

# Thermoplastic Polyurethane Elastomers Based on Polycarbonate Diols With Different Soft Segment Molecular Weight and Chemical Structure: Mechanical and Thermal Properties

A. Eceiza, M.D. Martin, K. de la Caba, G. Kortaberria, N. Gabilondo, M.A. Corcuera, I. Mondragon  
*Universidad País Vasco/Euskal Herriko Unibertsitatea, 'Materials + Technologies' Group,  
Dpto. Ingeniería Química y Medio Ambiente, Escuela Univ Politécnica, Pza Europa 1,  
20018 Donostia-San Sebastián, Spain*

**A series of thermoplastic polyurethane elastomers based on polycarbonate diol, 4,4'-diphenylmethane diisocyanate and 1,4-butanediol was synthesized in bulk by two-step polymerization varying polycarbonate diol soft segment molecular weight and chemical structure, and also hard segment content, and their effects on the thermal and mechanical properties were investigated. Dynamic mechanical analysis, thermogravimetric analysis, differential scanning calorimetry, Fourier transform infrared-attenuated total reflection spectroscopy and mechanical tests were employed to characterize the polyurethanes. Thermal and mechanical properties are discussed from the viewpoint of microphase domain separation of hard and soft segments. On one hand, an increase in soft segment length, and on the other hand an increase in the hard segment content, i.e., hard segment molecular weight, was accompanied by an increase in the microphase separation degree, hard domain order and crystallinity, and stiffness. In phase separated systems more developed reinforcing hard domain structure is observed. These hard segment structures, in addition to the elastic nature of soft segment, provide enough physical cross-link sites to have elastomeric behavior. POLYM. ENG. SCI., 48:297–306, 2008. © 2007 Society of Plastics Engineers**

## INTRODUCTION

Thermoplastic polyurethane elastomers are versatile materials that behave as cross-linked elastomers at room temperature but, unlike conventional elastomers, they can be processed, shaped, and formed upon heating via

numerous industrial processes [1, 2]. Polyurethane elastomers are linear segmented copolymers consisting of a relatively flexible component derived from a macrodiol, called the soft segment, and a relatively hard and stiff component derived from a diisocyanate and a chain extender, called the hard segment. Thermodynamic incompatibility of the so-called soft and hard segments leads to microphase separation, which is reflected in a rubber-like matrix containing hard microdomains. The domain structure formed by microscopic phase separation presents similar elastomeric properties to those shown for cross-linked rubber networks. The mechanical strength of this structure can be attributed to hard microdomains physically cross-linked through hydrogen bonding and dispersion forces, which act as filler-like reinforcement for the soft segment. At higher temperatures, a homogeneous melt can be formed, allowing the material to be thermally processed.

Polyurethanes are characterized by a complex morphology dependent upon the precise nature of the hard and soft segments, and their composition. In general, microphase separation is not complete [3–11]. That is, the coexisting microphases are not pure, but consist of mixed hard and soft segment units. The presence of intersegmental mixing within the microphases affects both morphology and mechanical properties of the materials. The inclusion of hard segments within the soft microphase, for example, can cause appreciable elevation of the soft microphase glass transition temperature, which will limit the applicability of the material as a low-temperature elastomer. The inclusion of soft segments within the hard microphase, on the other hand, decreases the hard microphase glass transition temperature. In the absence of appreciable hard segment crystallinity, the latter effect would generally depress the heat distortion temperature [8].

A correct design of the molecular structure becomes crucial as it provides the mechanical properties that meet customers' needs. The structure and weight fraction, molecular weight, polydispersity of hard and soft segments,

Correspondence to: I. Mondragon; e-mail: inaki.mondragon@ehu.es  
Contract grant sponsor: Diputación de Gipuzkoa; contract grant number: 0207/2005; contract grant sponsor: Ministerio de Educación y Ciencia, Spain, contract grant number: MAT2003-08125; contract grant sponsor: Gobierno Vasco/Eusko Jaurlaritza 'Etorrek 2005/BiomaGUNE 2005'; contract grant number: IE05-143.  
DOI 10.1002/pen.20905  
Published online in Wiley InterScience (www.interscience.wiley.com).  
© 2007 Society of Plastics Engineers