



Polymer-polymer Microfibrillar Composites: Effect of Nanofillers on Structure and Properties

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Microfibrillar composites (MFCs) are advantageous polymer-polymer composites with in situ formed reinforcing fibrils. The range of applications of MFCs is limited by their low thermal resistance and mechanical parameters of polymeric microfibrils, which are formed by melt or cold drawing of the polymer blend. This study addresses improving MFCs based on HDPE matrix with 20% polyamide 6 microfibrils using organophilized montmorillonite. The complex effect of the nanofiller on the structure and parameters of the MFCs is investigated.

Keywords: Microfibrillar Composite, Layered nanosilicate, Drawing.

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1. INTRODUCTION

Microfibrillar composites (MFCs) are polymer-polymer composites based on blends of ideally semi-crystalline polymers with a marked difference in melting points [1]. Their melt or cold drawing can transform the original spherical inclusions of dispersed polymer, such as polyamide or poly(ethyleneterephthalate) to fibre-like microfibrils, which are preserved during the subsequent processing step at lower temperature to only melt the matrix (usually polyethylene or polypropylene). The advantages of MFCs are their mechanical properties, which are analogous to those of glass or carbon fibre composites, and their lower density, zero abrasion of equipment, improved processability and cost effectivity. Further advantages represent fair recyclability and application of conventional processing equipment. Of importance is the very high interfacial bonding of the fibrils formed directly inside the matrix (created together with the matrix similarly to natural composites), which arises from the formation of a transcrystalline layer of matrix around the fibrils or chemical bonding in case of condensational polymers [2] and also through the use of the functionalized components. The limitations of MFCs include a reduced applicable temperature range, due to their relatively low thermal resistance, and a low strength and stiffness of the polymeric fibrils in comparison with inorganic or carbon fibres. These shortcomings can be successfully eliminated through the use of nanofillers (NF) of various geometries, i.e., by combination of MFC and nanocomposite concepts. In polymer nanocomposites [3], plate-, tube- or fibre-type nanofillers can significantly enhance the material's mechanical properties, influence the crystallinity and flow characteristics, and so on. Moreover, even more significant and complex changes can occur in the case of multiphase polymer systems [4], where the regulation of the phase structure by influencing the dynamic phase behaviour can be accompanied by the formation of new effective morphologies of the dispersed phase, increasing the toughening efficiency

[5]. As a result, systems with a unique balance of mechanical parameters may be obtained. Nanofillers close in size to that of the macromolecules also support drawing of the polymers [6], especially fibre formation due to the enhancement of the chains orientation along draw axis and the oriented crystallisation. As a result, the effect of using NF in MFC may be even more complex than the mere combination of reinforcement and structure directing effect. At the same time, the numerous, and in some cases contradictory, effects of NF must be perfectly harmonised to upgrade MFCs and/or to eliminate possible antagonistic effects. This study addresses with the potential of layered nanosilicate montmorillonite to improve an MFC based on the combination of an HDPE matrix with PA6 microfibrils.

2. EXPERIMENTAL

2.1 Materials

High density polyethylene (HDPE) HYA 800 (Exxon Mobil), copolymer ethylene-glycidymethacrylate (Aldrich), Polyamide/6 (PA6) Ultramid B5 (BASF), Clays based on natural montmorillonite: Cloisite 15A(modified with dialkyldimethylammonium chloride 95 meq/100g) (C15), Cloisite 30B (modified with alkylbis(2-hydroxyethyl)dimethylammonium chloride 90 meq/100g, with alkyl derived from tallow) (C30), (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 counter 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 adjustable take-up device. Dog-bone specimens (gauge length 40 mm) were prepared in a laboratory micro-injection molding machine (DSM). The barrel temperature was 200 °C, that of mold 70 °C.

2.3 Testing

Tensile tests were carried out at 22 °C using an Instron 5800 apparatus at a crosshead speed of 20 mm/min. At least 8 specimens were tested for each sample. Structure of fibrils was observed using scanning electron microscopy (SEM), HDPE matrix removed by boiling xylene for 10 hours.

3. RESULTS AND DISCUSSION

From Fig. 1 it can be observed that the addition of 3% C 30 (in the course of simultaneous mixing of all components) to the 80/20 HDPE/PA6 mixture leads to a minor increase in the stress at break, accompanied by a significant gain in stiffness with increasing draw ratio. The relatively higher parameters of the undrawn sample without nanofiller results from the significant fibril formation due to flow through the die; this effect is apparently reduced by the nanoclay. This is a consequence of the clay affecting rheological parameters of components.

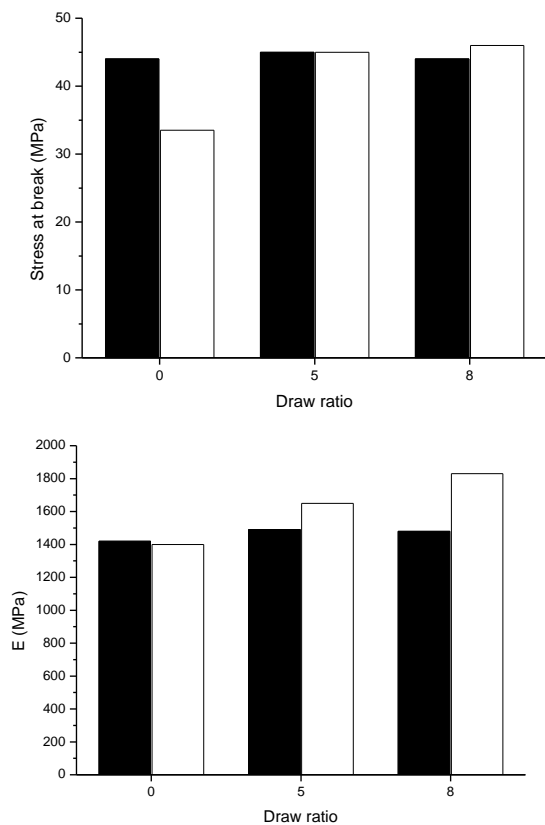


Fig. 1 – Stress at break and stiffness of HDPE/PA6 80/20 system without and with 3% clay (white) in dependence on draw ratio

From Fig. 2, it follows that with the analogous system containing pre-made polyamide nanocomposite containing 1 % C30 and an HDPE matrix with 5% of copolymer ethylene-glycidyl methacrylate (for reactive compatibilisation) the positive effect of NF occurs at a lower draw ratio only. This indicates a more complex effect of the nanoclay on these systems, which may include antagonistic effects.

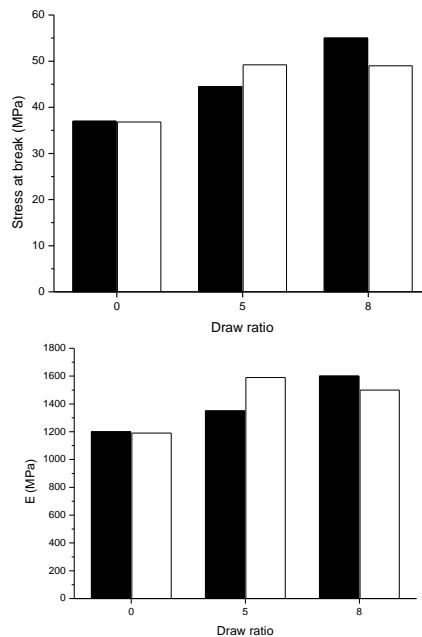


Fig. 2 – Stress at break and stiffness of HDPE/PA6 80/20 with 5% epoxidized HDPE and analogous system with PA6 nanocomposite (white) in dependence on draw ratio

Fig. 3, shows the microfibril structure of the above mentioned samples (Fig. 2). There is a marked effect of the nanoclay on the diameter and length of the microfibrils. The finer microfibrils formed in the case of PA6 nanocomposite result from the structure-directing effect of the clay in the multiphase system, which leads to a finer size of the PA6 domains in the original blend. At the same time, the length of the fibrils formed from the polyamide nanocomposite at a high draw ratio is lower than from neat PA6. The reduced parameters of this system at a high draw ratio (Fig. 2) are undoubtedly a consequence of the clay-affecting the elongational flow of PA6 and its ability to form fibrils. Additionally, the effect of the molecular weight of PA6 and effect of the nanofiller on crystallinity will be discussed.

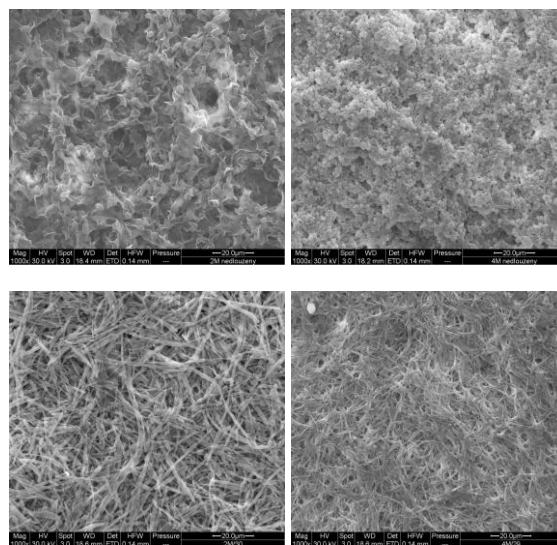


Fig. 3 – Structure of original blends (above) and PA6 microfibrils in HDPE/PA6 80/20 containing 5% epoxidized HDPE and analogous system with PA6 nanocomposite (right), draw ratio

of both samples was 8

4. CONCLUSIONS

The enhanced mechanical behaviour of microfibrillar composites with HDPE matrix suggests that nanofillers may be used to improve polymer-polymer composites. The explanation for the improved mechanical properties is the combination of reinforcement and structure-directing effects of the rigid nanoplatelets, which also affect the formation of polyamide fibrils dur-

ing melt drawing. At the same time, the complex effects of nanofillers must be harmonised to avoid antagonistic effects such as the unfavourable alteration of the rheological parameters of the components.

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