Structure–Property Relationships of Thermoplastic Polyurethane Elastomers Based on Polycarbonate Diols

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ABSTRACT: The phase-separation behavior and morphology of polycarbonate-based polyurethanes were investigated as a function of the soft-segment molecular weight and chemical structure and the 4,4′-diphenylmethane diisocyanate/1,4-butanediol based hard-segment contents. Polarized optical microscopy and atomic force microscopy images showed that the surface morphologies changed as the soft-segment molecular weight and hard-segment content varied and also when the sample preparation conditions were modified. An increase in the soft- and hard-segment lengths led to increased phase separation with respect to the lower molecular weight soft segment, and this showed an interlocked and connected morphology of intermixed soft and hard domains. The surface morphology of phase-separated polyurethanes with hard segments composed of more than four to five 4,4′-diphenylmethane diisocyanate units contained globular hard-segment domains formed by spherulites, in which the size and connectivity between the branched lamellae changed with the hard-segment size. Interlamellar areas related to the soft segment were seen in the spherulites. Variations in the hard-segment spherulites were observed for polyurethanes based on soft segments of different molecular weights. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3092–3103, 2008

Key words: atomic force microscopy (AFM); microstructure; polyurethanes

INTRODUCTION

Considerable attention has been devoted in recent years toward an understanding of the property–structure relationships in segmented polyurethanes.[1–3] These materials are usually randomly segmented copolymers of alternating flexible soft segments and more rigid, urethane-containing hard segments. In general, these materials derive their unusual elastomeric properties from the thermodynamic incompatibility of the polymer segments and their consequent microphase separation on a length scale comparable to the dimensions of the chain segments.

The mechanical properties of these materials are highly dependent on the degree of microphase separation.[1,4] This degree, however, not only is a function of the system thermodynamics but also depends on the ability of hard segments to pack correctly to form hydrogen bonds, and it is related to the chemical structure and composition of the copolymer.[5,6] Hard-segment packing is affected by some structural factors: the diisocyanate size and symmetry; the chain-extender length and functionality; and the polyol type, molecular weight, and functionality.[8–10] In addition, there is the distribution of hard-segment lengths, which is highly dependent on the stoichiometry and conversion of the condensation copolymerization.[11,12] The microphase-separation degree is also affected by the synthesis conditions, in bulk or in solution, with solvents of different polarities.[13] Finally, hard-segment packing is often a nonequilibrium process that depends on the thermal and mechanical history of a sample.[14–16] The understanding of these materials requires careful consideration of chemical and physical factors, opening a wide range of potential applications.

Microphase-separation and morphology studies of segmented polyurethane elastomers have been based mostly on small-angle X-ray scattering[8,9,11,17–25] and thermal characterization techniques.[8,9,15,20,22,26–28] Transmission electron microscopy (TEM) studies of stained films[24,29–31] have provided insight into the micromorphology of segmented polyurethanes. The experiments are limited by the inherent difficulties of sample preparation and/or the efficacy of staining, the possibility of beam damage, the low contrast between microdomains, and the possible misinterpretation of artifacts, so much of this work may be inconclusive. Morphologies containing spherical, cylindrical, or lamellar microdomains that depend on the

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