOA. For the foam with DEOA, 45.39 TDI pphp were fed, and for the foam without DEOA, 42.27 TDI pphp were fed.

Because the density of pure polyurea was required for the estimation of hard segment volume, a pure polyurea powder was produced by dissolving the 80/20 2,4/2,6 isomeric blend of toluene diisocyanate in acetone and slowly feeding in an excess of water while vigorously mixing. The acetone was then evaporated and the resulting powder was dried in a vacuum oven. One powder sample was produced with a calculated number average of 10 repeat units, and another was produced with an average of 30 repeat units. These powders were highly crystalline as shown by the WAXS pattern in Ref. [9]. To facilitate the estimation of density, the resulting powders were separated according to particle size, where one group was of ca. 1–3 mm in size and the other was of ca. 0.1 mm in size.

2.2. Methods

Atomic force microscopy (AFM) in tapping mode was utilized to study nanoscopic level structure. These experiments were performed on a Digital Instruments Scanning Probe Dimension 3000 Microscope using a Nanoscope IIIa controller and Nanosensors TESP (Tapping Etched Silicon Probe) type single beam cantilevers. These cantilevers had nominal lengths of ca. 125 μm, force constants of approximately 35 ± 7 N/m, and were used at oscillation frequencies at ca. 290 kHz. The samples were mounted and cured in epoxy (for 12 h at 60°C) as for transmission electron microscopy, and cross-sections were cryo-microtomed smooth and then examined by AFM. The procedure used for flexible polyurethane foams is described further in Ref. [9].

Density measurements on the polyurea powders were performed using a Denver Instruments Co. analytical balance model A-200DS and a Micromeritics Accupyc 1330 pycnometer. Argon was the expansion gas used for the pycnometer. Because the polyurea was in powder form, it was important to evaluate whether the pycnometer was correctly estimating the volume occupied by the sample. If the powder was too tightly packed, an over estimate of the volume would occur resulting in dependence of the density measurement on particle size. Two samples of different particle sizes were therefore used for each molecular weight polyurea powder, but no such variation was found.

Small angle X-ray scattering (SAXS) was utilized to provide quantitative characterization of the microphase separation for comparison with the AFM micrographs. Nickel filtered Cu K_α radiation having a wavelength of 1.542 Å was produced with a Philips model PW1729 generator operating at 40 kV and 20 mA. A slit collimated (0.03×5 mm) Kratky camera with a Braun OED 50 position-sensitive platinum wire detector was utilized for the scattering experiment. Because the apparent density of these foam samples did not vary with DEOA content, the beam path length was not corrected to account for the voids in the sample. Any error thus introduced to the absolute intensity of the SAXS profile is not expected to alter the relative comparisons for which this data was utilized.

3. Results and discussion

The properties of flexible polyurethane foams are well

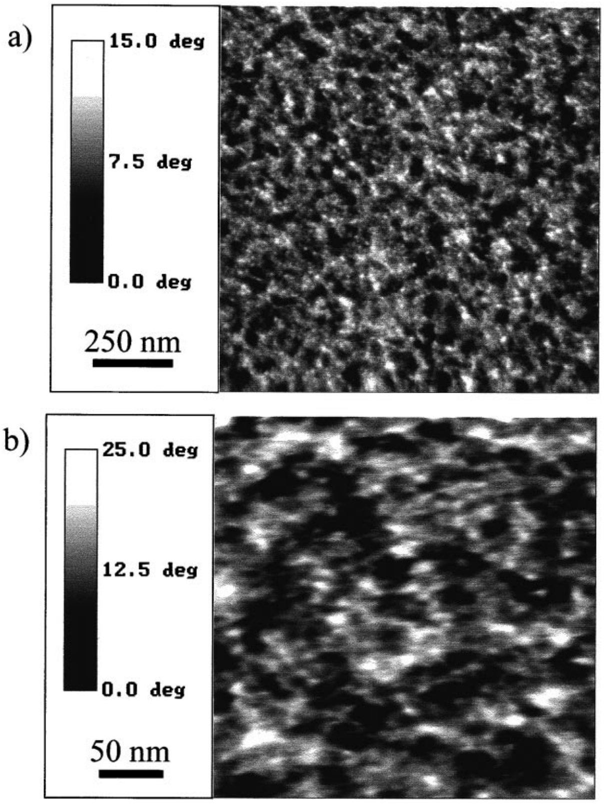

Fig. 2. AFM phase images of a molded foam with diethanol amine: (a) at low magnification; (b) showing the hard domain dispersion at high magnification.

known to be largely dependent on their microphase-separated morphology to the extent that alterations in that phase separation can have dramatic effects. This is discussed at length in Refs. [2,9]. However, many techniques have proven to be limited in the analysis of these materials by either the length scales that they study or their attainable resolution. For example, SAXS has proven to be valuable for studying the microphase separation, but it is not useful for evaluating phase separations on the scale of 500 nm [9]. TEM is another useful technique but obtaining adequate contrast for imaging in these materials at ca. 50 nm has proven to be difficult [10]. Phase imaging with tapping mode AFM, on the other hand, has been shown to be useful over a broad range of length scales because it relies upon stiffness variation in the local surface rather than upon electron density differences. Furthermore, TEM utilizes two-dimensional projections of ca. 100 nm thick sections and has a greater potential to convolute "*z*-axis" information. AFM, by contrast, only detects structure within 10 nm of the surface and so provides clearer imaging of the morphology in the plane of the other two axes. These differences enabled AFM to be used in other works to show for the first time how the microphase separation as shown by SAXS relates to the macrophase separation typically observed via TEM [5,9]. As discussed earlier, this occurs through the formation of lamellae-like hard domains, which have the potential to aggregate to form larger structures.

As can be seen in Fig. 1a, the molded foam without DEOA exhibits an even dispersion of aggregates (ca. 50 nm in size). In typical phase images from tapping mode AFM, higher offsets are usually generated by interactions of the tip with materials of higher dynamic modulus; therefore, in Fig. 1a the *lighter phases are richer in polyurea* and the *darker phases correspond to the polyol phase*. The polyurea aggregates of Fig. 1a are smaller than what is typically observed in slabstock systems [9], and this is attributed to the high content of ethylene oxide endcapping in the polyol used. Using polyols with higher concentrations of primary hydroxyl groups is known to improve the solubility of the hard segments in the polyol. Even at the low magnification of Fig. 1a, the aggregates appear to be geometrically anisotropic, and this is shown to be true in the higher magnification micrograph of Fig. 1b. As was shown in Ref. [5], it appears that the hard domains are actually lath-like, with dimensions of ca. 5 nm wide by 50–100 nm long. Moreover, Fig. 1b suggests what appeared at low magnification to be polyurea aggregates are the association of several of these lamellae-like polyurea hard domains. Fig. 1b also seems to attest to a high degree of interconnectivity between the larger polyurea aggregates. These micrographs suggest that the lamellae-like structures previously only observed in slabstock systems may also occur in molded foams when DEOA is not utilized. This suggests that the formation of lath-like structure is more dependent on the structure of the TDI-water based hard segment than upon the polyol system utilized.

Once DEOA is added, however, the morphology of the solid state is dramatically altered. As Fig. 2a reveals, the hard domains appear to be much smaller and very evenly distributed throughout the surface. No aggregates (ca. 50 nm) were observed in these samples, and the lower level of structure, that of the polyurea hard domains, can also be seen to be different. As observed by comparing Figs. 1a and 2a, the hard domains appear to be smaller (ca. 5 nm) and more geometrically isotropic in the foam with DEOA. This conclusion is borne out by comparing Figs. 1b and 2b. The hard domains in Fig. 2b are not the lath-like structures of Fig. 1b, and they have not aggregated as much as in Fig. 1b. Although a few anisotropic structures are observed in Fig. 2b, they are not as large and do not appear to occur as frequently. Fig. 2b also suggests a much lower degree of interconnectivity between the hard domains.

It is worth considering the significance of having no larger structures in the DEOA containing foams. Aggregations have been observed via TEM by other workers in materials with higher DEOA and TDI feeds [7], but they were found to occur irregularly in the sample in comparison to the aggregates of slabstock systems. It has been therefore hypothesized that aggregates occur in DEOA containing systems as a result of difficulties in keeping the liquid

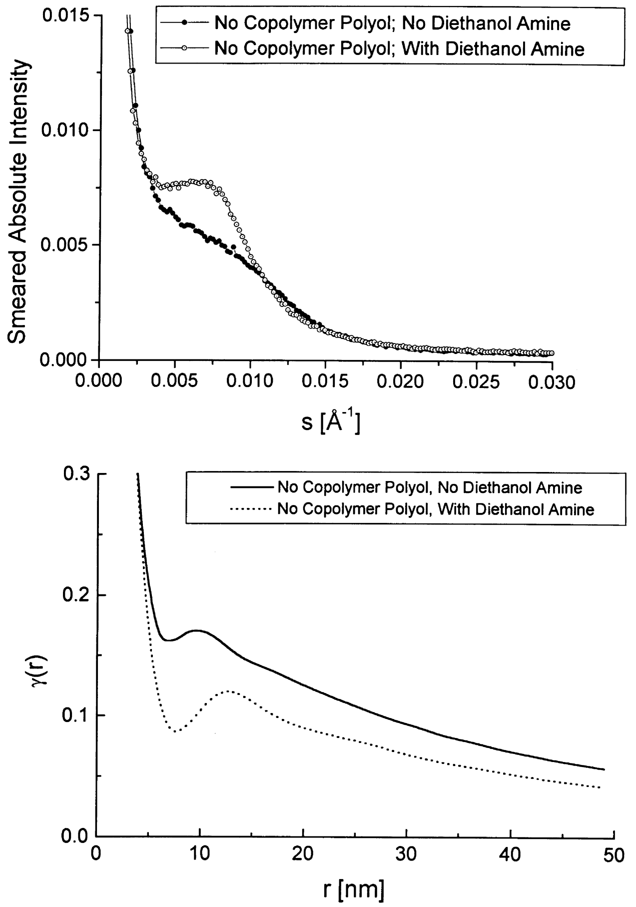

Fig. 3. (a) SAXS profiles for the foam samples with and without DEOA. (b) Three-dimensional correlation functions for the foam samples.

reactive mixture homogeneous while the foam is forming [7]. In slabstock foam, polyurea aggregates tend to form evenly throughout the material [2] as a result of association between lath-like polyurea hard domains which occur everywhere in the material [5]. In molded foams, when enough DEOA is added, the reactive mixture can phase separate even before the polyurea hard segments precipitate into hard domains. It is observed here that the sample without DEOA, which has a lower hard segment content (27 wt.%), forms aggregates evenly throughout the matrix; however, the DEOA containing sample (29 wt.% hard segment content) does not. This suggests that DEOA distinctly alters the mechanism of aggregate formation. Without the DEOA, the evenly distributed aggregates appear to form as the association of lamellae-like hard domains. However, considering the data of the other study [7], it is suggested that with DEOA a hard segment solubility limit in the polyol system must be surpassed to induce a phase separation leading to the formation of irregularly spaced aggregates. These samples were clearly below that limit and therefore exhibited no polyurea aggregation.

An interesting correlation to consider is that the SAXS of similar materials revealed that adding DEOA alters the interdomain spacing from ca. 9 nm without DEOA to ca. 12 nm with DEOA [3]. Fig. 3a and 3b shows that, for these foams, the interdomain spacing was 9.5 without DEOA and 12.7 nm with DEOA. Considering the morphology observed in Fig. 1b, this suggests that without DEOA, the SAXS spacing may be an indicator of the most probable distance between lamellae-like structures *within the polyurea aggregates*. This is hypothesized because it is observed in Fig. 1b that the spacing between the hard domains outside of the aggregates is ca. 30–50 nm which is much too large to explain the shoulder in the typical SAXS profile [3]. Moreover, where it could be measured within the aggregates of Fig. 1b, the distance between the lamellae was ca. 10 nm. On the other hand, Fig. 2b shows that with DEOA a ca. 13 nm spacing frequently occurs as the distance between the geometrically isotropic ca. 5 nm hard domains which are distributed evenly across the sample. *This may indicate that the ultimate result of the composition change that occurs with DEOA addition is a reduction in the association between hard domains.* The interdomain associations are weakened and so the hard domains themselves become more evenly dispersed and further apart, thus the reduced hard domain interconnectivity results in a polymer that exhibits a lower modulus (i.e. stiffness).

It can also be observed that the shoulder in the SAXS profile of Fig. 3a becomes much sharper when DEOA is added to the formulation. This suggests a more even periodic microstructure such as is observed in Fig. 2b in comparison to Fig. 1b. The less distinct shoulder of the SAXS profile without DEOA is similar to what is commonly observed in slabstock foams, and it suggests a broader distribution of interdomain distances and/or hard domain sizes throughout the sample. This corresponds well to Fig. 1b, wherein urea-rich domains (i.e. aggregates) are separated by ca. 30–50 nm urea-poor regions, and the aggregates themselves contain several lamellae which are spaced at ca. 10 nm.

As with an earlier AFM study on slabstock foams [3], the micrographs presented suggest a higher volume percent of hard segment material than would be expected from the formulation. To estimate the volume fractions, the densities of the respective phases in the foam are required, but the range of volume percents possible can be estimated by using the densities of the pure components. For that purpose, the densities of the polyurea powders described earlier were evaluated with a pycnometer. It was found that the pure polyurea had a density of 1.3 ± 0.002 g/cm^3 which was independent of both the particle size and the calculated molecular weight of the polyurea hard segment. The polyols used had densities of 1.0 g/cm^3. The foam without DEOA, having 27 wt.% hard segment material, would have a hard segment volume percent between 22 and 27%, depending on how organized the hard domains are relative to the packing that occurs in pure polyurea powder. Assuming that all of the DEOA becomes incorporated into the hard domains

[3], the foam with DEOA, which has 29 wt.% hard segment material, would result in hard segment volume percents between 23 and 29%. The micrographs, such as Fig. 1a, suggest volume percents higher than that range, and this is suggested to mainly result from the well-known difficulties associated with using two-dimensional micrographs to evaluate volume fractions. Additionally, three other factors in these materials might contribute further to this. Primarily, the intermixing of hard and soft material even in the larger aggregates makes characterization of domain sizes more challenging. Secondly, secondary interactions at the interface of every hard domain could lead to stiffening of the polyol, which would result in higher phase offsets, thus increasing the apparent size of the hard domains in the micrograph. Finally, material below the surface as deep as ca. 10 nm can induce offset in the tip, so some hard domain material just below the microtomed surface may appear in the image thus over representing the hard domains of the microtomed plane.

4. Conclusions

These results have shown that the use of DEOA in the formulation of molded flexible polyurethane foams has clear effects on the morphology of the solid state. The DEOA was shown to disrupt the formation of long (ca. 100 nm) lamellae-like polyurea hard domains. It also disrupts the formation of a consistent distribution of polyurea aggregates (ca. 50 nm in diameter) and instead yields a finer dispersion of isotropic ca. 5 nm hard domains. These changes reduced the observed hard domain interconnectivity that may ultimately lead to the reduced solid state modulus (i.e. stiffness) described elsewhere [3].

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References

[1] Herrington R, Hock K. Flexible polyurethane foams. 2. Midland, MI: The Dow Chemical Co, 1998.
[2] Dounis DV, Wilkes GL. Proceedings of the Polyurethanes 1995 Conference: SPI Polyurethanes Division, 26–29 September 1995:353.
[3] Kaushiva BD, Wilkes GL. J Appl Polym Sci 2000 in press.
[4] Dounis DV, Wilkes GL. J Appl Polym Sci 1997;65:525.
[5] Kaushiva BD, Wilkes GL. Polym Commun 2000 in press.
[6] Armistead JP, Wilkes GL, Turner RB. J Appl Polym Sci 1988;35:601.
[7] Lidy WA, Rightor E, Heaney M, Davis B, Latham L, Barnes G. Proceedings of the Polyurethanes World Congress‘97, 1997:95.
[8] Abouzahr S, Wilkes GL, Ophir Z. Polymer 1982;32:1077.
[9] Kaushiva BD, McCartney SR, Rossmy GR, Wilkes GL. Polymer 2000;41:285.
[10] Neff R, Adedeji A, Macosko CW, Ryan AJ. J Polym Sci B: Polym Phys 1998;36:573.