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Crystalline organization and toughening: example of polyamide-12

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Abstract

Improving the impact resistance of plastics is a key to many applications. Today, dispersing rubber and inorganic particles into semicrystalline polymers is widely used to increase their impact strength without greatly altering other interesting properties such as elastic modulus or chemical resistance. Yet, the underlying mechanisms controlling such toughening are controversial. Hitherto it has been often suggested that a critical distance between particles which controls the brittle-to-tough transition is an intrinsic property of the polymer. On the contrary, we demonstrate here that differences in crystalline organization of the matrix can induce dramatic changes in toughening efficiency. A thermal treatment and microscopic observations strongly suggest that crystalline orientation, size of crystalline grains and molecular organization at grain boundaries play a determinant role in the toughening mechanisms. These observations may have important implications for designing and manufacturing tough plastic materials.

Keywords: Toughening; Polyamide; Semi-crystalline polymers

1. Introduction

The impact resistance of semicrystalline polymers such as polyolefins or polyamides, is dramatically affected by the presence of defects or sharp notches which act as stress-concentrators and favor brittle fracture. In the past 50 years, great research efforts have been carried out to reduce the defect-sensitivity and improve the impact strength of these materials. Within this context, it was found that semicrystalline polymers can be considerably toughened by dispersing a second phase—usually rubber—in the semicrystalline matrix [1,2]. For instance, incorporating 20% of ethylene–propylene rubber particles into a polyamide-6 matrix can lead to a 10-fold increase in the impact resistance of notched specimens [3]. Such toughened semicrystalline plastics are now widely used in a large variety of demanding industrial applications ranging from automotive parts to off-shore pipes. Here, we present microscopic observations of toughened systems which bring a new insight into the mechanisms underlying the toughening of semicrystalline polymers.

In a very schematic way, the toughening strategy consists in modifying the polymer material to dissipate the impact energy by other means than crack propagation. In semi-crystalline polymers toughened with particles, both experimental [4–11] and theoretical [12–16] studies show that toughening results from a multiple step mechanism where cavitation and plastic deformation are crucial. When a crack propagates through an efficiently toughened system, voids are created inside or around the particles due to strong stress concentration at the front of the advancing crack. Particle cavitation and void formation generates a new stress distribution in the material which facilitates the initiation of plastic deformation of the matrix. As a consequence, the matrix ligaments confined between cavitated particles can undergo extensive plastic deformation which dissipates large amount of impact energy. The succession of particle cavitation, the initiation step, and matrix plastic deformation, the dissipative one, are now well-admitted mechanisms. However, the molecular parameters controlling their activation have not yet been clearly identified. The ability to predict toughening efficiency remains a controversial and challenging issue.

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Abundant literature has focused on the influence of particle dispersion on the impact resistance of toughened semicrystalline polymers. A first study by Wu on toughened systems of polyamide-6,6 indicates that toughening efficiency strongly correlates with the average ligament thickness, L_n, which is defined as the average surface-to-surface distance between two neighbored particles [17]. Such a length characterizes the confinement of the matrix. Experimentally, it is controlled by varying the concentration and size of the filler particles. In his work, Wu reports that for given temperature and impact conditions, extensive plastic deformation of the matrix is possible when L_n is lower than a critical value, L_c. Several groups have reported later the existence of a similar critical length in other matrices (polyamide-6 [3,19], highdensity polyethylene [20,21], isotactic polypropylene [18], polyethylene terephthalate [22]) using various rubber [3,17–20,22] and inorganic [21] fillers. For a given polymer matrix, this critical length, L_c, seems to be constant independently of the nature of the filler particles, filler content and particle size. Thus, it has been suggested that there exists a characteristic confinement length intrinsic to each semicrystalline polymer determining the onset of toughening efficiency. For instance, toughening at room temperature and under standard impact conditions should only be successfully achieved for L_n values lower than 300 nm in polyamide-6,6 [17] or 600 nm in high-density polyethylene [21], whatever the fillers are.

The microscopic picture proposed to explain the existence of an intrinsic critical confinement thickness, L_c, relies on the presence of highly oriented crystalline layers wrapping each particle with a well-defined thickness of about half L_c [6]. Due to their crystalline orientation, these so-called transcrystalline layers would exhibit a strong anisotropic behavior with directions of low shear yield stress parallel to the particle surface. In consequence, for ligament thickness lower than L_c, transcrystalline layers would percolate through the whole material enabling extensive plastic deformation of the matrix and high levels of toughness. Numerical mechanical models confirm that transcrystalline layers favor the plastic deformation of the matrix and indeed could bring toughness [16]. Experimentally, however, such layers have been observed in polyamide thin films prepared by spin-coating from solutions [6] but no studies have been reported for bulk samples. Here, we present transmission electron microscopy studies of bulk toughened polyamide-12 showing that there is no transcrystalline layers around particles. In injected samples, the crystalline organization of the matrix happens to be strongly determined by the processing conditions and particularly the local flow direction. In addition, this crystalline organization can be modified by a thermal treatment which also dramatically affects the toughening efficiency. Such processing and thermal history dependence suggests that the concept of an intrinsic critical length, although appealing, is very questionable.

2. Experimental

2.1. Materials

Semicrystalline polyamide-12 with $M_n = 25{,}000$ and $I_p = 2.3$ was provided by Arkema. Two impact modifiers were studied at various concentrations ranging from 0 to 30 wt%: reactive ethylene/propylene rubber (EPR*) and poly(styrene)-*block*poly(butadiene)-*block*-poly(methyl methacrylate) triblock terpolymer (SBM). Blending was achieved by extruding together the modifier and the semicrystalline matrix. Different particle dispersions were obtained by varying the concentrations and extruding conditions. In the case of EPR* which is very reactive, particle diameters are small (∼50–100 nm) and quite monodisperse. In SBM toughened systems, particle sizes are much larger (∼0.1–1 μm) and more polydisperse. More details about the use of SBM as an impact modifier will be published elsewhere [23]. Compositions and number average particle diameter, d_n, are given in Table 1 for some representative systems.

2.2. Processing and thermal treatment

Impact test bars were injected according to ASTM/ISO requirements. A thermal treatment was applied to some of the injected samples as follows. Test bars were first melted at 200 °C for 20 min in a mould and under a press to avoid contact with air. Melted bars were then slowly cooled under the press down to room temperature (1 °C/min). All the bars were dried in a vacuum oven at 50 °C for 24 h prior to this treatment and kept in a desiccator until they were tested. Notches were cut according to the specifications of ISO179, after the treatment and just before impact testing.

2.3. Characterization

Optical micrographs were obtained under crossed polarizers from thin (∼5 μm) microtomed sections on a LEITZ DMRXE microscope.

Particle dispersions and matrix crystalline organizations were characterized by transmission electron microscopy (TEM) using stained ultrathin sections. Ultrathin sections were cut by ultramicrotomy with a diamond knife at −100 °C. Osmium tetroxide (OsO_4) vapor was used to selectively stain SBM particles in PA12/SBM systems. An aqueous solution of phosphotungstic acid (H_3PO_4, $12WO_3$) and benzyl alcohol was used to stain the polyamide matrix and reveal the crystalline lamellae [24]. Benzyl alcohol acts as a dyeing assistant and helps diffusion of WO_3 which preferentially stains the amorphous polyamide layers. Experiments were carried out with a JEOL 100CX electron microscope at an acceleration voltage of 80 kV. For each blend, particle size distribution was obtained by image analysis with the ImageJ software [25] on 200–800 particles and over several tens of μm^2. The diameter, d, of each particle was estimated by: