Hysteresis and Mullins effect in thermoplastic polyurethane elastomers derived from hard segments of variable conformational mobility

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A study was made of how aspects of the mechanical responses of thermoplastic polyurethane elastomers (TPUs) vary with composition. Hard segment, soft segment and chain extender (CE) types were varied systematically. Hard segments were generated from 4,4'-methylene bis(phenyl isocyanate) (MDI), or from 4,4'-dibenzyl diisocyanate (DBDI)^{1,2}. A series of mechanical tests was designed to compare inelasticity of polymers under cycling to fixed and/or increasing extension. The materials were cycled between an extension of 3, and zero load, for 3 cycles. First cycle energy dissipation (E_{1H}) and Mullins Factor² (M) variations were computed. Notable features were: pronounced hysteresis, unrecovered strain and Mullins effect, whereby re-loading followed a stress-strain path closer to the unloading path than the original loading path. The dominant results from these tests were the differences between polymers based on the two hard segments DBDI, MDI. Neither M nor E_{1H} were influenced significantly by variation of strain rate. But for all materials, M and E_{1H} increased with increasing strain amplitude. For all combinations of chain extender (CE) and macrodiol, the residual strain and energy dissipation were highest for materials with hard segments of DBDI than for those of MDI, although neither M nor E_{1H} were influenced by the type of synthesis route (one-shot or prepolymer route). For small strain amplitudes, E_{1H} was higher for materials with hard segments of DBDI than for those of MDI. The highest E_{1H} values were found in the case of polymers based on the couple MDI – 1,4 butanediol (BG) while the smallest hysteresis values were for materials with MDI and chain extender diethylene glycol (DEG) which inhibits crystallization¹. For the MDI based materials the nature of CE did not influence significantly the shape of load-unload stress-strain cycles, in continuous or interrupted tests. In contrast, for the DBDI-based materials, the nature of the CE influenced significantly the shape of the stress-strain cycles. DBDI-based polymers showed lower strain recovery and strain energy recovery on cycling, and higher Young's modulus. The conclusion of the present work is that hard domain hydrogen bonding and crystallinity exert strong influences on inelasticity of PU elastomers The hard domains clearly do not act simply as rigid crosslinks for the soft domains. Stress-strain cycles reflect the resistance to plastic deformation occurring in the hard domains. This is enhanced by more pronounced hydrogen bonding achieved in the more mobile DBDI than in MDI, and especially so when the DBDI hard domains crystallize.

References

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