Composites Science and Technology 111 (2015) 9–16

Contents lists available at ScienceDirect

Composites Science and Technology

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

How do graphite nanoplates affect the fracture toughness of polypropylene composites?

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ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form 22 February 2015
Accepted 23 February 2015
Available online 27 February 2015

Keywords:
Graphite nanoplates
A. Polymer-matrix composites (PMCs)
B. Fracture toughness
B. Plastic deformation
D. Fractography

ABSTRACT

From a mechanical perspective, graphene and its derivatives, such as graphite nanoplates, graphite oxide, carbon nanofibers, or nanotubes, are envisioned as ideal nanofillers for polymer composites. Thus, tremendous research effort has been invested to determine the reinforcing mechanism of these nanofillers in the matrix: crack bridging, crystallization enhancement, or crack deflection are some possible mechanisms that have been proposed. In this work, a detailed analysis of the fracture mechanism of graphite nanoplate (GNP)/polypropylene composites was performed. Commercially available graphite nanoplates, composed of multiple graphene layers stacked together, were used to produce polypropylene nanocomposites by following a masterbatch technique. The fracture toughness was determined by applying the S_{pb} parameter method and the fracture mechanism was identified to be void nucleation and growth. We demonstrate how GNPs affect and improve the fracture toughness of polypropylene. This improvement is caused by the debonding of the GNP agglomerates, which promotes the matrix plastic deformation during the fracture process.

1. Introduction

In the last decade, graphene-based nanostructures have been extensively studied as part of a novel generation of composite materials. Their outstanding mechanical properties and extraordinary surface area make these nanoscale materials ideal as nanofillers. Although recent efforts have been made to scale-up the production of graphene [1] or modified graphene [2], only graphite nanoplates (GNPs), which consist of stacked graphene layers bound to each other by van der Waals forces, can currently be produced at the scales needed for use in composite materials and structural applications.

The addition of a small amount of nanofiller can lead to a significant improvement in mechanical properties. Stiffness and strength can be enhanced when nanofillers are homogeneously dispersed [3] and there is a strong interphase between nanofillers and polymer matrix [4,5]. Tremendous research effort has been invested to determine how the nanofiller affects the mechanical and fracture behavior of a polymer [6–11]. The most effective way to toughen semi-crystalline polymers is the cavitation or nucleation of voids [12,13]. One approach to achieve this toughening effect is the addition of nanoparticles. However, if these nanoparticles have a strong interaction with the host matrix then the cavitation or debonding and consequent void nucleation could be hindered [14]. Such materials would have extrinsic rather than intrinsic toughening mechanisms, i.e., crack bridging [15], crack deflection [16], etc.

One of the main problems in analyzing the effect of a nanofiller in a thermoplastic matrix is the difficulty of characterizing the fracture toughness. In the case of ductile polymers, fracture toughness is generally determined by the *J*-integral versus crack growth resistance (*J*–*R*) curve, in which the value of the *J*-integral is plotted against the crack extension. To measure the *J*–*R* curve, a multi-specimen technique is commonly used [17]. A set of pre-cracked test specimens of the same size, geometry, and material are tested until the crack grows to a certain length. As a single test is needed for each point of the *J*–*R* curve, a large number of tests and specimens are needed to obtain the whole curve. Additionally, in the case of polypropylene (PP), measurement of the crack extension is extremely difficult because of the presence of fine-scale fracture-surface features or microstructural inhomogeneities [18]. To

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http://dx.doi.org/10.1016/j.compscitech.2015.02.017
0266-3538/

overcome these drawbacks, Sharobeam and Landes proposed the S_{pb} parameter method [19–21], in which the crack length is estimated indirectly throughout the whole mechanical test; only one single pre-cracked specimen plus one notched specimen are used to measure the whole *J–R* curve. This low material consumption makes this method ideal for materials produced in small batches, such as nanocomposites.

In the work presented here, we analyze the toughening effect of graphite nanoplates in a polypropylene matrix made by a simple extrusion-compounding process, followed by an injection-molding process. The S_{pb} parameter method is used to analyze the fracture toughness of the resulting PP/GNP composites. To identify the plastic deformation zone that appears ahead of the crack tip in the specimen during the fracture test, a full-field strain analysis is carried out by digital image correlation. The fracture mechanism is identified by scanning electron microscopic (SEM) analysis of the fracture surfaces.

2. Methods

2.1. Materials and preparation of nanocomposites

A commercial polypropylene homopolymer (Borealis HB601WG), with a density of 900 kg/m^3 and a melt flow index (230 °C/2.16 kg) of 2.2 g/10 min (ISO 1133), was used for the production of PP/GNP nanocomposites. Graphite nanoplates were purchased from Avanzare (Logroño, Spain) and used with no further treatment. The individual GNPs have a particle size of 2 × 5 μm and are less than 10 nm thick.

2.1.1. Compounding and injection molding

A polypropylene masterbatch with a content of 5 wt.% GNPs was prepared by using an industrial extrusion-compounding machine (Coperion ZSK 26, 26 mm diameter co-rotating twin-screw). The polymer pellets and the GNPs were introduced through the extruder's main gravimetric feeder and side-feeder, respectively. The screw speed was 500 rpm and the temperature of mixture was increased from 170 °C in the feeding zone up to 190 °C at the nozzle. The compounding was extruded through a 2-mm diameter die at a constant output rate of 5 kg/h, producing 10 kg of masterbatch. The extruded material was quenched immediately in a water bath at room temperature, dried, and cut into pellets.

Masterbatch pellets were dried at 80 °C for 4 h prior to processing. Composites of different GNP weight fractions were prepared by diluting the masterbatch with neat PP by using an injection molding machine (JSW 85 EL II) with a 35-mm diameter reciprocating screw, at a screw speed of 120 rpm. The temperature profile was increased from 225 °C at the barrel up to 255 °C at the nozzle. A specific steel mold was used at 30 °C to obtain normalized specimens for flexural tests, by following the specifications of the standard ISO 178, in the form of prismatic bars with dimensions of 125 × 13 × 5 mm^3.

2.2. Particle size analysis and dispersion of the graphite nanoplates

SEM analysis of the as received GNP was performed by using an EVO MA15 Zeiss scanning electron microscope. The agglomerate size distribution was analyzed with the help of the image processing software, ImageJ. The lateral size and thickness of a minimum of 200 GNP agglomerates were measured. To analyze the degree of dispersion, samples of the produced materials were cooled in liquid nitrogen and immediately broken at high speed by impacting with a Charpy pendulum. The cryo-fractured surfaces were analyzed by using scanning electron microscopy (EVO MA15, Zeiss) after they had been sputter-coated with a thin layer of gold.

2.3. Differential scanning calorimetry and dynamic mechanical analysis

Differential scanning calorimetry (DSC) was performed on a DSC Q200 (TA Instruments), to obtain information about the effect of the nanofiller on the crystallization behavior of the PP matrix. During the measurements, the samples were heated from 20 to 220 °C at a rate of 10 °C/min, held at 220 °C for 0.5 min to eliminate any previous thermal history, and then cooled to 20 °C at a rate of 10 °C/min. Then, after being kept at 20 °C for 0.5 min, the samples were heated to 220 °C at a rate of 10 °C/min.

Dynamic mechanical analysis (DMA) were carried out by using specimens with dimensions of 17.5 × 13 × 5 mm in single cantilever mode. The tests were performed on a Q800 (TA Instruments) in a temperature range of −150 to 150 °C, at a frequency of 3 Hz, and a heating rate of 1.5 °C/min.

2.4. Mechanical characterization

Characterization of flexural properties was conducted under ambient conditions by using a Zwick Roell Z 10 kN. At least ten specimens of each composition were measured. Tests were carried out following standard ISO 178 with a cross-head speed of 2 mm/min. Specimens were tested in a three-point bending configuration with 57 mm between supports.

The characterization of the fracture behavior of PP nanocomposites was carried out by using a three-point bending test, at room temperature, by using an Instron 3384 at a cross-head speed of 1 mm/min. Single-edge-notch bending (SENB) specimens, with dimensions of 62.5 × 13 × 5 mm^3, were tested with a span-to-width ratio of 4. To apply the S_{pb} parameter method two types of specimens were tested; reference and pre-cracked specimens. A schematic representation of the SENB specimens tested is shown in Fig. 4a. In this work, one reference and three pre-cracked specimens were tested for each GNP concentration. All the specimens had blunt notches machined with a disk-cutting machine. In the case of the reference specimens the blunt notch length, a_b, was 10.4 ± 0.1 mm and for the pre-cracked specimens a_b = 3.3 ± 0.1 mm. Then, in the pre-cracked specimens, the notch was sharpened by tapping with a razor blade to extend the crack length with a sharp crack with a length, a_{sp}, of 1 mm. Thus, the pre-cracked specimens had total crack lengths, a_p, of 4.3 ± 0.2 mm, as confirmed by examining every specimen under an optical microscope. A detailed explanation of the S_{pb} parameter method can be found in Refs. [19–22].

2.5. Digital image correlation and fractographic analysis

To perform a digital image correlation (DIC) study, one side of every SENB specimen was painted white and then lightly sprayed with black paint to obtain the random speckle pattern that is required for DIC analysis. Images were taken every 3 s during the test. The area of analysis (13 × 6.5 mm^2) was located immediately ahead the root of the blunt notch (Fig. 4a). The acquired images were evaluated by using the Vic-2D 2009 Digital Image Correlation software (VicSNAP, Correlated Solutions Inc., Columbia, SC, USA).

After fracture tests, specimens were cooled in liquid nitrogen and immediately broken at high speed by impacting with a Charpy pendulum. This procedure ensured that brittle fracture surfaces were generated, to allow the easy identification of the ductile fracture surface generated during the fracture test. The surfaces of