



Toughening plastics by crack growth inhibition through unidirectionally deformed soft inclusions



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ARTICLE INFO

Article history:

Received 15 April 2013

Received in revised form

7 August 2013

Accepted 11 August 2013

Available online 19 August 2013

Keywords:

Toughening mechanism

Soft inclusions of high aspect ratio

Crack growth inhibition

ABSTRACT

We demonstrate that without changing the filler content mechanical properties of commodity plastics with immiscible soft inclusions can be decisively enhanced, simply by pressure induced flow processing in the solid state. As an example, we have chosen acrylonitrile-butadiene-styrene (ABS), where shape and orientation of the soft fillers were changed by processing, resulting in an array of aligned and oriented nanosize deformed rubber domains. These deformed domains effectively controlled the propagation of cracks inside the solid matrix and were responsible for a multifold increase of tensile and impact toughness. Thus, appropriate processing allows manufacturing plastics with high impact resistance in accordance with engineering needs.

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1. Introduction

Transforming through simple processing steps standard materials into high performance products allows in a cost-effective and versatile way to adapt materials properties to engineering needs without the necessity of developing new materials. Along these lines, strategies for transforming commodity plastics, which often suffer from low ductility, insufficient for many engineering applications, into products of high toughness are explored. For decades, higher ductility and thus higher toughness was typically achieved by adding immiscible soft inclusions, for example, rubbery particles, into plastics such as acrylonitrile-butadiene-styrene (ABS) or epoxy resins. Toughness, which is related to the amount of energy of an impact dissipated in the sample, increases with the volume fraction of soft inclusions. However, increasing the amount of soft material added causes a reduction of the tensile strength of the material. Thus, one has to search for possibilities to enhance mechanical properties even without changing the filler content, preferably through simple but appropriate processing routes.

Acrylonitrile-butadiene-styrene (ABS) resin represents one of the most successful examples of toughening plastics by integrating soft fillers [1,2]. ABS is realized by blending a bulk matrix of random styrene-acrylonitrile (SAN) copolymer with rubbery polybutadiene (PB). Due to phase separation, the incorporated viscoelastic PB molecules assemble in numerous isolated spherical domains with a size ranging from 100 nm up to a few micrometers. As a consequence, the impact toughness is raised from about 2 kJ/m² to about 10 kJ/m², ensuring a wide range of applications of ABS, e.g. in automobile industry, where it replaced metals in crash bars. Based on the success of ABS, the mechanism of toughening by soft inclusions has attracted much attention and various theories have been proposed thereafter [3–9]. As a general rule, for a given domain size, impact toughness improves with the increase in rubber content [10]. However, due to the addition of a rubbery component, such improvement is always at the expense of a loss in tensile strength.

As one efficient and attractive approach for introducing soft objects, nano-meter sized micelles have been added into a hard epoxy matrix [11,12]. Changing the shape from spherical to wormlike micelles through synthetic routes was shown to lead to an effective enhancement of toughness due to so-called “crack blunting” [13]. This suggests a general concept for toughening plastic materials by inclusion of soft objects of high aspect-ratio, e.g. soft inclusions like “oval disks” attained either by synthesis or through processing.

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Anisotropic and rigid particles with high aspect ratio, e.g. sheet-like clays [14–16], or most recently graphene [17–19], have been shown to significantly enhance modulus and strength of several commodity polymers. However, in contrast to rigid fillers, highly non-spherical soft inclusions having a glass transition temperature (T_g) lower than the application temperature have not yet been successfully fabricated. Being easily deformable, such fillers will tend to minimize their surface energy and maximize conformational entropy by attaining a spherical shape. However, when the surrounding elastic matrix is put under tension these spherical domains can be deformed, but typically only up to a few percent until the elastic matrix polymer fails due to brittle failure (cracking).

Here, we present a simple approach for making plastics tougher without increasing the rubber content and thus without decreasing the tensile strength. We simply change the morphology of the rubber phase from spherical into disk-like domains by a processing step in the solid state. To this end, we employed pressure-induced-flow (PIF) processing of ABS, which is a simple and effective method to generate arrays of soft filler particles with high aspect ratio (i.e. rubber inclusions of anisotropic shape) within a solid matrix. Here, as a consequence of compression, flow within materials like ABS was caused in the solid state at temperatures below the glass transition (see Fig. 1a). The thereby generated large quantities of PB rubber inclusions were uniformly oriented with respect to the flow direction of PIF. A similar approach of solid-state-processing of polymers has been employed for poly(styrene-*block*-*n*-butylmethacrylate) (PS-*b*-PBMA) block copolymers [20], thermoplastic polyurethane [21], semi-crystalline polyethylene [22] and polypropylene [23]. PIF processing has the additional advantage of being energy efficient as it can be performed even at relatively low temperatures, typically 10–50 °C below glass transition (T_g) or melting temperature (T_m) of semicrystalline polymers, and thus

may avoid severe thermal degradation, especially decisive for some biomaterials. Generally, PIF-processing is a robust and versatile approach which can easily be implemented in various fabrication approaches, using conventional industrial processing techniques, for toughening diverse commodity plastics.

2. Experimental section

2.1. Materials and samples preparation

The SAN (styrene-acrylonitrile) resin (brand D-178) used in experiments was purchased from Zhenjiang Guoheng Chemical Co., LTD, China. The glass transition (T_g) of the SAN matrix is 117 °C, as measured by dynamic mechanical spectroscopy, for an acrylonitrile content of 25 wt. % and 75 wt. % of polystyrene. Polybutadiene was synthesized by emulsion polymerization resulting in about 27 wt. % of these PB molecules being grafted to SAN and had a T_g of –80 °C as measured by dynamic mechanical spectroscopy. The molecular weight (M_w) of PB was 8.1×10^4 g/mol. The ABS resin was prepared by mixing 10 wt. % of PB into a SAN matrix. At 200 °C, the melt index of the resultant ABS resin was 1.7 g/10 min for 5000 g, as measured by a melt flow rate detector (RLS-400 melt flow rate detector, Kexin Test Instrument Co., LTD, Changchun, China), according to the ASTM D-1238 standard test. ABS is an amorphous polymer, and both SAN and PB are not able to crystallize, as verified by DSC curves before and after PIF processing.

2.2. Pressure-induced flow (PIF) processing

Samples for mechanical testing were prepared by first injecting the 200 °C hot ABS resin into a mold (80 mm × 10 mm × 15 mm) at 50 °C (which is below glass transition temperature of SAN) at an injection pressure of 10 MPa, and no other special annealing

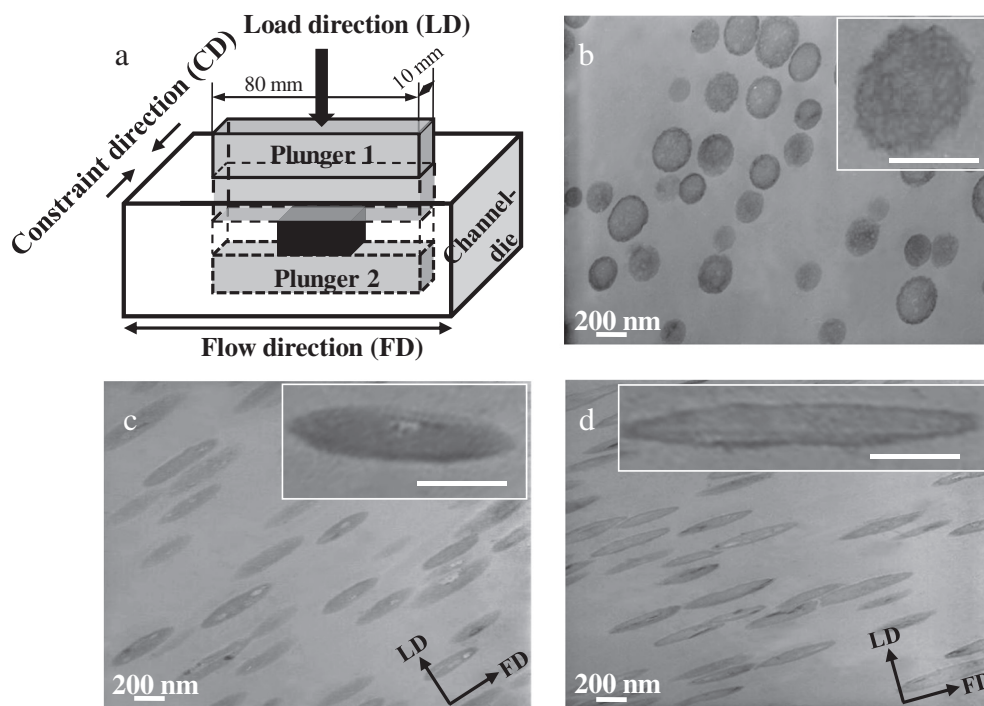


Fig. 1. Microscopic characterization of array of rubber inclusions obtained by pressure-induced flow (PIF) processing. (a) Schematic drawing showing the channel die used for the PIF processing procedure. The sample between the plungers is marked in black. Load direction (LD), flow direction (FD) and constraint direction (CD) are indicated. (b) Transmission electron microscopy (TEM) images of an ordinary acrylonitrile-butadiene-styrene (ABS) resin having a 10 wt. % content of polybutadiene (PB), demonstrating spherical domains (rubber inclusions) consisting of PB stained by OsO_4 . (c, d) TEM images of oriented rubber inclusion array in ABS after PIF-processing, with width to thickness ratio $AR = 2.56$, and $AR = 4.78$, respectively. The scale bar represents 200 nm in all cases.

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