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Material Properties

J-integral evaluation of nanoclay-modified HDPE/PA6 microfibrillar composites

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ABSTRACT

Microfibrillar composites (MFC) are polymer-polymer composites with many advantages, including good dispersion and bonding of in-situ generated fibrils. Recently, it has been shown that their performance can be enhanced by suitable addition of organophilized montmorillonite (oMMT) provided the numerous oMMT-induced effects are harmonized. This work deals with evaluation of resistance against unstable crack propagation (J-integral) in combination with Charpy and tensile impact strength methods, and SEM observation of fibrils shape and size and fracture surfaces. The results indicate that addition of PA6 inclusions and oMMT to relatively ductile HDPE reduces toughness evaluated using Charpy and J-integral. The fact that tensile impact strength is not reduced by oMMT indicates the importance of the impact testing mode for MFC. Of importance is the fact that formation of PA6 fibres reinforced with oMMT practically does not reduce toughness. Hence, the drawn oMMT-modified system with significantly higher stiffness and practically unchanged fracture resistance can be obtained. Combination of the complex effect of oMMT and in-situ fibrils reinforcement present a tool to attain polymer systems with enhanced well-balanced properties.

1. Introduction

Microfibrillar composites (MFC) are polymer blends with the minority phase in the form of fibrils produced by cold or melt drawing of suitable polymer mixtures like HDPE/PA6 [1–3]. These polymer/polymer composites are a special case of polymer modification - a transition between polymer blends and composites. The advantage of MFC is fair dispersion and adhesion of in-situ formed fibres and no abrasion of processing equipment [4]. Their main disadvantage associated with limited parameters of polymeric fibres may be eliminated by nanofillers (NF), as shown recently in HDPE/PET/CNT system [5] and our study on HDPE/PA6/oMMT [6,7]. NF can even enable melt drawing by elimination of unstable extrusion in the case of the biodegradable PCL/PLA system [8,9]. Specific features of MFC containing relatively ductile fibres undoubtedly influence their fracture behaviour [10–12]. While the energy absorption in a system containing short rigid (mostly glass or carbon) fibres consists predominantly in fracture and pull-out of fibres [13,14], in MFC deformation and fracture of fibres is also of importance [15]. In contrast to analogous composites with short rigid fibres, where fracture behaviour has been studied intensively [13–16], fracture toughness of MFC has been studied only rarely [12]. The work of Li et al. [12] dealing with PE/PET MFC indicates optimal PET fibres content 10–20% and importance of microfibres characteristics. Addition of polymeric or natural fibres can improve impact resistance, especially in melt-mixed composites with a matrix of low ductility [17,18]. In a PP-matrix system, a positive effect on toughness was found with a combination of PET fibres and nano-$CaCO_3$ particles [19]. The present work deals with the effect of fibrils formation on toughness expressed as the fracture mechanics concept, *J*-integral, of HDPE/PA6 MFC and analogous clay-modified system [6], i.e. in composite with dual reinforcement.

2. Experimental

2.1. Materials

High density polyethylene (HDPE) HYA 800, melt index 0.7 g/10 min (190 °C, 2.16 kg) (Exxon Mobil); polyamide 6 (PA6) Ultramid B5, M_n ~ 42000 (BASF); clay based on natural montmorillonite

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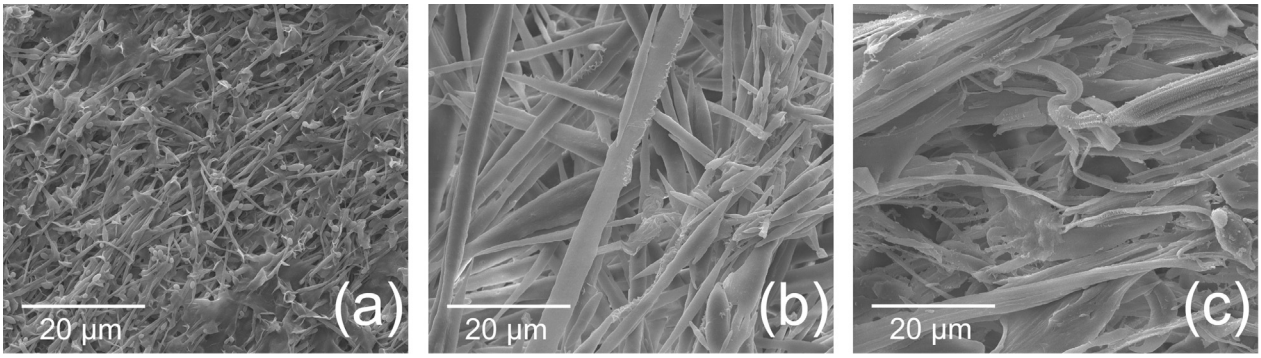

Fig. 1. SEM images of PA6 fibrils, draw ratio = 7: (a) HDPE/PA6 80/20; (b) HDPE/PA6/oMMT 80/20/2; (c) HDPE/PA6/oMMT 80/20/3.5.

(oMMT) Cloisite 30B (modified with alkylbis(2-hydroxyethyl) dimethylammonium chloride 90 meq/100 g, with alkyl derived from tallow) (Southern Clay Products, Inc.)

2.2. MFC preparation

Prior to mixing, PA6 and clay were dried at 85 °C and 70 °C, respectively, for 12 h in a vacuum oven. Mixing proceeded in a co-rotating segmented twin screw extruder (L/D 40) Brabender TSE 20 at 400 rpm and temperature of respective zones 230, 235, 240, 245, 245 and 250 °C. The extruded bristle was melt-drawn using an adjustable take-up device. The draw ratio is a ratio between the velocity of take-up rolls and initial velocity of the extruded bristle. Dumbbell specimens (gauge length 100 mm) were prepared by injection moulding in an Engel Victory 200/50 machine. Analogous smaller specimens with gauge length of 40 mm were prepared using a micro-injection moulding machine (DSM). The barrel temperature was 200 °C, and that of mould 70 °C.

2.3. Characterization

Tensile tests were carried out at 22 °C using an Instron 5800 apparatus at crosshead speed of 50 mm/min. At least 10 specimens were tested for each sample. The Young's modulus (E), maximum stress (σ_m) and elongation at break (ε_b) were evaluated; the corresponding variation coefficients did not exceed 10%, 2% and 20%, respectively. Charpy impact (a_{cN}) was measured with one-side notched specimens of dimensions 60 × 10 × 4 mm using a Zwick hammer with energy of 4 J (variation coefficient 10–15%). Tensile impact strength (a_t) was measured with one-side notched specimens, using a Zwick hammer with energy of 4 J (variation coefficient 10–15%). The reported values are averages of twelve individual measurements.

Rheological characterization was conducted using an ARES apparatus (Rheometric Scientific, Piscataway, NJ) with the parallel-plate geometry at 200 °C using an oscillatory shear deformation at frequency range of 0.1–100 rad/s. The amplitude of oscillation was 3%, i.e. within the range of linear viscoelasticity.

2.4. J-integral determination

J-integral was selected for determination of toughness. An instrumented Charpy impact pendulum (CEAST Resil Impactor, Italy) with nominal energy 7.5 J, speed (v_H) 1.5 m/s and support span (s) 40 mm, was used to perform the procedure at room temperature according to Seidler-Grellmann [20]. Testing specimens corresponding to ISO 179-1/1 type (length, L = 80 mm; width, W = 10 mm; thickness, B = 4 mm) were prepared by injection moulding. The notches of depth (a) 2 mm and tip radius 0.2 μm were prepared with a razor blade. In the impact tests, the load-deflection (F-f) diagrams were recorded and the initial deformation energy (A_G) up to the maximum impact load was separated into elastic (A_{el}) and plastic (A_{pl}) parts. The values of the J-integral were determined using the following equations (1)–(3), proposed by Sumpter and Turner [21,22]:

$$J_{Id}^{ST} = \eta_{el}\frac{A_{el}}{B\ (W-a)} + \eta_{pl}\frac{A_{pl}}{B\ (W-a)}\cdot\frac{W-a_{eff}}{W-a} \tag{1}$$

where

$$\eta_{el} = \frac{2F_{gy}s^2(W-a)}{f_{gy}E_dBW^3}\cdot f^2(a/W)\left(1-\nu^2\right) \tag{2}$$

$$\eta_{pl} = 2 - \frac{(1-a/W)\cdot(0.892-4.476\ a/W)}{1.125+0.892\ (a/W)-2.238\ (a/W)^2} \tag{3}$$

and a_{eff} is crack length at the onset of unstable crack propagation measured using light microscope equipped with metering table.

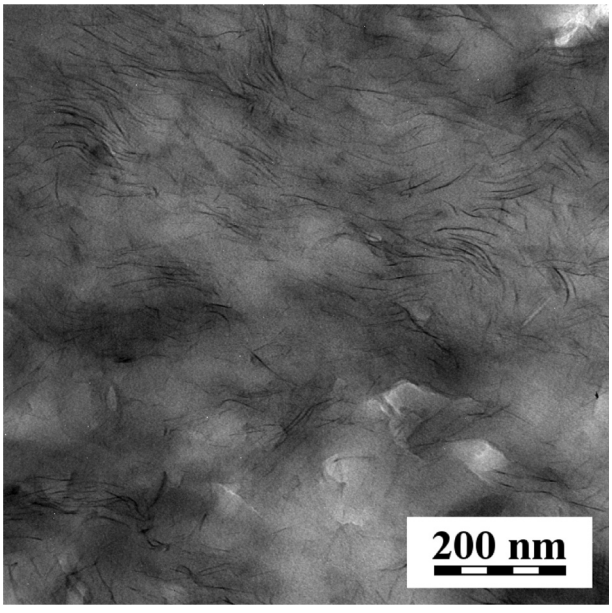

Fig. 2. TEM image showing the degree of clay dispersion in PA6 fibre and presence of HDPE subinclusions inside; HDPE/PA6/oMMT 80/20/3.5 system.