Influence of Cross-Linking on the Hysteresis Behavior of Poly(urethane–diacetylene) Segmented Copolymers

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ABSTRACT: The influence of hard-domain cohesion on the hysteresis behavior of a number of different poly(urethane–diacetylene) segmented copolymers has been examined. The hard domains of these materials were selectively cross-linked in the solid state by polymerizing the diacetylene groups contained within their hard segments. For elastomers with weakly associated hard segments, it was found that low levels of cross-linking significantly reduced the amount of hysteresis that they exhibited at low strains. In this case it was postulated that premature breakup of the hard domains due to weak hard-domain cohesion was partially responsible for the high hysteresis values observed at low strains. This mode of energy loss could therefore be eliminated by diacetylene cross-linking. For elastomers with crystalline hard domains and highly interlocked microstructures, it was found that cross-linking via the formation of poly(diacetylene) chains increased the level of hysteresis regardless of the level of cross-linking. In this case, elongation can only occur by irreversible disruption of the microstructure, and this mode of energy loss is enhanced by diacetylene cross-linking.

Introduction

For many years, it has been recognized that the enhanced mechanical properties of segmented polyurethanes are directly linked to the two-phase microstructures of these materials.[1] The presence of thermodynamically incompatible hard and soft segments alternating along the same polymer chain leads to microphase separation and the formation of distinct hard-segment domains. At low hard-segment contents, the hard domains act as multifunctional virtual cross-links, thereby preventing chain slippage and imparting elastomeric properties to the flexible soft-segment phase. The virtual nature of the hard-segment domains, however, also results in materials that exhibit high energy loss and heat buildup during mechanical cycling. This high level of hysteresis, which is characteristic of most segmented polyurethanes, has been attributed to a number of factors including nonaffine deformation, plastic deformation of the hard domains, irreversible disruption of the microstructure (particularly in materials with interlocked hard-segment domains), irreversible orientation of the hard-segment domains, and irreversible strain-induced soft-segment crystallization.[2-8] Given the wide variety of deformation processes possible in these materials, it is not too surprising to find that it is oftentimes very difficult to determine the dominant mechanism responsible for hysteresis in segmented copolymers.

Our group has recently developed[9] a new class of segmented polyurethanes that contain reactive diacetylene groups within their hard segments. In such materials, the diacetylene groups remain inactive during film or fiber formation but can be subsequently reacted in the solid state to produce hard-segment domains covalently linked together with fully extended poly(diacetylene) chains. The conversion of the diacetylene groups to poly(diacetylene) chains is a topochemical, lattice-controlled process and therefore occurs without significant disruption of the hard-domain organization or the morphology of the segmented copolymer. Thus, it is possible to introduce well-defined covalent cross-links within the hard domains without modification of the molecular or supermolecular organization of the polymer. We have previously shown[10] that this chemistry can be used to dramatically modify the mechanical behavior of these materials by selectively increasing the cohesion of the hard domains. For example, selective cross-linking of the hard segments was found to prevent premature breakup of the hard domains and, in some cases, activate new strengthening mechanisms such as strain-induced crystallization of the soft segments.

In this paper, we examine the influence of diacetylene polymerization within the hard domains on the hysteresis behavior of these materials. A comparison is made of segmented copolymers with different hard-segment structures and different levels of phase separation and hard-domain ordering. Since the hard segments can be systematically cross-linked without disruption of the morphology, it is possible to ascertain the importance of hard-domain mechanical integrity and cohesion in determining the level of hysteresis displayed by these materials.

Experimental Section

Details concerning the synthesis and sample preparation of the poly(urethane–diacetylene) segmented copolymers can be found in our previous publications.[9] The soft segments are poly(tetramethylene oxide) (PTMO) having an average molecular weight of either 1000 or 2000, whereas the hard segments are based on either 4,4′-methylenebis(phenyl isocyanate) (MDI) or hexamethylene diisocyanate (HDI) and either 2,4-hexadiyne-1,6-diol or 5,7-dodecadiyne-1,12-diol (chain extender). The molar ratio of the diisocyanate, PTMO, and chain extender used in the polymerization reaction is approximately 2:1:1. The elastomers are designated by the monomers used to synthesize them. For example, HDI-5,7-1000 refers to an elastomer synthesized from HDI, 5,7-dodecadiyne-1,12-diol, and PTMO of molecular weight 1000. The HDI-based elastomers represent well-phase-separated materials (soft-segment glass transition temperatures of ca. −70 °C) with highly crystalline hard domains. The MDI-based materials, on the other hand, are less phase separated (soft-segment glass transition temperatures of −50 °C) and exhibit significantly less ordered hard domains.

Polymerization of the diacetylene groups contained within the hard domains was accomplished by exposure to high-energy electrons from a Van de Graaff electron accelerator operated at 2.6 MeV. Mechanical measurements were made on an Instron Model 1122 using elastomeric or pneumatic grips to prevent slippage of the samples. In order to allow comparison with work done on conventional segmented polyurethanes, hysteresis experiments were performed by using the approach described many times in the literature.[2-8] The hysteresis measurements were made by loading and unloading specimens at a constant cross-head speed of 50 mm/min to an increasing strain level for

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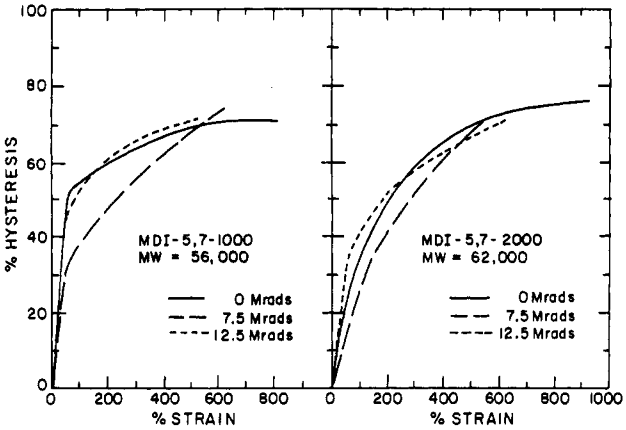

Figure 1. Percent hysteresis vs strain as a function of radiation dosage for MDI-5,7-1000 (M_w = 56 000) and MDI-5,7-2000 (M_w = 62 000).

each successive cycle. The end of a cycle was taken as the point where the material displayed zero stress on the unloading curve. The percent hysteresis was calculated from the ratio of the area bounded by the loading–unloading curves to the total area under the loading curve.

Results and Discussion

An examination of the effects of diacetylene polymerization on the mechanical properties of the MDI-5,7-based elastomers has previously shown[10] that the ultimate tensile strength of samples with relatively low molecular weights increases dramatically after optimum radiation treatments (typically 7–10 Mrad). The tensile strengths of higher molecular weight samples, on the other hand, were found to only increase slightly after optimum radiation treatment. In general, it was found that as the ultimate tensile properties of the MDI-5,7-based materials improved by either increases in molecular weight or via suitable annealing treatments, the effect that cross-polymerization had on increasing the tensile strength became less significant. The dramatic improvement in the tensile strength of the lower molecular weight materials was attributed to an enhancement of the mechanical integrity of the hard domains due to the cross-links introduced by diacetylene polymerization. This, in turn, establishes a more effective elastic network in a material that, due to its low molecular weight, normally suffers from weakly associated hard domains. The higher degree of chain entanglement and the greater number of hard segments anchored in hard domains in the higher molecular weight samples make these materials less vulnerable to premature hard-domain breakup and therefore less responsive to cross-linking.

In light of the above comments, we now present the hysteresis data for the MDI-5,7-based materials. Figure 1 displays the strain dependence of the percent hysteresis for samples of MDI-5,7-1000 and MDI-5,7-2000 with relatively low molecular weights. The ultimate tensile strength of these materials was found to essentially double after exposure to a 7.5-Mrad dosage of electron radiation.[10] This represents the optimum radiation dosage as larger dosages were found to significantly reduce the tensile strength. Looking first at MDI-5,7-1000, one can see that the hysteresis value of the as-prepared material rises quickly to ca. 50% and then slowly increases to a level of ca. 70% with increeasing strain level. This is typical behavior for a segmented polyurethane, although the hysteresis value at low strains is somewhat larger than what has been reported for conventional MDI–butanediol–PTMO elastomers with similar hard-segment contents (they usually exhibit ca. 40% hysteresis at 100% strain).[2,5] After cross-linking with a 7.5-Mrad dosage, however, this material exhibits a significant reduction in its percent hysteresis at all strain levels below 500% strain. Further cross-linking within the hard domains (12.5-Mrad dosage) creates a material with a hysteresis behavior very similar to that of the starting material. Thus, as the level of cross-linking via the diacetylene groups increases, the hysteresis value first drops dramatically and then returns to its original value.

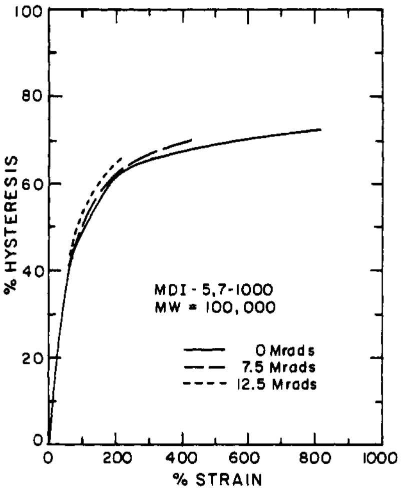

Figure 2. Percent hysteresis vs strain as a function of radiation dosage for MDI-5,7-1000 (M_w = 100 000).

Similar results were obtained for the low molecular weight sample of MDI-5,7-2000. Again it can be seen that cross-linking levels that produce the largest increase in ultimate tensile strength also lower the precent hysteresis at all strain levels. With higher cross-linking levels, the percent hysteresis actually becomes larger than that of the starting material, at least at strains less than ca. 200%. Note that the hysteresis curve of MDI-5,7-2000 shows a more gradual increease with increasing strain than that of MDI-5,7-1000. The level of hysteresis at low strains is also lower than for MDI-5,7-1000 but becomes larger at higher strains. This behavior is expected[7] due to the higher soft-segment content of MDI-5,7-2000, which produces a less interlocked hard-domain morphology and better facilitates strain-induced crystallization of the soft segments. The presence of some residual strain-induced soft-segment crystallites is most likely responsible for the higher hysteresis values observed at high strains. Irreversible strain-induced soft-segment crystallization is a common phenomenon in segmented polyurethanes with high molecular weight soft segments.[11]

The hysteresis behavior of a higher molecular weight sample of MDI-5,7-1000 is presented in Figure 2. In this case, the strain dependence of the percent hysteresis does not change significantly with increasing radiation dosage, i.e., increasing level of diacetylene cross-linking with the hard domains. The level of hysteresis below 150% strain for the as-prepared polymer is also seen to be lower than that for the as-prepared sample of the low molecular weight sample of MDI-5,7-1000. These results suggest that the elastic network is more firmly established in the higher molecular weight sample and therefore less susceptible to partial disruption of the hard-segment domains. A more effective network would be expected to result in a more uniform loading of the microstructure and therefore less premature hard-domain disruption.

For these results, it can be inferred that the initial high level of hysteresis observed in the low molecular weight MDI-5,7-based materials is in part due to weakly associated

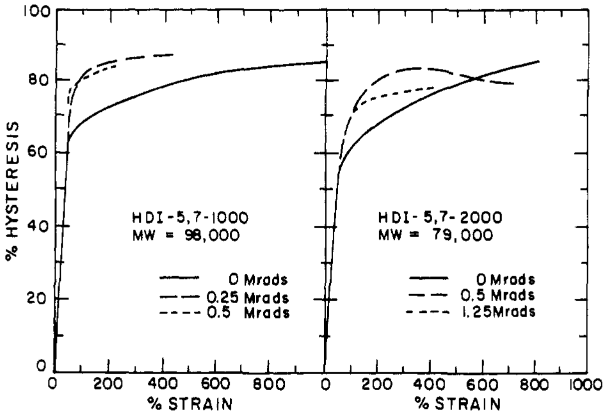

Figure 3. Percent hysteresis vs strain as a function of radiation dosage for HDI-5,7-1000 (M_w = 98 000) and HDI-5,7-2000 (M_w = 79 000).

hard-segment domains. As the elastomer is stretched, some of the hard segments are pulled free from the hard domains, thereby eliminating their contribution to the elastic network and preventing full elastic recovery. Partial cross-linking of the hard segments prevents this mode of hard-domain disruption, the net result being a material with a higher ultimate tensile strength that exhibits a lower energy loss during mechanical cycling. The fact that the level of hysteresis is still high even after partial cross-linking of the hard domains, however, suggests that this is not the only source of hysteresis in this material. Higher levels of cross-linking render the hard domains excessively rigid and unable to deform during elongation without breaking bonds or grossly disturbing the hard-domain organization. The bundles of cross-linked hard segments created within the hard domains would tend to respond as individual entities, making irreversible deformation of the hard domains more likely as there would be no mechanism to restore these structural units to the hard domains once they have broken free. Overall, this creates a less deformable material that offers a higher resistance to elongation and exhibits higher hysteresis levels.

The hysteresis curves of the HDI-5,7-based elastomers are presented in Figure 3. The higher levels of hysteresis found in these materials at low strains support the conclusion that they form a more interlocked hard-domain morphology. This is clearly the case for HDI-5,7-1000, which also exhibits a much higher level of permanent set at all strain levels when compared to the other elastomers. For example, HDI-5,7-1000 shows a permanent set of 200% after stretching to a strain level of 400%, whereas all of the other elastomers obtain permanent set values of only ca. 100% at this strain level. Since the microstructure of this elastomer does not allow strain-induced soft-segment crystallization to occur,[10] the high level of permanent set is clearly due to plastic deformation of a substantially interconnected hard-domain microstructure. As expected, the higher soft-segment molecular weight of HDI-5,7-2000 results in a less interlocked hard-domain structure and hence a slightly lower level of low-strain hysteresis than HDI-5,7-1000. The high levels of hysteresis displayed by both of these materials, however, clearly indicate that elongation cannot take place without irreversible restructuring of the polymer's microstructure. Thus, irreversible deformation of the microstructure occurs throughout the entire elongation process.

In both cases, cross-linking of the hard domains via the diacetylene groups produces a significant increase in the percent hysteresis exhibited by these materials at nearly all strain levels. This is in sharp contrast to the MDI-5,7-based materials where it was found that cross-linking initially lowered the level of small-strain hysteresis. Note that the radiation dosages required to induce cross-linking are much lower than those used for the MDI-based materials. This is due to the fact that the hard domains of the HDI-5,7-based materials are highly crystalline as opposed to the poorly ordered hard domains of the MDI-5,7-based materials. The poly(diacetylene) chains formed during irradiation of the HDI-based materials are therefore more effective at linking a large number of hard segments together. The increase in hysteresis level observed in the HDI-5,7-based materials coupled with the large increase in modulus[10] that also accompanies cross-linking suggests that the crystalline hard domains are becoming more resistant to deformation and are therefore supporting higher stress levels during the early stages of elongation. The higher stress levels, in turn, force the microstructure to deform more drastically and in a more irreversible manner, hence the higher hysteresis levels.

These results coupled with recent mechanical and optical studies suggest that the high levels of hysteresis exhibited by the diacetylene-containing segmented polyurethanes at strains below ca. 200% are related to an unlocking of the original microstructure via the breakdown of a small fraction of hard- or soft-segment material that is placed under locally high stress levels during elongation. These morphological interlocks can take the form of interconnected hard-segment domains or regions of hard- and/or soft-segment material that are locally interlocked via their irregular spatial arrangement or by chain entanglements or interlocking chain loops.[12] When the local stress levels experienced by these interlocks are large enough to cause their failure, they force a local irreversible disruption of the microstructure which then allows further elongation of the material by gradual extension and alignment of the soft segments (when not inhibited by the overall microstructure) and by stress-biased orientation of the hard domains.

These conclusions are supported by in situ visible dichroism studies which clearly show[13] that the integrity of the hard-domain molecular organization is, for the most part, preserved at strain levels below ca. 200% for all of the poly(urethane–diacetylene) elastomers. This implies that these morphological interlocks can be systematically eliminated at progressively higher strain levels without catastrophically altering the structure of the hard domains (at least below strains of ca. 200%). In other words, failure of an interlock most likely occurs by the dislodging or cleavage of a structurally intact aggregate of hard segments from a hard domain and not by complete reorganization of the entire hard-domain molecular organization. In addition, the hard domains were found to orient with the poly(diacetylene) chains aligning into the stretch direction but the levels of residual hard-domain orientation exhibited by these materials at strains below 100% were quite small. Thus, the high levels of hysteresis developed at small strains cannot be caused by irreversible hard-domain orientation or by gross reorganization and disruption of the hard domains. This latter phenomenon was only observed at strain levels greater than ca. 200%.

The development of more cohesive hard domains via diacetylene cross-linking is only effective at reducing hysteresis when weakly associated hard-segment domains provide an additional source of energy loss by premature hard-domain breakup. In this case, suitable levels of cross-linking eliminate this mode of energy loss and lower the level of small-strain hysteresis. A significant reduction in hysteresis via this mechanism would only be expected in materials with poorly ordered hard-segment domains and a less interconnected hard-domain morphology. By preventing premature hard-domain breakup, the material can elongate primarily by orientation of the hard domains and by extension of the more flexible soft-segment phase. In some cases, this can enhance the ultimate tensile properties of the elastomer by allowing other strengthening mechanisms such as strain-induced soft-segment crystallization to occur. The effect of cross-linking on materials with highly interlocked microstructures and more cohesive crystalline hard domains, on the other hand, is just the opposite. In this case, hysteresis is increased regardless of the level of diacetylene cross-linking. Since a highly interlocked hard-domain microstructure results in local stress levels that can only be alleviated by an irreversible breakup of the hard domains and/or the polymer's overall microstructure, this mode of energy loss is enhanced by covalently linking the hard segments together.

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Registry No. (5,7-Dodecadiyne)(MDI)(PTMO) (block copolymer), 130434-56-9; (5,7-dodecadiyne)(HDI)(PTMO) (block copolymer), 130434-57-0.