

Influence of Diethanolamine (DEOA) on Structure–Property Behavior of Molded Flexible Polyurethane Foams

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ABSTRACT: In this study, the viscoelastic and morphological properties of molded foams were investigated to determine the influence of varying the concentration of diethanolamine (DEOA), a commercially utilized crosslinking agent. FTIR and WAXS analyses showed that DEOA had a disrupting effect on the bidentate hydrogen bonding within the hard domains of the polymer. DMS revealed that DEOA softens the foam above the T_g of the soft segment but only causes minor changes in the degree of microphase separation. Annealing treatments were shown to remove the DEOA influence on the microphase separation as well as some of the softening effect. FTIR was used to show that bidentate hydrogen bonding is enhanced through the annealing of DEOA foams. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 202–216, 2000

Key words: polyurethane; foam; structure; property; diethanolamine

INTRODUCTION

Polyurethane foam is widely utilized in many applications including thermal insulation, furniture, packaging, and novelty applications. Often, these uses demand altering the large initial foam “bun” into complex shapes, and it has proven more economical in many cases to produce foams by casting the reactive mixture into molds of the desired form rather than by the traditional slabstock method. This eliminates the time and waste involved in trimming and shaping large buns of foam. Furthermore, molded foams can be made to meet a broad range of property specifications by including inserts for support, varying zones of hardness, or with liners or skins of fabric or plastic. Therefore, while slabstock operations dominate the volume of the flexible foam produced, the

technique of molded foam production is gaining popularity.

Changing from slabstock to molded foam processing involves switching modes of production from a continuous method to a semibatchwise operation in which each mold is essentially a reactor. Molded operations usually involve many individual molds being rotated through the production cycle from being charged with reactants to product removal and preparation for another charging. Since the volume of the batch is fixed by the mold size, and since the number of molds is essentially fixed by the size of the process, decreasing residence time in the molds (or demold times) is an effective way to increase production.¹

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 diisocyanate is typically used in

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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 poly(ether polyol). Because the polyol usually has a functionality between two and three, 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 another pseudo or physical crosslinking point that is, instead, dependent upon strong intermolecular interactions (i.e., hydrogen bonding) for its cohesive strength.

To achieve lower demold times, the formulation of a molded foam varies significantly from that of a traditional slabstock. The polyols used for each are different in three ways: First, the polyol of a molded foam tends to be end-capped with poly(ethylene oxide) for increased reaction rates. Second, the polyol molecular weight is generally higher than what is used in slabstocks (ca. 5000 MW in molded compared to ca. 3000 MW in slabstock), thus yielding faster viscosity buildup as the gelation reaction proceeds. Finally, filler particles are sometimes added to formulations to increase load-bearing properties. The predominant filler currently used is termed "copolymer polyol" (CPP), and it is a particulate dispersion produced via the free-radical copolymerization of styrene and acrylonitrile in a poly(ether polyol). Since the reaction of either the styrene or the acrylonitrile free radicals with the polyol is not favored, the dispersion is stabilized by also copolymerizing the SAN with poly(ether polyol) molecules functionalized with a vinyl moiety. This process produces a stable dispersion of SAN particulates that are typically about 0.3–0.5 μm in size. The influence of CPP on the structure–property relationships in molded foams was addressed in another work by the authors.²

Because the filler particulate aids in cell opening, the CPP component does play a particularly important role in facilitating this work. In another study from this laboratory on molded foams without CPP, workers reported in ref. 3 that the

increased rate of crosslinking provided by diethanolamine (DEOA) prevents more cells from opening than which occurs without DEOA.³ This was observed as a significant decrease in airflow through a foam sample. The samples from that study showed that compressive load bearing increased as DEOA concentration increased in the formulation; however, because all levels of the structure contribute to the macroscopic properties of foams, it was not possible to absolutely distinguish whether the observed increase in load bearing was due to the higher content of closed cells or due to the presence of the crosslinking agent, DEOA.³ Filler particles such as those of the CPP are known to have destabilizing effects on the cell windows as they become thinner, thus offsetting the stabilizing effect of the DEOA. Therefore, to obtain a set of foams which have the same airflow characteristics but vary in their DEOA content, CPP was included in the formulations reported here.

Another major difference between molded and slabstock formulations is the presence of the crosslinking agent DEOA. Typically, this component is fed at concentrations between 1.0 and 2.0 parts per hundred parts polyol (pphp). Because of its low molecular weight, this is a small weight fraction; however, in total number of functionalities added, at these levels, the DEOA is of approximately equal importance as are the polyol and water. Using typical feed proportions from a formulation as a basis for calculation makes this clear. For example, 100 g of a 5000 MW poly(ether polyol) with a functionality of 2.4 would only provide about 0.048 mol of hydroxyl groups for reaction; however, only 2 g of DEOA provides 0.057 mol of reactive groups. This component is added to increase the degree of covalent crosslinking in the foam, thus more quickly adding the dimensional stability required for the foam to be pulled out of the mold and, therefore, decreasing demold times.

Simultaneously, however, DEOA has a single amine and two alcohol functionalities, and since they, respectively, produce urea and urethane linkages upon reaction with isocyanate, it can be seen that DEOA might play a significant role in the development and organization of the polyurea hard domains. Typical flexible polyurethane foams are phase-separated systems composed of the polyol ("soft") matrix with polyurea hard domains interspersed throughout. These hard domains organize in a specific way due to hydrogen bonding, sometimes termed "*para*-crystalline" or-

dering, and variation of their size and concentration has been shown to have profound influence on the overall properties of the foam. In the molded foams studied here, it is therefore anticipated that the DEOA will have its impact by changing the makeup and molecular packing of the hard domains and thereby influencing overall properties.

Several other components in the formulation must be discussed when considering a molded foam. While toluene diisocyanate (TDI) is widely utilized in both slabstock and molded foam formulations, the concentration of isocyanate in a foam has significant influence on its final properties. A foam that has a stoichiometric ratio of TDI to other components is said to have an isocyanate index of 100. It has been shown that producing foams with less than a stoichiometric feed, about 85–90, for example, significantly reduces the level of covalent crosslinking in the system, resulting in a substantial softening of the foam.^{3,4} For example, at 30°C–35% RH, the 85 index foam exhibited a 43% lower load bearing than that of the 100 index foam.⁴ Foams produced above the stoichiometric feed, about 105–110, for example, typically produce harder foams, exhibiting load bearings about 21% higher than that of the 100 index foam.^{3,4} This increase in load bearing with the higher index foams has been attributed to a faster viscosity increase, resulting in less phase separation of the hard segments from the polyol.^{3,4} To avoid such variation, therefore, the concentration of TDI in this study was increased as DEOA is added to maintain a stoichiometric feed ratio (100 index).

Since catalysts in foam formulations are blended to balance the gelation and blowing reactions so that the foam has the right properties, changing the reactivity of the polyol components and the presence of DEOA requires alteration of the catalyst blend. Surfactant concentration has also been modified relative to a slabstock formulation to provide for cells of the desired size for seating applications (ca. 1 mm diameter) that open at the appropriate time. Both the catalyst and the surfactant concentrations have been maintained at constant levels for all the samples studied here.

The thermal history of these foams is the final variable to be considered. A typical molded foam is produced by injecting a reactive mixture into about a 68°C mold. The mixture expands to fill the mold within 1 min and the foam is left to cure for about 4–5 min. The foam bun is then removed

from the mold and mechanically crushed twice between rollers to further aid cell opening. Once the reactive blend is injected into the mold, the mixture heats itself to about 140°C within 120 s of injection and then ambiently cools after the crushing steps. Molded foam buns are typically only about 4–6 in. thick and cool within hours. Slabstock buns are usually several feet thick and cool much more slowly over several days. Remaining at higher temperatures for so much longer could allow slabstock foams to cure further and possibly achieve a higher degree of phase separation than that of the molded foams. A rapid viscosity increase due to cooling might prevent similar phase separation in molded systems than that which occurs in slabstocks and ultimately reduce the overall level of hard domain ordering in the foam. As the organization of the hard domains is crucial to mechanical properties, the usefulness of an annealing step to the production of the foams was therefore also addressed in the present work by annealing some samples for 2 h at 130°C.

In light of this discussion, it is clear that DEOA may have a significant impact on the composition of the hard segments by coreacting with the isocyanate simultaneously with the water and polyol. Such alteration in the structure of the hard segments could have dramatic effects on the way that they order within the hard domains, and variation of that packing is known to strongly alter the mechanical properties of a foam. From this discussion and the earlier results from this laboratory,³ it is clear that the relationships among formulation, structure, and properties are not completely understood. Therefore, since DEOA is so widely utilized commercially, this work seeks to further elucidate such relationships and to further clarify the results of our earlier study.

EXPERIMENTAL

Materials

Five 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, Texas. 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,

Table I Variation of DEOA and TDI 80 in the Five Samples

Sample Names	DEOA Added	Total TDI 80 Added
McD2.0/MaD2.0	2.35 (2.0) pphp	46.45 pphp
McD1.7/MaD1.7	2.0 (1.7) pphp	45.2 pphp
McD1.3/MaD1.3	1.5 (1.275) pphp	43.42 pphp
McD0.9/MaD0.9	1.0 (0.85) pphp	41.64 pphp
McD0.0/MaD0.0	0.0 pphp	40.1 pphp

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 $15 \times 15 \times 4.5$ in. was used, which was heated to 68°C prior to injection of the reactive mixture.

These foams were based on 62.86 parts of an experimental ethylene oxide endcapped poly(ether polyol) produced by Dow Chemical which was based on a glycerine/sucrose mixed initiator and had a functionality of about 2.4 and a molecular weight of 5000. The foams were also based on 37.14 parts of Voranol® 4935 (Dow Chemical), a copolymer polyol containing 35 wt % styrene/acrylonitrile random copolymer (60/40 styrene/acrylonitrile) particles. These particles were about $0.5\text{--}1.3 \mu\text{m}$ in diameter. Five different concentrations of DEOA were used: 0.0, 0.85, 1.275, 1.7, and 2.0 pphp. Total water in each foam was 3.82 pphp. Three catalysts were used: 0.15 pphp of Dabco® 33LV (Air Products and Chemicals), which is 33% triethylenediamine 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 to obtain the desired cell structure: 0.5 pphp of DC5043 and 0.5 pphp of DC5169. The 80/20 2,4/2,6 isomeric blend of TDI was used at a stoichiometric feed rate. Therefore, to maintain stoichiometry, the TDI was decreased in proportion to the decrease of DEOA for each sample as shown in Table I.

Methods

Dynamic mechanical analysis (DMA) was carried out using a Seiko Model 210 in the tensile mode. The samples were heated from -120 to 350°C at

a rate of $0.5^\circ\text{C}/\text{min}$, from which the storage modulus (E') and $\tan \delta$ data were collected at a frequency of 1 Hz. Bar-shaped samples were cut from the foam with die punches and had dimensions of approximately $5 \times 5 \times 15$ mm with a grip-to-grip distance of 10 mm. Well below the T_g of the soft segment (at ca. -100°C), the storage moduli were then normalized to 3×10^9 Pa to remove the effect of varying density, which is only a function of the cellular structure.⁵

Mechanical properties were investigated through compressive load relaxation. Samples, having dimensions of $3.5 \times 3.5 \times 1$ in., were cut from the foam bun using a band saw equipped with a smooth "wavy edge" saw blade to eliminate tearing. Each sample was first dried under a vacuum and at 40°C for 3.5 h in order to equilibrate each sample to an equal level of moisture content. The samples were then placed in an environmental chamber preset at the testing conditions for about 60 min. The latter involved compressing a foam square at 300 mm/min using a 2-in. diameter indenter to 65% compressive strain three times and maintaining compression after the third time. The load relaxation was then tracked. This was performed on an Instron Model 4400R with a 25-lb_f load cell produced by a Transducer Techniques Model MDB-25. The environment chamber produced by Russells Technical Products used a Watlow 922 microprocessor for environmental control. Tests were performed at low humidity and low temperature (30°C –15% RH), at low humidity and high temperature (100°C –15% RH), and at high humidity and high temperature (100°C –70% RH).

Small-angle X-ray scattering (SAXS) was utilized to evaluate the presence of microphase separation. This was performed with a Phillips Model PW1729 generator operating at 40 kV and 20 mA and a slit collimated (0.03×5 mm) Kratky camera with nickel-filtered $\text{CuK}\alpha$ radiation having a wavelength of 1.542 \AA . The detector utilized was a Braun OED 50 position-sensitive platinum wire detector. Scattering data were corrected for parasitic scattering and normalized using a Lupolen standard. Because apparent density varied, the beam path length for the nonquenched and noncrushed foam samples ("S" series in Table I) was also corrected based on density relative to the apparent density of sample C80-Su1.5. The foam samples were cut approximately 8 mm thick and compressed to approximately 2 mm. These data were analyzed using the TOPAS program developed by Dr. Stribeck at the University of Ham-

burg. Dr. Stribeck has graciously posted TOPAS for free downloading on the world wide web at <http://www.chemie.uni-hamburg.de/tmc/stribeck/index.html>.

The cellular structure of the foams was evaluated and compared using scanning electron microscopy (SEM). Thin slices (3–4 mm) of foam were adhered to aluminum stubs using silver paint and allowed to dry. A thin layer of gold was then applied to the surface of the foam using an SPI model 13131 sputter coater. Micrographs were taken using a Stereoscan 100 SEM (Cambridge Instruments, Ltd.) operating at 20 kV and at a magnification of approximately 30 \times .

To explore the ordering within the hard domains, the technique of wide-angle X-ray scattering (WAXS) was applied via a Phillips Model PW1720 generator with a Warhus camera. Nickel-filtered CuK α radiation was used with a wavelength of 1.542 Å and pinhole collimation with a diameter of 0.5 mm. Foam samples varied in density; therefore, they were cut to thicknesses which would expose about 3.2 mg of material to the beam and then were compressed to about a 2-mm thickness. Sample-to-film distance was 7.7 cm and exposure times were about 10 h.

Fourier transform infrared (FTIR) was also used to evaluate hydrogen bonding in the hard domains.⁶ FTIR spectra were collected on a Nicolet 510 spectrometer utilizing a Spectra-Tech ATR attachment Model 0012-405 using a horizontal ZnSe crystal. Spectra were analyzed using Omnic 3.0 software, and all scans were normalized by the corrected peak height at 2970 cm⁻¹, which corresponds to a CH₃ absorbance. For quantitative analysis, the ratio of the absorbance of the 1640–1650-cm⁻¹ peak to the 1710-cm⁻¹ peak was used. This provides a measure of the ratio of hydrogen-bonded polyurea carbonyl groups to polyurea carbonyl groups which have not formed hydrogen bonds, and it serves as an internal calibration for each spectrum. Using this ratio allows the level of hydrogen bonding in one sample to be compared with another one with good precision (ca. 3% error).

Extraction experiments were carried out on selected samples to compare the level of crosslinking (gel fraction). Samples were submerged in a succession of DMF solutions of LiCl. Lithium chloride solutions are used to increase the rate of extraction for these materials by disrupting the level of hydrogen bonding, thus facilitating the evaluation of the amount of extractable material in a given sample. The succession consisted of two

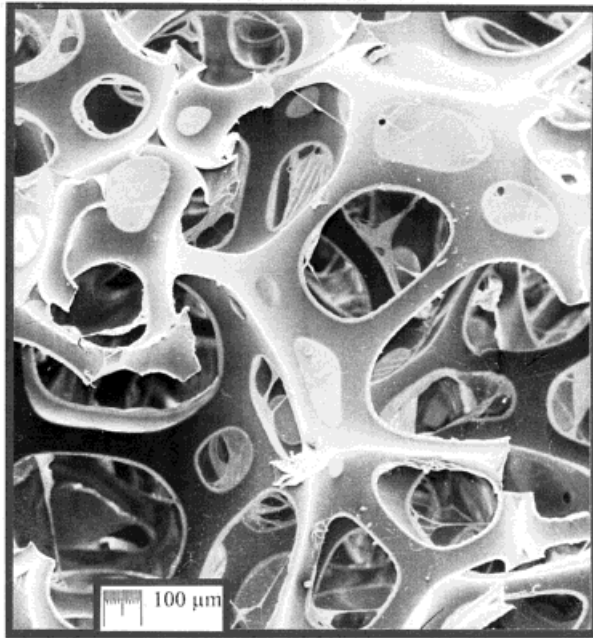
submersions at 10 wt % LiCl, one at 6 wt % and one at 3 wt %, followed by three submersions at 0 wt %. The period of each submersion was 4–5 days. The samples were then repeatedly evacuated at 40°C for 2 weeks followed by 2 days at 80°C. Samples were weighed throughout the drying process until a stable weight was achieved. The level of weight lost via extraction provides an index of the sol fraction while the remaining extracted matrix represents the gel fraction.

RESULTS AND DISCUSSION

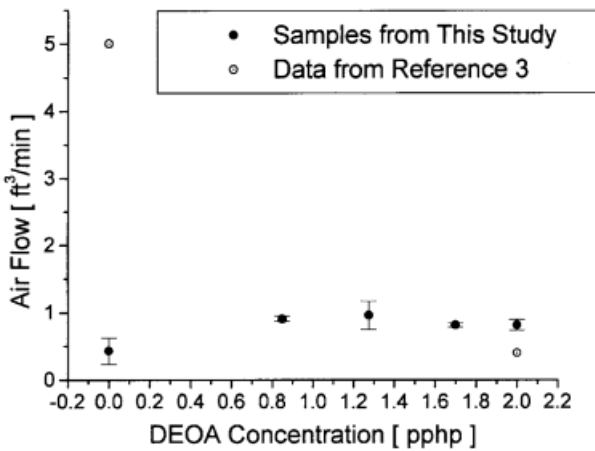
Since macroscopic tests on foams convolute the properties of the solid polymer with the character of the cellular structure, it is important in systematic comparisons to evaluate how much either are being changed. For example, scanning electron micrographs of the foam, such as that of MaD2.0 shown in Figure 1(a), allow for comparison of the size of the cells and of the number of closed cell windows observed. However, examining these samples via SEM revealed no difference in either of those characteristics; therefore, micrographs of the other samples are not presented here. Airflow measurements were used to more qualitatively evaluate cell openness, and those data can be seen in Figure 1(b). In contrast to the data reported earlier from this laboratory,³ our new results clearly show that these samples have essentially the same degree of openness in their cellular structure. Another measure of the cellular structure is the core density, and all of these samples had an apparent density of 1.86 ± 0.04 lb/ft³. Without observing differences among the apparent densities, the air-flow measurements, and the SEM examinations, it is inferred that the cellular structures of the samples in this study are sufficiently equivalent to allow any major variations of the other foam properties to be attributed to differences in the polymer itself.

Mechanical Properties

The mechanical properties of these samples were investigated through tensile DMA and compressive load-relaxation studies. The DMA storage moduli for the nonannealed samples are shown in Figure 2. These data reveal that in the rubbery region even the addition of small amounts of DEOA to the foam results in significant softening. It also shows that there is a softening at about 125°C, which corresponds to the glass transition



(a)



(b)

Figure 1 (a) Scanning electron micrograph of MaD2.0. (b) Variation of airflow measurements as a function of DEOA concentration.

of the SAN reinforcing filler particles.² The annealed samples showed identical trends of softening with increasing DEOA concentration, so those storage moduli are not presented.

The 65% compressive load-relaxation studies were performed at low temperature and low humidity, where hydrogen bonds would be expected to be strongest, and at high temperature and high humidity, where hydrogen bonds would be most disrupted. The results of these tests are shown in

Figure 3(a,b). At low temperature and low humidity [Fig. 3(a)], the nonannealed foams are observed to have significantly lower load bearing with increasing DEOA content. For example, the initial compressive load on the nonannealed foam with 0.0 DEOA pphp is about 6.5 kg_f, but with 2.0 DEOA pphp, it is about 2 kg_f. This trend was also observed in the foams at high temperature and high humidity [Fig. 3(b)], wherein the foams at 0.0 DEOA pphp are approximately twice as hard as the foams at 2.0 DEOA pphp. The shape of the load-relaxation curve at 100°C is different from that at 30°C due to being in thermal proximity to the glass transition of the SAN reinforcing filler.^{2,7} The annealed foams revealed an identical trend of significant softening with increasing DEOA content at both environmental conditions, so those load-relaxation curves are not presented. This dramatic softening influence of DEOA is the opposite of what was observed in our earlier study,³ and it points out the importance of considering the cellular structure in systematic work on foams. Because a restricted airflow in a foam would result in a higher compressive load bearing, it is suggested that the trend of DEOA increasing foam hardness observed in the earlier work³ is due to the higher closed-cell content of the foams and not to changes in the polymer itself.

Observing the softening effect of DEOA is the major trend to consider from the compressive load-relaxation work, but there are some minor points to also note. For example, the annealing does not appear to influence the overall rate of relaxation, but DEOA does. This is shown in Figure 4(a), which reveals that, although the an-

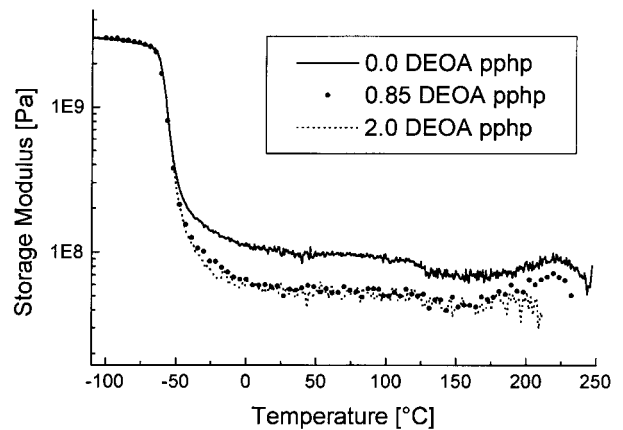


Figure 2 DMA storage moduli at 1 Hz for nonannealed foams of varying DEOA content.

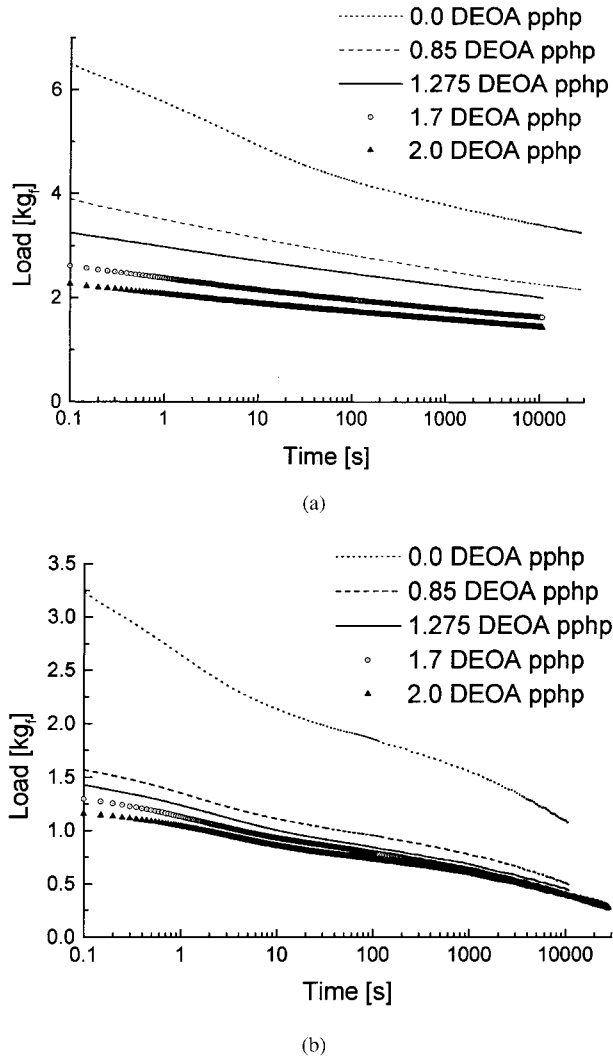


Figure 3 Load-relaxation data at 65% compression for nonannealed foams at (a) 30°C-15% RH and (b) 100°C-75% RH.

nealed foam data overlays the nonannealed foams, increasing DEOA content in a foam significantly reduces its total 3-h load relaxation at 30°C-15% RH. At 0.0 DEOA pphp, the foams exhibit about a 45% load relaxation, whereas at 2.0 DEOA pphp, they relax at about 30%. However, as shown in Figure 4(b), at 100°C-75% RH, the data reveal no variation of the percent relaxation with respect to DEOA content. This strongly suggests that whatever influence the DEOA has in reducing the percent load loss it is undetectable or removed in the high-temperature/high-humidity environment. This is suggestive that the DEOA may be influencing the hydrogen-bonding properties of the polymer and, more specifically, of the hard segments.

Another observation from the load-relaxation work is that the annealing of the foams does not alter that softening trend, but it does have some effect on the load bearing at each DEOA concentration. As shown in Figure 5, at 30°C-15% RH, the annealing has very little effect on the foams below about 1.3 DEOA pphp, but above that DEOA content, the load bearing is improved by as much as about 15% in the 2.0 DEOA pphp foams. This reveals that the annealing is improving the load bearing but only in foams with higher levels of DEOA. A similar trend is seen in the 100°C-75% RH results, where at no DEOA the annealing

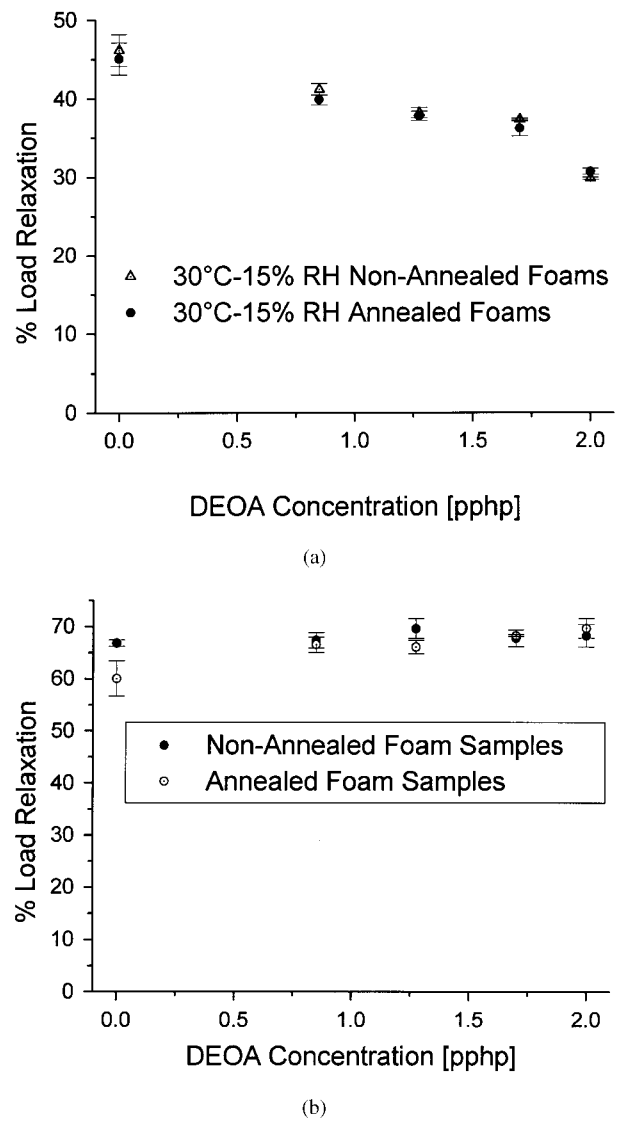


Figure 4 Percent load relaxation data at (a) 30°C-15% RH and (b) 100°C-75% RH. This was calculated by comparing the load bearing at 0.1 and 10,000 s after compression to 65%.

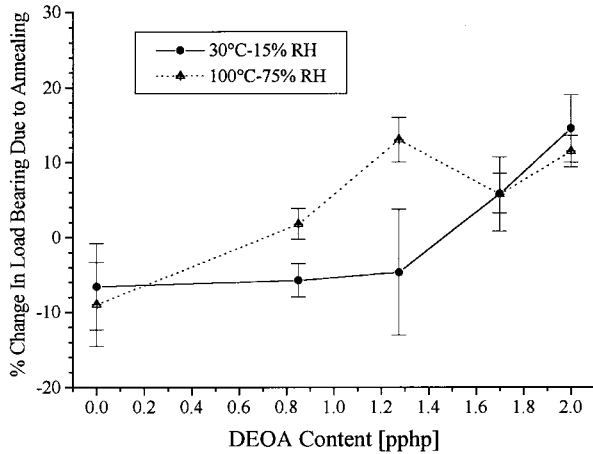


Figure 5 Percent change after annealing in the initial load bearing at 65% compression for the foams measured at 0.1 s after compression.

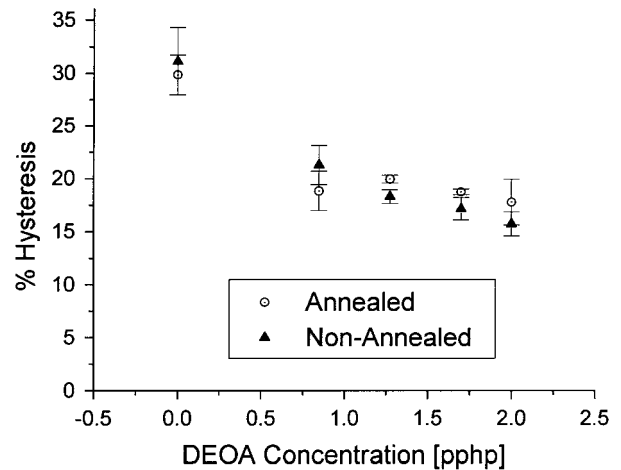
seems to have no influence, but at higher concentrations, the annealing does appear to increase the load bearing. Thus, the annealing seems to be significant in improving foam properties only in the higher DEOA concentrations that were examined here.

In addition to these observations, the percent hysteresis also comes from the load-relaxation work, and it is calculated as the percent difference in the area below the loading and unloading curves of the second 65% compression. At 30°C–15% RH, as Figure 6(a) reveals, the amount of energy dissipated during a compression cycle decreases systematically with higher DEOA concentrations. This suggests that DEOA reduces the dependence of these materials on the hydrogen bonding for their properties. It is interesting that up to 1 DEOA pphp the annealing treatment seems to have little discernible effect, yet above that concentration, the annealing marginally increases the hysteresis of the foams. As shown in Figure 6(b), this subtlety is lost at 100°C–75% RH, a condition where much hydrogen-bonding lability exists in the foam. No significant difference can be observed between the annealed and nonannealed materials, but the consistent decrease of hysteresis with increasing DEOA content remains. This decrease from about 35% at 0.0 DEOA pphp to about 25% at 2.0 DEOA pphp should emphasize that the DEOA is clearly changing the viscoelastic properties of the foam. Since hysteresis in these materials is frequently associated with hydrogen bonding, Figure 6(a,b) suggests that DEOA reduces the extent to which

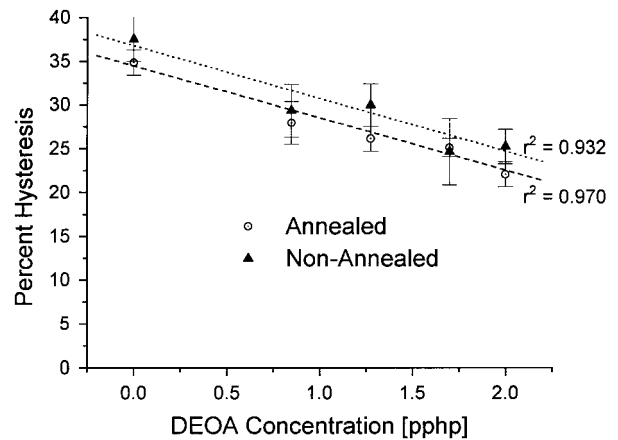
the foam depends upon these cohesive physical bonds for its mechanical properties.

Structure and Morphology

The above analysis of the mechanical properties of these foams has presented an intriguing question. The theory of rubber elasticity states that higher levels of covalent crosslinking should increase the modulus or stiffness of the polymer. Yet, this study has so far demonstrated that if influences of the cellular structure are removed 2.0 DEOA pphp reduces the load bearing (i.e., stiffness) of the foam by nearly 50%. This dichotomy is further established by the fact that DEOA can be proven to increase the level of covalent crosslinking by using solvent extraction to probe



(a)



(b)

Figure 6 Percent hysteresis at (a) 30°C–15% RH and (b) 100°C–75% RH.

how much material was covalently bound into the three-dimensional network. As Figure 7 reveals, the weight fraction of extractables is substantially decreased as DEOA content is increased, decreasing from about 13 wt % at 0 DEOA pphp to about 4.5 wt % at 2 DEOA pphp. This is interpreted to mean that the DEOA does significantly increase the amount of material becoming bound into the covalent network. Figure 7 also reveals that the level of extractables is not substantially changed by the annealing step. Clearly, then, the DEOA is increasing the level of covalent crosslinking, and so the question of how softening results from the addition of DEOA must be answered from another change in the polymer.

The properties of flexible polyurethane foams are well known to be largely dependent on their microphase-separated morphology to the extent that alterations in that phase separation can have dramatic effects. This was discussed at length in refs. 8 and 9. SAXS is one technique which has to be frequently used to examine the microphase separation of these materials. The shoulder in the SAXS profiles of Figure 8(a) shows that even the highest concentrations of DEOA studied did not prevent these systems from phase separating. On the contrary, the profiles of Figure 8(a) show that increasing DEOA content systematically increases the observed scattering intensities of the foam samples. This might occur through either an enhancement of the phase separation or through an increase in the hard-segment content of the foam. Considering the increase in TDI fed, it is suggested that the latter is more probable.

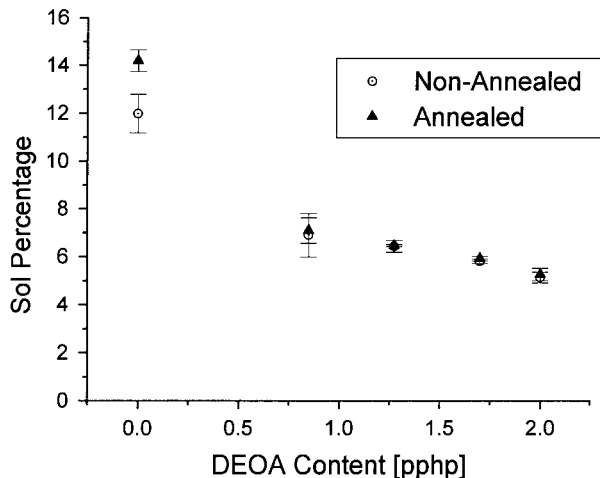
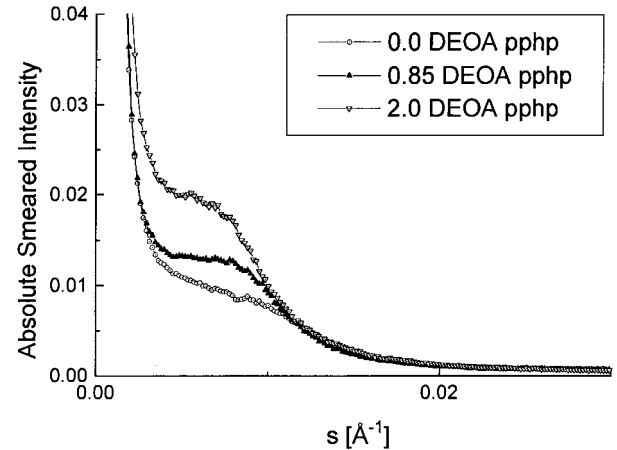
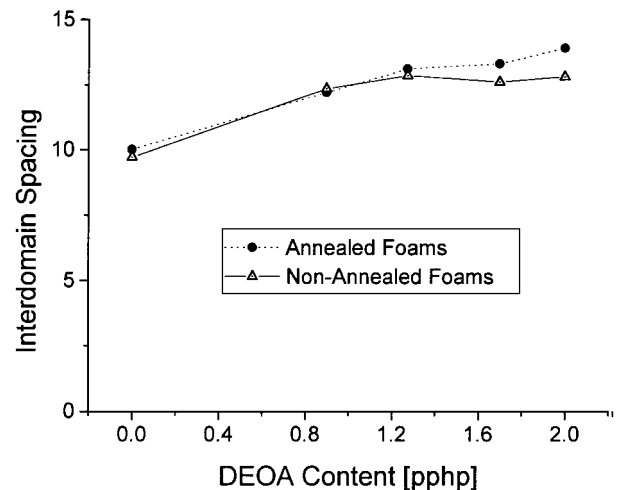


Figure 7 Solvent-extraction results for foams of varying DEOA content.



(a)



(b)

Figure 8 (a) SAXS profiles for nonannealed foams of varying DEOA content. (b) Influence of DEOA on the SAXS interdomain spacings of annealed and non-annealed materials.

The profiles do show distinct movement to lower angles (i.e., longer interdomain spacings) with increasing DEOA concentration. This was examined further using the three-dimensional correlation function analysis described in ref. 10. That analysis provides a way to better estimate the interdomain spacing which underlies the scattering profile, and the results of this are shown in Figure 8(b), where it can be seen that the spacing between hard domains systematically increases from about 10 nm at 0.0 DEOA pphp to about 13 nm at 2.0 DEOA pphp. It also shows that annealing may have a subtle influence on the interdomain spacings, but only at DEOA feed concentrations above 1 pphp. Two separate but conceptu-

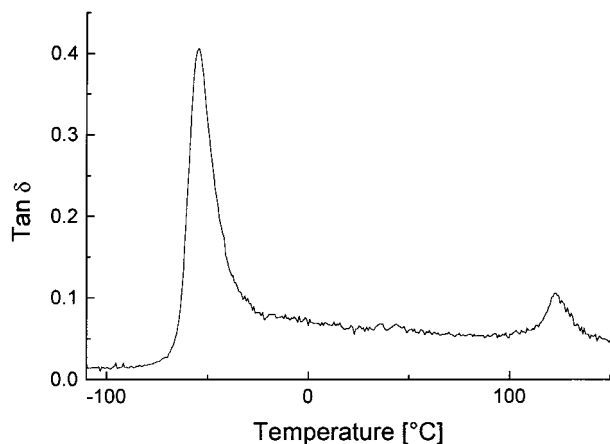


Figure 9 DMA tan δ curve for the 0.0 DEOA pphp nonannealed foam.

ally valid hypotheses would explain this increase in spacing. If the DEOA and whatever reacts with it reside completely in the polyol phase and the hard domains are essentially unchanged, the resulting increase in the polyol phase volume fraction might distribute the hard domains further apart. On the other hand, the interdomain spacing relates the most probable distance from the center of one domain to the center of the next. Therefore, if the DEOA and its coreactants reside more so in the hard domains, then increase of the hard-domain volume would result in their centers being further from each other. This latter explanation may be supported by the increasing intensities observed in Figure 8(a). The SAXS thus provides strong evidence that the microphase separation is being altered somehow by including DEOA in the formulation; however, information from another technique is required to provide a satisfying interpretation of that change.

Examination of the polyol glass transition is one way to evaluate whether the DEOA and whatever reacts with it resides in the soft or hard phases of the polymer. The very flexible poly(ether polyol) chains are usually observed to have very low glass transitions (ca. -55°C by DMA at 1 Hz), and, so, relatively small amounts of hard-segment material becoming mixed with it can restrict chain mobility and result in higher glass transition values. Using this technique to evaluate polyol purity was established by other workers.¹¹ A typical DMA tan δ curve may be observed in Figure 9. This shows the dominant relaxation is that of the polyol at about -55°C and that a minor relaxation peak occurs at about 125°C which is attributable to the styrene-co-acrylonitrile reinforcing filler.²

Complete understanding of the DEOA influence on the polyol glass transition requires consideration of the results in both a numerical and graphical form. As Table II shows, the nonannealed materials show that without DEOA the polymer attains a level of phase separation that exhibits a polyol glass transition peak at $-54.0 \pm 0.3^{\circ}\text{C}$. However, as DEOA content is increased, the location of the tan δ peak shifts to ca. $-52.4 \pm 0.3^{\circ}\text{C}$. After annealing, however, all the samples, regardless of DEOA content, have their tan δ peaks centered on -54°C . This suggests that whatever level of phase separation is attained by the 0.0 DEOA pphp foam is regained by the foams with DEOA after the annealing step. The reality of this somewhat subtle difference is demonstrated in Figure 10(a,b), which examines the polyol glass transition region. Figure 10(a) shows that the onset of the glass transition for all the nonannealed foams begins at about the same temperature (ca. -65°C). However, the peaks of these relaxations move systematically higher with increasing DEOA content. Furthermore, the tail of the relaxation extends to higher and higher temperatures as the DEOA concentration is increased, which suggests the distribution of chain mobility in the polyol is broadening. This is established by Figure 10(b), which shows that all the foams which were annealed have their glass transitions centered upon the same temperature. Furthermore, as the DEOA level is increased, Figure 10(b) clearly shows that the tan δ peak is broadening and increasing in height. These data suggest that the DEOA initially affects the level of phase separation obtained in the polymer, but that this influence is removed via annealing. Furthermore, because the polyol is reaching the same level of mobility in the annealed foams regardless of DEOA content, *it is suggested that the DEOA and its coreactants largely reside within the hard domains.* However, the annealing does not

Table II Influence of DEOA on Polyol Glass Transition Temperature

DEOA Content (pphp)	Nonannealed Tan δ Peak	Annealed Tan δ Peak
0.0	$-54.0 \pm 0.1^{\circ}\text{C}$	$-54.1 \pm 0.3^{\circ}\text{C}$
0.85	$-53.2 \pm 0.3^{\circ}\text{C}$	$-53.8 \pm 0.7^{\circ}\text{C}$
1.275	$-52.7 \pm 0.2^{\circ}\text{C}$	$-54.3 \pm 0.1^{\circ}\text{C}$
1.7	$-52.3 \pm 0.4^{\circ}\text{C}$	
2.0	$-52.4 \pm 0.3^{\circ}\text{C}$	$-54.2 \pm 0.5^{\circ}\text{C}$

change the wider distribution of molecular mobility shown by the broader $\tan \delta$ peaks and this suggests more permanent alterations changes in the microphase-separated morphology.

WAXS and FTIR are two complementary techniques which can be used to evaluate structure and ordering in the hard domains of flexible polyurethane foams.⁹ As shown in Figure 11(a), the WAXS pattern of the 0.0 DEOA pphp foam exhibits a 4.7-Å reflection overlying an amorphous halo. As shown in ref. 9, this indicates that bidentate hydrogen bonding is present and that the hard domains possess an internal order of a somewhat *para*-crystalline nature. However, as Figure 11(b) shows, this reflection is no longer visible at 2.0 DEOA pphp, revealing that the no short-range

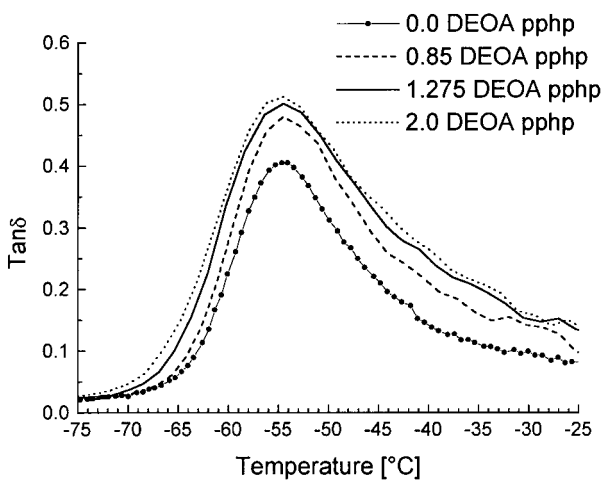
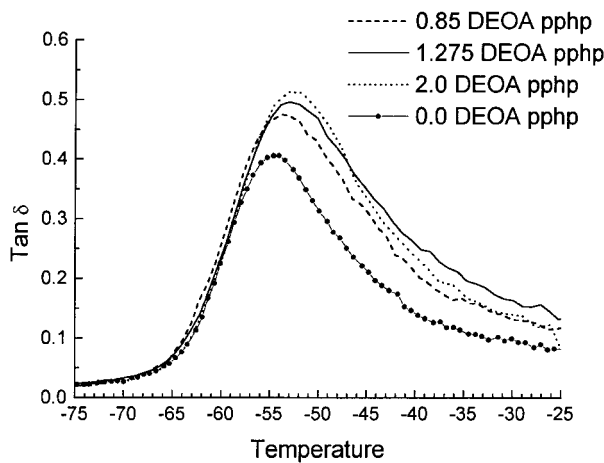


Figure 10 Polyol glass transition region from DMA $\tan \delta$ curves for foams of various DEOA content: (a) nonannealed samples; (b) annealed samples.

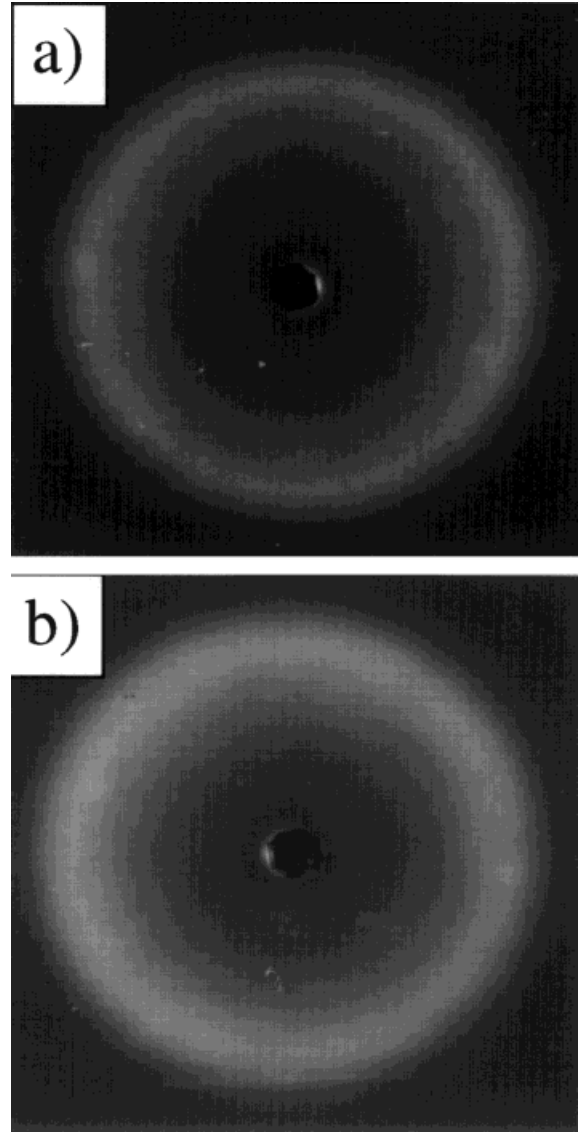
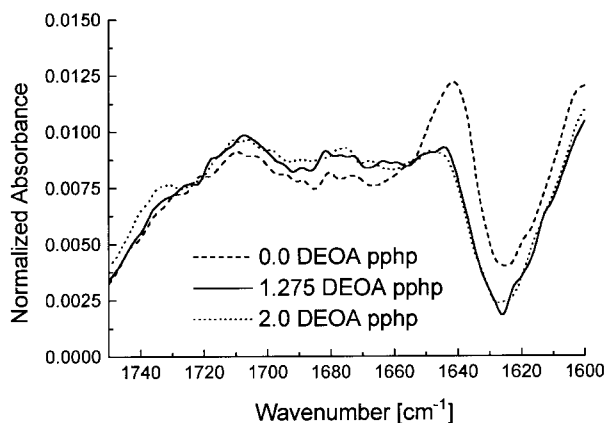


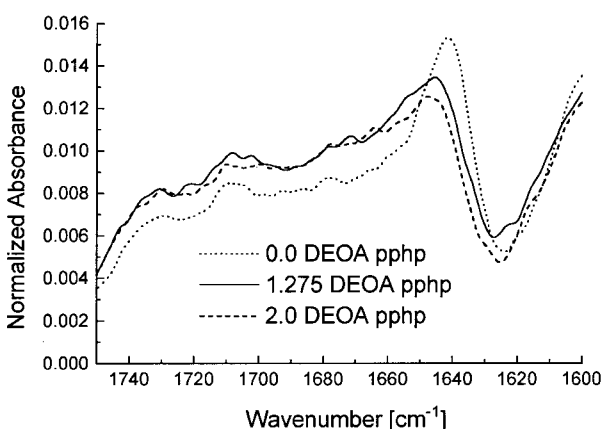
Figure 11 WAXS patterns for foams with (a) 0.0 DEOA pphp and (b) 2.0 DEOA pphp.

periodic spacing exists within the hard domains when DEOA is present. Because the 4.7-Å reflection could not be brought back after annealing and additional heat treatments, it is concluded that this disorder is due to alterations in the covalent structure of the hard segments themselves. Furthermore, because this occurred at even the lowest levels of DEOA content studied (0.85 pphp), it is suggested that the DEOA reacts early in the sequence of foam reactions, incorporating itself internally in the hard segments and, ultimately, in the polyurea hard domains as well.

The hypotheses proposed above are supported by the FTIR results. As shown in Figure 12(a), the



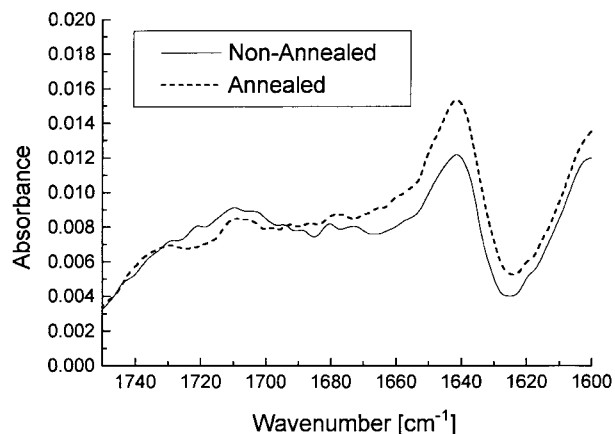
(a)



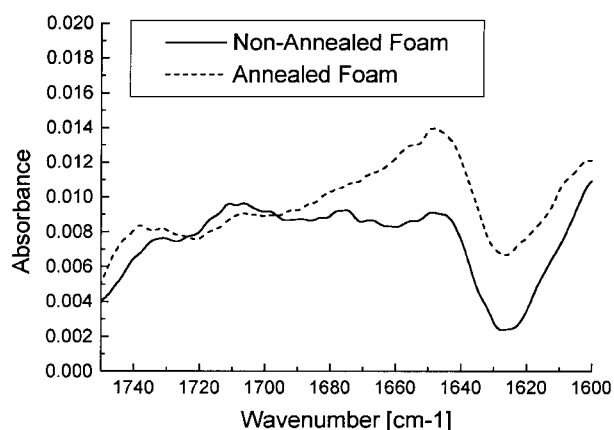
(b)

Figure 12 FTIR spectra showing the carbonyl vibration region for (a) nonannealed and (b) annealed foams.

overall character of the carbonyl region is dramatically altered even at the lowest levels of DEOA used here. All spectra have been normalized for these qualitative comparisons using the CH_2 peak at 2969 cm^{-1} . The outstanding peak at ca. 1640 cm^{-1} indicates the presence of bidentate hydrogen bonding. By comparing the height of that peak with the vibration at 1710 cm^{-1} , which arises from carbonyl groups that are not hydrogen-bonded, it can be observed that without DEOA hydrogen bonding is much more prevalent. With DEOA, the bidentate vibration appears to be of the same significance as that of the free carbonyl vibration. However, with annealing, the situation changes as shown in Figure 12(b). It can be observed that hydrogen bonding is significant after annealing for all the samples as judged by the height of the 1710-cm^{-1} absorbance. What is important to notice, however, is that, even after



(a)



(b)

Figure 13 Influence of annealing on the FTIR spectra of (a) 0.0 DEOA pphp foams and (b) 2.0 DEOA pphp foams.

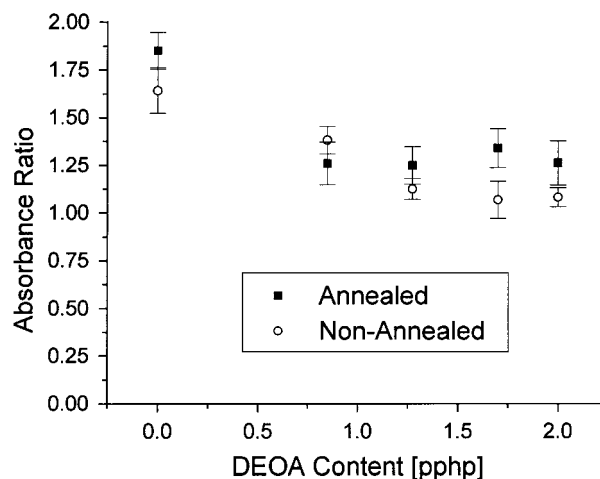


Figure 14 Ratio of hydrogen-bonded carbonyl peak height to the free carbonyl peak height as a function of DEOA content.

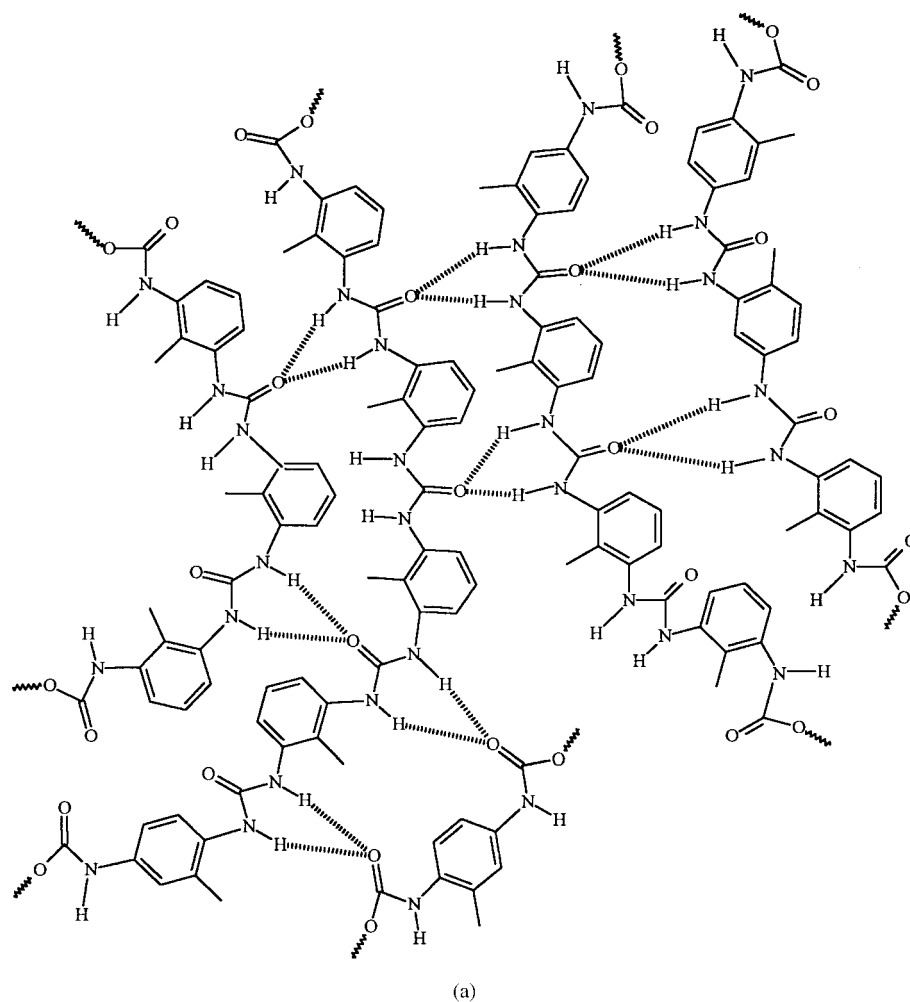


Figure 15 Schematic representation of polyurea segment packing in a hard domain (a) without DEOA and (b) with DEOA.

annealing, no foam with DEOA in it regained an absorbance at about 1640 cm^{-1} , but, rather, they only exhibit weaker peaks at about 1645 cm^{-1} . This is significant because it indicates that those peaks have become more convoluted with the monodentate hydrogen-bonding vibrations in the region of $1650\text{--}1660\text{ cm}^{-1}$. This indicates that although some level of hydrogen bonding is obtained through the annealing step the covalent alterations that DEOA makes on the chemical structure of the hard segments may preclude a return to true bidentate hydrogen bonding.

FTIR also brings an explanation as to why foams with higher levels of DEOA show the most influence during the annealing step. As Figure 13(a) shows, the character of the carbonyl region is not altered for a foam without DEOA. The 1640-cm^{-1} peak is still predominant in compari-

son to the free carbonyl vibration. However, for the foam with 2.0 DEOA pphp, Figure 13(b) illustrates that its carbonyl spectra are dramatically altered. The annealing step brings significant monodentate hydrogen bonding into a material which formerly had levels that were approximately comparable to the amount of nonassociated carbonyl groups. This can be made more quantitative by taking a ratio of the peak height at $1645\text{--}1640\text{ cm}^{-1}$ to the peak height at 1710 cm^{-1} . Two major observations can be made from the data that this provides in Figure 14. First, as DEOA is increased in a foam, whether or not it is annealed, the level of hydrogen-bonded carbonyl groups systematically decreases. This is concluded to be the source of the decreasing hysteresis observed in Figure 6(a,b). Another observation is that the annealing makes a more signifi-

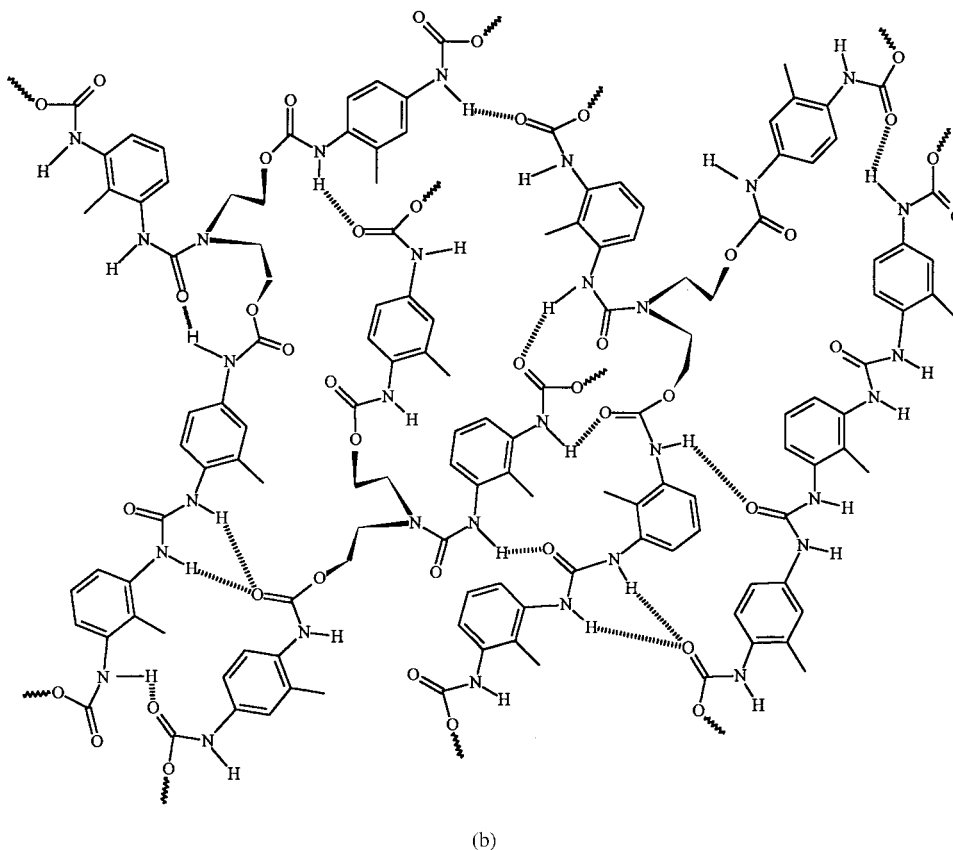


Figure 15 (Continued from the previous page)

cant difference to the hydrogen bonding in the material at and above 1.3 DEOA pphp than it does below that level. The similarities in this regard between Figure 14 and Figure 6(a) cannot be a coincidence. It is therefore concluded that the annealing treatment does somewhat improve the phase separation of the polymer as shown by DMA, but that the largest effects on the mechanical properties are made by increasing the level of hydrogen bonding in the system.

CONCLUSIONS

These results have shown that the use of DEOA in the formulation of molded flexible polyurethane foams has clear and related effects on the morphology and properties. The DEOA was shown to reside largely in the hard domains and to alter their "para-crystalline" ordering. This results in lower rubbery moduli and lower overall load-bearing properties. Without DEOA, each hard domain in the foam serves as a point of crosslinking but relies completely upon physical

associations for its cohesive strength. When DEOA is added, it becomes incorporated in the hard segments and, ultimately, in the hard domains as well, so that each hard domain now also contains some covalent crosslinks. Since the DEOA resides largely in those domains, the overall number of crosslinking points are not increased in the polymer. *Thus, the softening occurs because DEOA alters the chemical structure of the hard segments, reducing their ability to form the bidentate hydrogen bond which typically increases foam stiffness.*

This idea is presented as a very simplified schematic diagram in Figure 15(a,b). As Figure 15(a) shows, without DEOA, it is fairly easy to conceive of ways for the hard segments to pack so that poly(urea carbonyl) groups are able to associate with both hydrogens of an adjacent polyurea. This well-ordered packing provides a structure which yields the 4.7-Å reflection in WAXS.⁹ Figure 15(b) attempts to illustrate that adding DEOA alters two main features of the hard segment: Most clearly, it reduces the number of polyurea groups and increases the number of polyurethane link-

ages in the hard segment. Even where a polyurea link has been generated from the amine of the DEOA, only a single hydrogen is available for association with any adjacent carbonyl groups. This change reduces the likelihood for forming the strong bidentate hydrogen bonding between hard segments, and the loss of short-range ordering in the hard domains results in the WAXS pattern exhibiting no detectable reflections. These oversimplified schematics thus convey the idea that DEOA disrupts a manner of molecular packing in the hard domains that typically leads to strong associations.

This increase of the covalent nature (but not the crosslink density) of the network was also seen to result in lower mechanical hysteresis. Additionally, DEOA alters the initial degree of phase separation which results in subtle increases in T_g before annealing. However, the near-equilibrium degree of phase separation was shown to be uninfluenced by the addition of DEOA as shown by the annealing steps. Finally, it was also observed that foams containing the highest DEOA concentrations have the most to gain in terms of properties from an annealing step.

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