

Polymer Communication

Uniaxial orientation behavior and consideration of the geometric anisotropy of polyurea hard domain structure in flexible polyurethane foams

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Received 10 May 1999; received in revised form 16 November 1999; accepted 29 November 1999

Abstract

Atomic force microscopy (AFM) and wide angle X-ray scattering (WAXS) were used to examine the morphology of hard domains in flexible polyurethane foams and plaques based on slabstock formulations. In plaque samples that were uniaxially deformed to 50% elongation, WAXS was utilized to demonstrate transverse hard segment orientation relative to the axis of deformation. AFM was utilized to directly observe the morphology of the foams and plaques. Micrographs from this technique present, for the first time in polyurethane foam systems, lamellae-like structures ca. 0.2 μm long and ca. 10 nm across. These structures are believed to be precipitates of polyurea hard segments and are considered to be responsible for the orientation behavior presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyurethane foam; Hard domain morphology; Atomic force microscopy

1. Introduction

Flexible polyurethane foams are currently utilized in a broad range of applications in such areas as furniture, packaging and transportation. Although polymer composition varies with each different product, this chemically complex family is united by utilizing a urethane linkage to covalently bond hard segments with soft segments. This linkage is typically formed from the reaction between the isocyanate functionality of one component with the hydroxyl group of another component. By controlling the composition of each component, two solid-state phases are expected. This two-phase morphology provides the key to controlling performance of the final product and gives the manufacturer versatility in tuning properties as desired by varying the composition or content of one or the other phases.

One phase of typical water-blown foam systems is based upon the reaction of water with a diisocyanate such as toluene diisocyanate (TDI). This reaction initially produces a carbamic acid which then decomposes yielding heat, carbon dioxide, and an amine functionality [1]. The heat

and carbon dioxide contribute to the expansion of the gas bubbles in the reactive mixture and so play important roles in the development of the foam's cellular structure. On the other hand, a disubstituted urea product results from the reaction of the amine with other isocyanate groups. A "hard segment" results from several isocyanate groups covalently bonding through the urea linkages, and solid-state phase separation in typical systems arises from the precipitation of these segments into "hard domains." A more detailed discussion of the morphology and composition of these polyurea-based hard domains may be found in Ref. [11].

An additional structure is also sometimes observed in these 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 [1,2]. These larger aggregates 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 [1,3,4]. This difference results from the chemistry of the typical components used in each. Whereas both molded (HR) and slabstock flexible foams most commonly utilize TDI (fed at an 80/20 2,4/2,6 isomer ratio), the polyol used for each is one major formulation

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difference. The higher primary hydroxyl content in molded foam polyols provides a much faster reaction rate and therefore requires a different blend of catalysts as well as lower potency surfactants to obtain an open-celled foam. Also, increasing the ethylene oxide content of the polyol dramatically alters the miscibility of water and other reaction components. Furthermore, it is believed that variation of the ethylene oxide/propylene oxide (EO/PO) ratio also has profound effects on the solubility of the hard segments in the polyol matrix of the final foam. It is therefore deduced that the larger aggregates (urea balls) may form as either the hard segments or the urea precipitates or some combination of both reach a molecular weight or a concentration that surpasses a solubility limit which varies depending on the chemical system being utilized [1,2].

In examining how these materials behave during mechanical deformation by using FTIR linear dichroism techniques, workers [5] have shown initial hard segment orientation transverse to the direction of elongation in flexible slabstock foams followed by transformation to parallel orientation parallel to the stretch direction at higher uniaxial deformations. This somewhat surprising orientation behavior has also been consistently well noted in segmented polyurethane elastomers [6–9]. It has been explained by suggesting that hard domains are associating with one another to form lamellar-like structures which then dissociate under shear yielding and rupturing at the higher elongations. This dissociation causes the transformation of the hard segment orientation from partially perpendicular to partially parallel to the deformation axis [5–9]. Considering the interdomain distances typically observed via small-angle X-ray scattering (SAXS) (7–11 nm), this orientation behavior suggests that these spacings may not result from a dispersion of small, geometrically isotropic hard domains. It instead indicates that such spacings may be the distances between lamellar-like formations, and that much larger lateral dimensions of the lamellae exist. However, well-defined lamellar-like structure on any larger scale in polyurethane foams has not been unambiguously observed via microscopy. Recent work by Neff et al. [10] has attempted to utilize TEM to probe the scale lengths below that of the polyurea aggregates which are ca. 50–200 nm. By degrading the samples with the electron beam, image contrast was enhanced enough for the micrographs to suggest the presence of evenly distributed anisotropic structures on the order of 1 nm across with lengths ca. 4–6 nm [10]. Given the beam damage, and thus the pronounced local chemical changes, required to induce the formation of an observable structure, the question remains whether such structures occur in a polyurethane foam under typical conditions. Also, the chemistry and space filling considerations suggest that the observed domains might contain only a few hard segments oriented parallel to the long axis of the polyurea precipitate. Therefore, hard domain structure on that level would not explain the orientation behavior observed, and it does not provide an explanation for how the micro-

phase separation (as observed via SAXS, ca. 7–11 nm) relates to the macrophase separation (typically observed via TEM, ca. 50–200 nm). This discussion brings up the question of how well dispersed the hard domains actually are in polyurethane foams [11]. One would, however, expect that the level of hard domain dispersement or its inverse, domain connectivity, would depend on the relative composition or volume fractions of the respective hard and soft segment components. In fact, an earlier report from this same laboratory addressed this issue for segmented urethane elastomers [12]. Of interest is whether such domain connectivity exists in urethane foams and what is the nature of the morphological texture of the respective hard segment regions. This report will attempt to address this topic.

Given the wide use of polyurethane foams and elastomers, and the dependence of their properties on these hard domains, it can be seen that it would be valuable to understand their morphology. In particular, it would be of great importance to understand how the hard domains relate to the larger urea ball structures. In a recent publication, the authors have presented strong evidence that the WAXS 4.7 Å reflection frequently observed in these materials results from ordered packing of hard segments via bidentate hydrogen bonding which is commonly detected via FTIR [11]. This local packing provides a Bragg spacing that is perpendicular to the long axis of the hard segments, and that spacing yields the observed WAXS reflection. A postulate to be tested in this study is that if such a link exists, the orientation behavior previously observed through linear dichroism should also be detectable with WAXS. This would be observed as the 4.7 Å reflection becoming more concentrated in the meridional regions of a uniaxially deformed sample. This study will therefore utilize samples characterized in another work to further elucidate the hard domain morphology between the scale lengths of SAXS and TEM.

2. Experimental materials and methods

2.1. Materials

Samples of flexible water-blown polyurethane foams were made with conventional slabstock formulations [1]. These samples were based on 100 parts of Voranol™ CP 3322 (Dow Chemical), a triol containing 88% propyleneoxide and 12% ethyleneoxide with terminal secondary OH-groups. The foams also used four parts of water and TDI 80 (an 80/20 mixture of the 2,4/2,6 isomers) fed at an isocyanate index of 105. Dimethylethanolamine was used as a catalyst for the water–isocyanate reaction at a concentration of 0.2 parts per hundred polyol (pphp). Stannus octoate was used as a polyol–isocyanate reaction catalyst also at 0.2 pphp. The surfactant used was TEGOSTAB™ BF 2370 (Goldschmidt), and it was fed at a concentration of 1.5 pphp. BF 2370 is a siloxane–polyether block copolymer

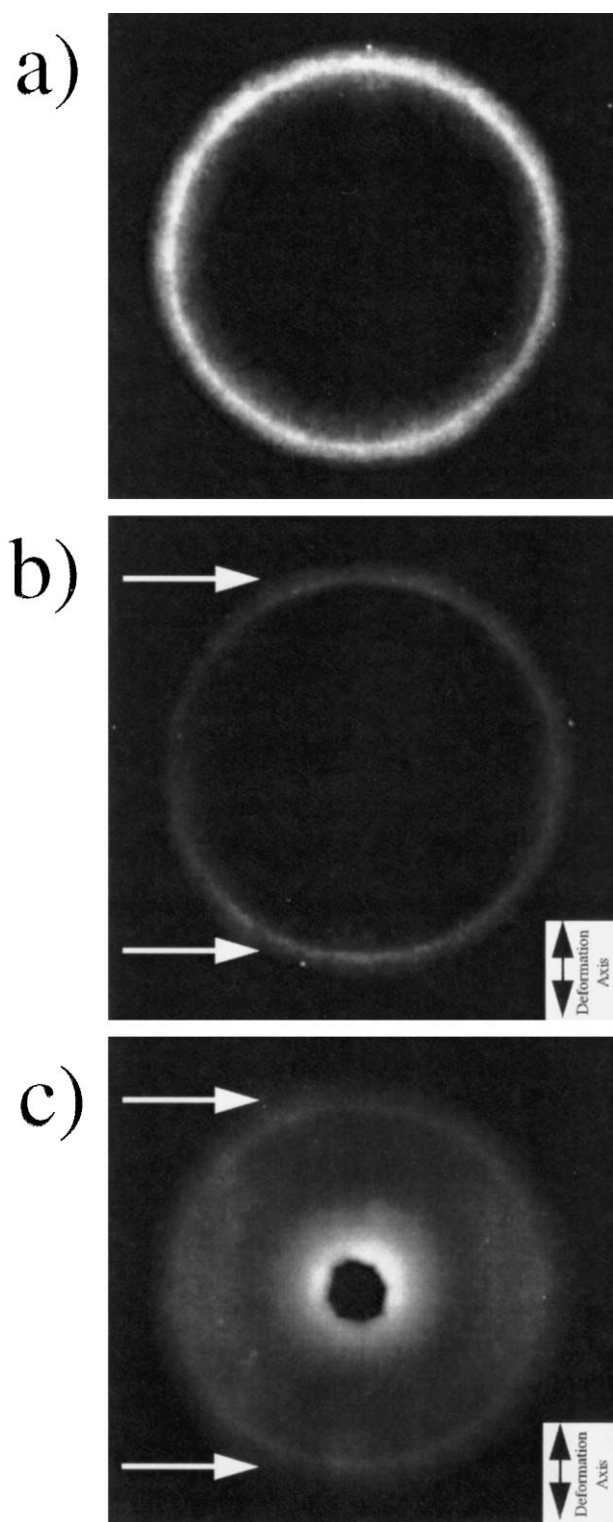


Fig. 1. Consideration of the geometric anisotropy of the polyurea hard domain structure in flexible polyurethane foams.

with an average molecular weight of 8800. The precise structure of BF 2370 is given in Ref. [11].

One foam was made that was allowed to fully develop with an additional 15 min cure at 140°C to remove tackiness. This sample is named “SSu1.5.” Two foams of the

same formulation were also mechanically compressed to examine possible influences that the removal of cellular structure may have on the development of microphase separation in the solid state. One of these was crushed at 80 s to match the time at which a 0.0 surfactant pphp foam spontaneously collapsed. The other foam was crushed at 106 s, the rise time to final height for that foam formulation. For these samples, small quantities of material were taken from the reacting foam and then quenched or crushed. This was done to assure that the entire sample had a uniform thermal and morphological history characteristic of their respective times of quenching or crushing. The crushed samples shall be referred to as “C80-Su1.5” and “C106-Su1.5.”

2.2. Methods

To explore the ordering of the hard domains, the WAXS technique was applied using a Philips model PW1720 generator equipped with a Warhus camera. Nickel filtered CuK radiation was used with a wavelength of 1.542 Å and pinhole collimation with a diameter of 0.020 in. Samples were mounted in a uniaxial extension device designed to fit in the camera and expose the gauge section of the sample to the X-ray beam. Sample time was ca. 3 h.

Atomic force microscopy (AFM) in tapping mode was also used to study nanoscopic level structure. These experiments were performed on a Digital Instruments Scanning Probe Microscope using 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 mounted and cured in epoxy for TEM at 60°C were cryomicrotomed smooth and then examined by AFM. The procedure used for flexible polyurethane foams is described further in Ref. [11].

3. Results and discussion

As stated earlier, in Ref. [11] the authors presented evidence that ordered packing within the polyurea hard domains, which occurs as bidentate hydrogen bonding observed via FTIR, is the source of the 4.7 Å reflection observed via WAXS. As already discussed, FTIR linear dichroic evaluations of foams and elastomers have well demonstrated that the hard domains initially orient transverse to the extension direction [5–9]. Such behavior is believed to be only truly explained by the presence of lamellar-like hard domains in the polymer. Furthermore, there must be enough such domains in the material to dominate the FTIR linear dichroic measurements of orientation.

Fig. 1 presents three WAXS patterns of the slabstock formulation samples which were crushed into plaques, C80-Su1.5 and C106-Su1.5. The deformation axis of the samples is always kept vertical. In Fig. 1a, a typical

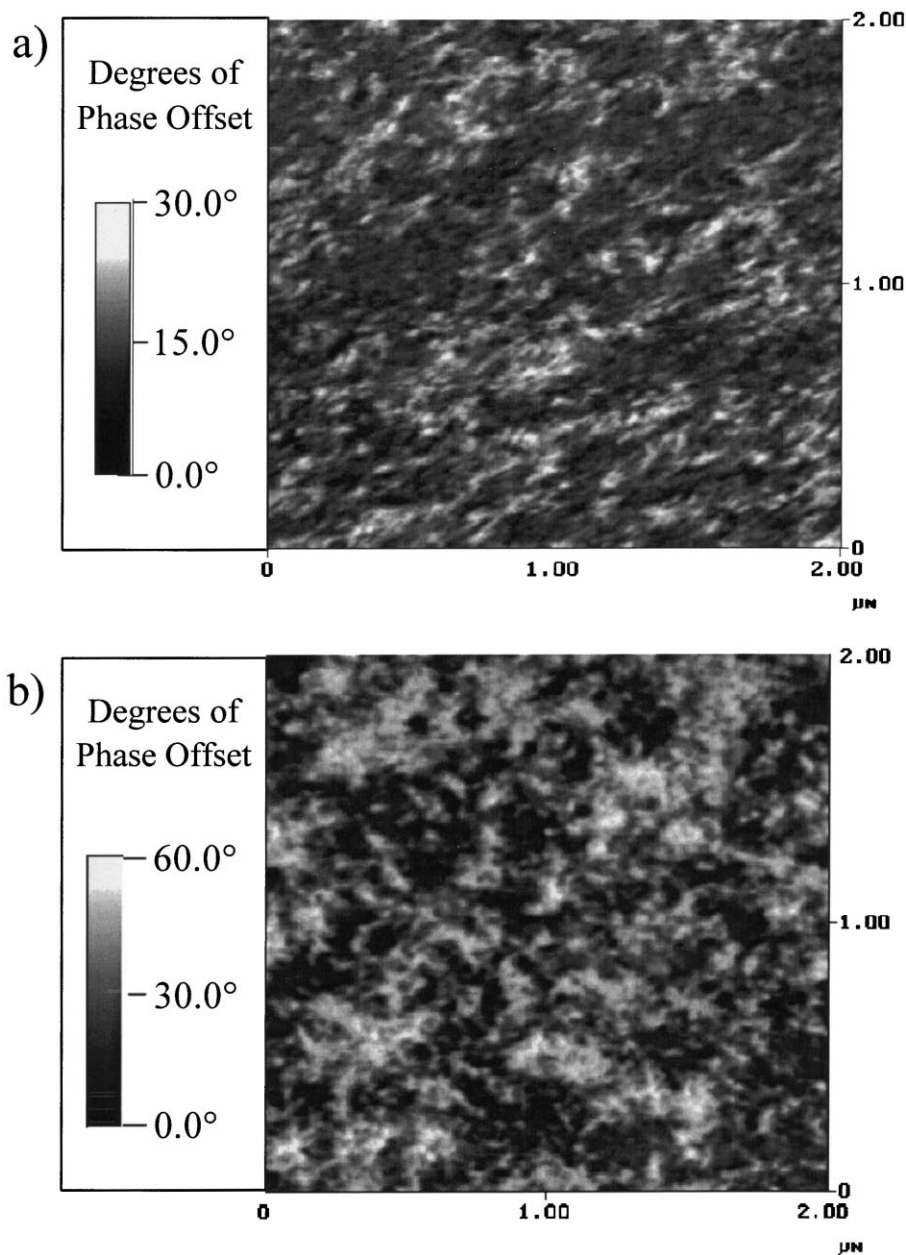


Fig. 2. Consideration of the geometric anisotropy of polyurea hard domain structure in flexible polyurethane foams.

WAXS pattern of an undeformed polyurethane foam material may be seen from sample C80-Su1.5, wherein a 4.7 Å reflection is observed with no azimuthal intensity dependence. This single maximum overlays an amorphous halo seen as a diffuse ring. Such uniformity is indicative of samples with no orientation. Fig. 1b, however, shows the same sample extended at room temperature to only 50% elongation. It may be observed in that pattern that there is an intensification of the 4.7 Å reflection around the meridional centerline. However, on the equatorial axis, the reflection has lost enough intensity that it is difficult to differentiate it from the underlying amorphous halo. This is evidence of transverse orientation of the hard segments in the polymer, providing strong support of behavior

observed via FTIR linear dichroism. This behavior is also seen in Fig. 1c from sample C106-Su1.5 also extended to 50% elongation. Given the large morphological differences between these two samples, discussed at length in Ref. [11], this suggests that the formation of lamellae occurs widely in typical slabstock polyurethane foam polymers.

To find further information regarding the morphology of the hard domains, the technique of tapping mode AFM was applied. A phase image of the sample C80-Su1.5 is shown in Fig. 2a. This is a higher magnification view than any published in Ref. [11]. The most important observation to make is that the higher phase offset features on this surface, which correspond to the polyurea hard domains, are not at all spherical in shape. Instead, it can be observed that thin

lath-like aggregations are pervasive throughout the material. *It should be noted that the apparent orientation of the lath-like structures observed in Fig. 2a was a local phenomenon, and that larger scale phase images and planar axis WAXS patterns revealed no distinct large scale planar orientation which might be induced by squeezing the sample into a plaque.* Where it could be measured in Fig. 2a, these lath-like structures had dimensions of ca. 18 nm across and range in length to as large as ca. 0.3–0.5 μm , and they were spaced ca. 30 nm from center to center. Interdomain distances from SAXS are typically 7–11 nm, and it is suggested that the discrepancy largely arises because these measurements were made on domains away from the larger aggregates. It can be observed in Fig. 2a and b that the laths are smaller and closer together within the large aggregations where consistent measurements are difficult to make. Also, if the laths are not normal to the cutting plane for the microtome, estimations of their size will contain error. Finally, it should also be noted that C80-Su1.5 was shown in Ref. [11] to have an atypical distribution of its aggregates. In TEM, 2D projections of the thin sections reveal dark aggregates that are usually interpreted as polyurea rich domains; however, AFM does not convolute “z-axis” information but provides clear imaging of the morphology in the plane of the other two axes. Fig. 2a clearly exhibits the formation of lath-like structure, and it suggests that large aggregations of polyurea hard segments may be clusters of these lath-like hard domains.

Fig. 2b is another phase image from AFM of a typical slabstock foam, SSu1.5. It is observed in Fig. 2b that the polyurea aggregations are larger and more evenly distributed across the surface, and this more even distribution relative to C80-Su1.5 is consistent with what was shown in Ref. [11]. Upon closer inspection, however, it can be seen that similar if somewhat shorter lath-like domains can be observed throughout the image. At some places, these lamellae-like structures even appear to bridge between larger polyurea aggregations. This suggests a higher level of connectivity than would be expected considering that these materials contained only 29 wt% hard segment material (24 vol%). It is hypothesized that this connectivity would lead to considerable stiffening of the polymer. It can be observed, especially in Fig. 2b, that more hard segment material appears to be present than just 24 vol%, and this appearance is suggested to be the result of three main factors. Primarily the hard and soft domains are somewhat intermixed so that even the larger aggregates can be seen to contain some amount of polyol. This makes visual estimation of volume fractions difficult. Secondly, higher phase offset is induced by any stiff material, and it is likely that some polyol is stiffened through secondary interactions at the interface of every hard domain. This is supported by the observation of many domains in the image which induced

intermediate phase offsets. Finally, material below the surface as deep as ca. 100 Å 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

This study has shown that the polyurea hard domains do develop lamellar-like structure in typical slabstock flexible polyurethane foam systems. It is suggested that these lath-like structures develop as the polyurea hard segments precipitate into hard domains. Furthermore, it also appears from this examination that polyurea balls (macrophase aggregations) are clusters of these lamellae. This indicates that the polyurea balls may either form as developing lamellae spatially interfere with each other or as several lamellae grow out from a single nucleation site. Current work is examining the thermal stability of these lamellae and their orientation. Also materials based on a molded foam formulation will be used to examine whether the anisotropic hard domain morphology is ubiquitous in these materials or just isolated to systems wherein polyurea balls typically occur.

Acknowledgements

This work has been financially supported by the Dow Chemical Company and Goldschmidt AG, and their support is gratefully acknowledged. We also thank Helmut Schator of Goldschmidt AG for directing the slabstock foaming experiments at Goldschmidt AG. Finally, we acknowledge the contributions and many helpful discussions of Dr Gerd Rossmly.

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