Quantifying tie-chain content in semicrystalline polyolefins with vapor-flow small-angle neutron scattering.

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A long-standing fundamental concept in our understanding of the mechanical properties of semicrystalline polymers is that of tie chains—molecules which form part of two adjacent crystalline lamellae and function as crosslinks between them. Although characterization methods targeting crystalline regions are well established, quantifying the properties of the interlamellar amorphous region remains challenging. This technique establishes a crucial link between semicrystalline polymer mechanical properties and calculations of tie-chain content based on molecular architecture. Here, we compare both notch test results and a primary structural parameter [1] with tie-chain content calculated by applying equilibrium swelling theory to vapor-flow SANS data for two ethylene-hexene copolymers and a linear polyethylene.

Crosslinks in gels are routinely characterized by applying equilibrium swelling theory to gravimetric absorption data: the entropic cost of crosslink extension opposes the free energy of mixing [2]. Tie molecules similarly restrict solvent absorption, but there are several disadvantages to quantifying the swelling of semicrystalline materials gravimetrically. First, gravimetric measurements do not differentiate between solvent uptake by extralamellar (grain boundary) and interlamellar amorphous material. Second, the amorphous layer swelling ratio must be determined indirectly, by assuming that the molar volumes of the permeant and amorphous polymer are additive during mixing.

Small-angle scattering experiments directly measure the interlamellar amorphous layer swelling [3,4]. When using deuterated solvent vapor, neutron scattering in particular offers the further advantage of a large increase in scattered intensity, independently related to the interlamellar solvent volume fraction. There is also a clear indication of any solvent-induced change in the crystalline structure at high vapor activities; these data points are excluded from the equilibrium swelling calculations. Examining the effect of short chain branch content on the rate and extent of swelling-induced crystallization may provide additional insight into mechanical behavior.

References:

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