236a Structural Origin of Thermomechanical Behavior in Semicrystalline Ionomers

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Ionomers are nonpolar polymers incorporating a minor amount of ionic functionality; prototypical examples are ethylene copolymerized with a minor amount of methacrylic acid or acrylic acid, followed by partial or total neutralization to create E/MAA or E/AA ionomers. The ionic groups associate within the nonpolar matrix material to form nanometer-scale aggregates, which act as physical crosslinks and radically alter both the solid-state [1] and melt [2] behavior. However, E/(M)AA ionomers possess structure on a second length scale: the ethylene sequences crystallize, generating polyethylene-like crystals with a typical 10 nm spacing. The ionic aggregates reside within the amorphous layers between primary polyethylene crystals [3]. Also, the ionic associations hinder a large fraction of the ethylene sequences from crystallizing upon initial cooling; these sequences subsequently form interlamellar secondary crystals upon aging at room temperature [4].

The complex structure of these materials leads to equally complex thermomechanical behavior, even in the linear viscoelastic limit, with the acid comonomer content and neutralization levels both exerting profound effects. In typical ethylene copolymers (such as ethylene/hexene), increased comonomer content leads to a reduction in the room-temperature modulus, due to a reduction in crystallinity. By contrast, in high-acid E/(M)AA copolymers, the room-temperature modulus INCREASES with comonomer content, due to vitrification of the amorphous layers [5]. Neutralization creates a heterogeneity within these amorphous layers, which then comprise a polyethylene-like matrix (with a glass transition temperature comparable to that in low-density polyethylene, as shown by dynamic mechanical thermal analysis) and the ionic aggregates, which themselves immobilize a significant fraction of incorporated or adjacent organic material. Room-temperature aging then generates secondary crystals with a typical thickness of 3 nm, which serve to reinforce the amorphous layers and generate a material with a room-temperature modulus far in excess of that for either the nonionic copolymer or the material immediately following primary crystallization.

With increasing temperature, this reinforced amorphous phase can be softened either by melting of the secondary crystals or devitrification of the ionic aggregates; these two processes both occur between room temperature and 80C, but which occurs first depends on the material (acid content and neutralization level) and its thermal treatment (melting point of the secondary crystals). At 80C, the material consists of the remaining primary crystals and soft amorphous interlayers physically crosslinked by the ionic aggregates. Using the Davies composite model [5], we can extract the modulus of the amorphous layers from the overall modulus and the known crystallinity and crystal-phase modulus; the results at 80C can be satisfactorily collapsed as a master curve against ion content, and are adequately described by rubber elasticity theory, taking each ionic group to be an effective crosslink.

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[2] N.K. Tierney and R.A. Register, Macromolecules, 36, 1170 (2003).

[3] R.A. Register and S.L. Cooper, Macromolecules, 23, 318 (1990).

[4] Y.-L. Loo, K. Wakabayashi, Y.E. Huang, R.A. Register, and B.S. Hsiao, “Thin Crystal Melting Produces the Low-Temperature Endotherm in Ethylene/Methacrylic Acid Ionomers”, Polymer, posted on Web, May 11, 2005.

[5] K. Wakabayashi and R.A. Register, “Micromechanical Interpretation of the Modulus of Ethylene-(Meth)Acrylic Acid Copolymers”, Polymer, John D. Hoffman Memorial Special Issue, to appear.