European Polymer Journal 71 (2015) 221–230

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Effect of *in-situ* formed core–shell inclusions on the mechanical properties and impact fracture of polypropylene

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ARTICLE INFO

Article history:
Received 28 April 2015
Received in revised form 1 July 2015
Accepted 30 July 2015
Available online 31 July 2015

Keywords:
Polypropylene
Core–shell
Liquid crystalline polymer
Ionomer
Impact fracture

ABSTRACT

To obviate the reduction of stiffness in rubber toughened and yield strength in rigid particle toughened iPP, various strategies were adopted. Here, we report on the static and impact properties of isotactic polypropylene (iPP) with *in situ* formed (rigid thermotropic liquid crystalline core)–(soft copolymer shell) inclusions (RCSS inclusions). We found that, at constant soft shell thickness (t_s) and stiffness (E_s), the elastic modulus of iPP/RCSS (E_c) increased with the total RCSS volume fraction (v_{RCSS}), and, at constant v_{RCSS}, the E_c increased with E_s. At constant t_s and E_s, the yield strength of iPP/RCSS (σ_{yc}) decreased with the v_{RCSS} and, at constant v_{RCSS} and t_s, the σ_{yc} decreased with E_s in an agreement with the simple micromechanics models of Matonis and Small. At small v_{RCSS}, the changes in E_c and σ_{yc} with v_{RCSS} contributed simultaneously to the significant enlargement of the crack tip plastic zone size, enhancing the impact fracture toughness in terms of the apparent critical strain energy release rate (G_c'), substantially, without significantly reducing stiffness and yield strength. The SEM fractography revealed extension of the RCSS inclusions into fibrous shape providing an additional means for dissipation of mechanical energy stored in the fracturing solid. Experimental data agreed reasonably well with the prediction based on a simple mixed mode fracture model proposed earlier.

1. Introduction

For the increasing number of structural applications of plastics in automotive, sporting goods, appliances and IT hardware, high stiffness at elevated temperature and good fracture resistance at high strain rates or low temperatures are desired the most. Various toughening strategies were used over last 30 years [1–20]. In rubber toughened polymers, the enhanced fracture toughness is usually offset by the reduced elastic modulus, enhanced creep compliance and reduced high temperature properties [5]. The use of rigid particulate fillers with controlled interfacial adhesion can prevent this problem to some degree, though rigid fillers usually increase viscosity and density [3,8,10,11,14]. Simultaneous enhancement of low temperature impact resistance without significant penalty in high temperature properties can be achieved by adding both rigid and soft inclusions with controlled spatial arrangement of the rigid and elastomer component [5]. It has also been shown that addition of small volume fraction of short deformable fibers can enhance fracture toughness of brittle polymers at high strain rates, substantially [21]. Toughening of polymers with preformed core–shell inclusions [3,22,23] suggests that dispersing a small amount of deformable rigid core–soft shell (RCSS) inclusions may provide the desired improvement of low temperature toughness while preserving the hight temperature properties [15,17,18].

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http://dx.doi.org/10.1016/j.eurpolymj.2015.07.057
0014-3057/© 2015 Published by Elsevier Ltd.

Isotactic polypropylene (iPP) offers a good balance of properties at reasonable cost [24]. Enhancing fracture resistance of iPP at low temperatures or high strain rates is usually achieved by rubber toughening strategy consisting of either physical mixing with elastomers or by reactor copolymerization with ethylene producing impact copolymers (ICPPs) [24–26]. It has already been shown that a desired balance of the low temperature fracture toughness and high temperature stiffness of PP can be achieved by incorporating small volume fraction of rigid core–soft shell inclusions with engineered elastomer shells [5,6,17]. It has been speculated that, in addition to the delocalized shear-yielding most effective during crack initiation, further enhancements of the low temperature fracture resistance of iPP may be achieved by introducing additional deformation mechanism active also in the later stage of the fracture process.

Cold-drawing of thermotropic liquid crystalline polymers (TLCP) was shown to produce high modulus fibers. Hence, it seems reasonable to assume that drawing the rigid core–soft shell (RCSS) inclusions under the stress field in the region ahead of the crack tip can result in the *in-situ* formation of high modulus fibrils [27,28]. Hence, one can hypothetise that this process will result in an additional dissipation of strain energy near the crack tip resulting in a reduction of the crack driving force and, at the same time, may even result in stabilization of microcracks by bridging the crack planes with the drawn microfibrils. Among the necessary conditions to activate these effects optimal size, properties of core and shell polymer and interfacial adhesion of the RCSS inclusions to the matrix. All of these can be engineered to some extent by minimizing Gibbs energy of mixing the three components and the kinetics of the preparation process.

The major obstacle in achieving a desired dispersion of thermotropic liquid crystalline polymer (TLCP) in the iPP is the poor compatibility of the two polymers [29]. The use of block copolymers with segments capable of specific interactions with the individual components is of particular relevance to the work described in this paper [29–32] to obviate the compatibility issue. Graft copolymers of a TLCP with poly(ethylene-*r*-acrylic acid) ionomer (EAA) partially neutralized to the Na^+-salt (NaEAA) were prepared previously [33–36]. Varying the extent of EAA neutralization, size of the cation and the TLCP content in the reacting melt provided a range of graft copolymers (NaEAA-*g*-TLCP) with varying molecular structure [35].

The critical strain energy release rate, G_{Ic}, for the short fiber reinforced composite consists of the contributions from breaking, debonding and pulling-out the fibers and the matrix fracture [21]. The G_{IC} for polymers with uniformly distributed short deformable fibers oriented perpendicularly to the fracture plane, without fiber pull-out can be expressed as:

$$G_{Ic} = \upsilon_{ff} \cdot \frac{5L_c \cdot \sigma^2_{B_f}}{6E_f} + 2D[1 - (d + D)^2 \upsilon_f^2]\sigma_{ym}\left(\varepsilon_{mb} - \frac{1}{2}\varepsilon_{ym}\right) + G_{Ic}f^2, \tag{1}$$

where d is the diameter of the formed fibril and D is the average spacing of fibrils, υ_f is volume fraction of fibers, υ_{ff} volume of fractured fibers, υ_m volume fraction of matrix, L_c critical length, L fiber length, L/d aspect ratio, L_c/d critical aspect ratio, τ_a interfacial shear strength, σ_{Bf} fiber tensile strength, σ_{ym} matrix yield strength, E_f fiber tensile modulus, ε_{ym} deformation at yield point and ε_{mb} matrix elongation at break, respectively. The first two terms on the right hand side of Eq. (1) represent contribution from a narrow layer near the crack plane and the third one is the contribution from the matrix away from the crack plane where no fibers are formed.

In this paper, we report on the effect of *in-situ* formed rigid TLCP core–soft (TLCP-g-NaEAA) shell inclusions on the elastic modulus, yield strength and impact fracture toughness of iPP at 23 °C. Effects of the shell modulus (E_s) and thickness (t_s), the total RCSS volume fraction, υ_{RCSS}, on the tensile modulus, E_c, yield strength, σ_{yc}, and the apparent critical strain energy release rate, G'_c, measure under impact loading at 23 °C are reported. Scanning electron microscopy (SEM) of fracture surfaces from the impact tests and those prepared by breaking single edge notched rectangular bars in liquid nitrogen was used to prove fibrillation of the RCSS inclusions on the crack plane.

2. Experimental

The TLCP used was the wholly aromatic co-polyester RD501™ (Ticona, USA) composed of terephthalic acid (TA), hydroquinone (HQ), hydroxybenzoate (HBA) and hydroxynaphthanoate (HNA), $T_g = 112$ °C, $T_m = 222$ °C. The iPP (Mosten EB501, Chemopetrol Litvinov, CZ) MFI = 0.5 g/10 min (230 °C/21.6 kg), $E_m = 1.5$ GPa, and $\sigma_{ym} = 35$ MPa was used as the matrix. A poly(ethylene-*r*-acrylic acid) ionomer containing 15 wt.% acrylic acid and ~35 mol% of the acrylic acid neutralized to the Na^+ salt, (NaEAA) (Iotek™ 8000, ExxonMobil Chemicals, USA) MFI = 0.8 g/10 min, $\rho = 0.957$ g/cm^3, $\sigma_{yi} = 19$ MPa, $E_i = 0.3$ GPa, tensile impact strength = 570 kJ/m^2 and $T_m = 83$ °C was used as the soft component of the NaEAA-g-TLCP copolymer. The NaEAA-g-TLCP copolymer was prepared by reactive melt blending of the TLCP and NaEAA in a BUSS 30 single screw kneader (BUSS, AG, Switzerland) at 300 °C and 40 rpm following the procedure described by Son and Weiss [35,36].

The TLCP, iPP and NaEAA pellets were pre-dried in a vacuum oven at 70 °C for 12 h prior to use. Single step melt blending of iPP with TLCP, NaEAA and/or NaEAA-g-TLCP was carried out using a Brabender LabStation 2000 (Brabender OHG, Germany) co-rotating twin screw extruder ($L/D = 36$, 50 rpm, 250 °C). The *in-situ* formation of rigid-TLCP-core-soft-NaEAA-g-TLCP-shell inclusions was achieved by mixing the NaEAA-g-TLCP copolymer with the iPP and TLCP in a one step process and keeping the TLCP-g-NaEAA copolymer to the added TLCP volume fraction ratio constant. The RCSS inclusion volume fraction (υ_{RCSS}) was the sum of the volume fractions of the TLCP and the NaEAA-g-TLCP. The pelletized compounds were dried in a vacuum oven at 70 °C for 12 h and then compression molded into 1 mm and 4 mm thick 150 mm × 150 mm sheets using a hot press (Fontijne, NL). The molding protocol consisted of 5 min preheating without pressure at 220 °C, 2 min compression at 133 kN load at 220 °C followed by cooling under pressure at a rate of 20 °C/min for 10 min.