Nanofiller-Modified Microfibrillar Composites: Origin of Complex Effect of Nanoparticles with Different Geometry

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ABSTRACT

Microfibrillar composites (MFCs) are polymer – polymer composites prepared by drawing of suitable polymer blends, where application of various nanofillers have strong potential to eliminate basic disadvantage of MFC arising from limited parameters of polymer components. Due to complexity of NF acting, both synergistic and antagonistic effects may occur. This arises, e.g. from NF-affected interface parameters. This work deals with comparison of the effect of particular, platy and tubular inorganic nanofillers on performance of MFC based on the HDPE matrix with in-situ formed PA6 fibrils. The best results were achieved with organophilized montmorillonite. Tubular halloysite, except of slightly lower mechanical parameters, showed different dependence on the mixing protocols and composition. In the case of nanosized silica spheres, the MFC behaviour exceeded the reinforcing potential of single components, but using functionalized HDPE only. The antagonistic effects reflected in decrease of mechanical properties in spite of drawing and fibril formation, were found using some mixing protocols and compositions for all 3 types of NF, but were most marked in the case of spherical NF. These negative effects arise most probably from affecting of crystallinity of semicrystalline polymer components in the interfacial area by different NF localization and ordering caused, e.g. by different extent and course of NF transfer between the polymer components. The explanation of crucial effect of reduced modulus of the thin (~1μm) interfacial layer due to different fraction of PE spherulites at the surface of the PA6 fibrils is based on the finite element analysis. This original concept represents a tool for explanation of analogous antagonistic effects in multicomponent polymer systems and their rational design.

***Keywords*:** blend, melt drawing, microfibrillar composite, nanofiller, finite element analysis

MFC PREPARATION

Materials: PA6 (Ultramid B5), HDPE (HYA 600 and HYA 800), ethylene-glycidylmethacrylate copolymer (PEGMA), organophilized montmorillonite (MMT - Cloisite 30B), halloysite nanotubes (HNT), hydrophobized nanosilica (NS – Aerosil R 972)

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

Clay addition protocols applied: (a) simultaneously with other components; (b) application of pre-made PA6 nanocomposite (prepared in extruder, temperatures 260, 260, 260, 260, 260, and 265°C); (c) application of HDPE/PEGMA nanocomposite (temperature of all zones 200°C); (d) combinations of (a) and (b), (a) and (c) or (b) and (c). The application of pre-blends is indicated by round brackets. The ratio of HDPE/PEGMA was 95/5 w/w and that of HDPE or HDPE/PEGMA to PA6 80/20 w/w in all systems studied.

The structure of the fibrils was examined using scanning electron microscopy (SEM) with a Vega (Tescan) microscope); the HDPE matrix was removed using a Soxhlet extraction apparatus with boiling xylene for 10 hours.

INTRODUCTION

In the area of polymer nanocomposites, many studies have shown that the comprehensive affecting of polymers by nanofillers (NF) is more marked in multicomponent-matrix systems [1]. In this case, NFs do not only bring combination of reinforcement with replacement of classical

compatibilizers but may induce formation of morphologies associated with synergistic effects [2,3]. Recent results indicate that application of various NF can be beneficial in microfibrillar composites (MFC) produced by melt- or cold-drawing of suitable polymer blends [4,5]. The effect of NF is quite complex; important is also influence on components rheology and thus parameters of fibrils and arrangement of NF in the interfacial area due to its migration between phases in the course of mixing and melt drawing. This work deals with comparison of the effect of spherical, platy and tubular inorganic nanofillers on performance of MFC based on the HDPE matrix with the in-situ formed PA6 fibrils.

Table 1 Effect of nanofiller addition on mechanical properties HDPE/PA6 80/20 blends and related microfibrillar composites

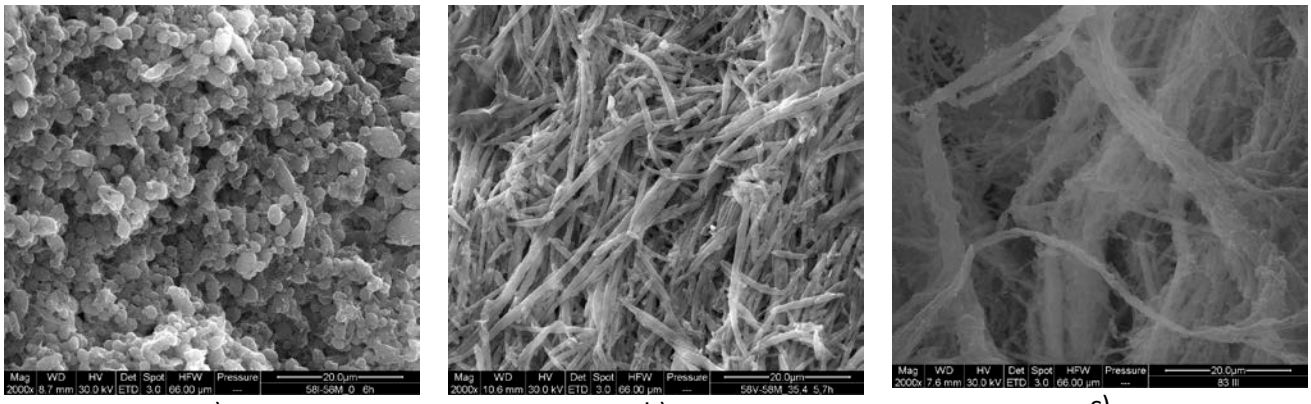
Sample composition	Draw ratio	Max. stress (MPa)	Break strain (%)	E Modulus (MPa)	Toughness ($kJ.m^{-2}$)
HDPE	1	35 ± 1.3	52 ± 9	1120 ± 110	25 ± 2.1
HDPE/PA6	1	44 ± 2.1	5.5 ± 2.6	1400 ± 165	21 ± 2
HDPE/PA6	7	45 ± 2	8.5 ± 1	1520 ± 103	20.5 ± 3.2
HDPE/PA6/3% MMT	7	46 ± 2	7.5 ± 1	1850 ± 105	18 ± 2.6
(HDPEF/3% MMT)/(PA/1% MMT)	8	54 ± 1.8	10.5 ± 0,8	1890 ± 95	45 ± 3
HDPE/(PA6/1% MMT)	7	36 ± 2	11 ± 0,9	1410 ± 75	18 ± 2
HDPE/PA6/2.5% HNT	8	41.5 ± 2	9 ± 0.8	1420 ± 98	-
HDPEF/PA6/2.5% HNT	8	46 ± 2.4	14 ± 0.5	1510 ± 55	-
HDPE/PA6/3% NS	1	47 ± 2	9 ± 0.7	1590 ± 62	-
HDPE/PA6/3% NS	7	38 ± 2.1	10 ± 0.9	1320 ± 70	-
HDPE-F/PA6/3% NS	6	48 ± 2	10 ± 1	1540 ± 105	-

HDPEF - HDPE/PEGMA ratio 95/5 w/w, brackets indicate pre-blended components

RESULTS AND DISCUSSION

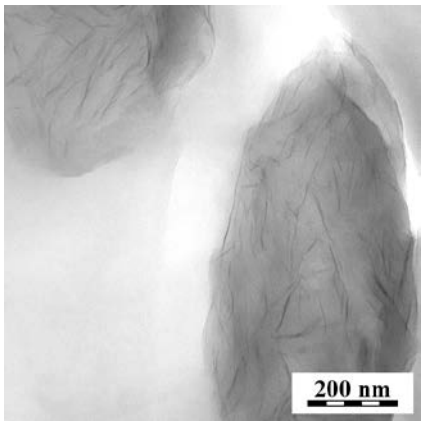
The results in Table show that drawing can lead to expected increase in mechanical parameters, but also to parameters not corresponding to dual reinforcement (by NF and PA6 fibrils) or even lower than those of the undrawn system. The latter effect is most marked for the nanosilica-modifed system having unexpectedly high parameters of the undrawn sample. Similar decrease of stiffness of NF-modified MFC and analogous multicomponent polymer systems was found without plausible explanation in the literature [6].

This different mechanical behaviour of the drawn samples occurs in spite of similar extent of transformation of spherical inclusions to fibers (Fig. 1) reinforced by NF and the predominant NF localization inside PA6 fibers (Fig. 2) or in both polymer components in the case of NS. This final structure is achieved in the case of all mixing protocols applied. The crystallinity of both polymer components, evaluated using DSC and XRD, is practically unchanged as well. At the same time, these results indicate the importance of mixing protocols, optimal composition, and NF geometry. This leads to different extent of clay migration between polymer phases, which may affect final clay localization and ordering in the interfacial area and its parameters. We consider significant importance of low-modulus interfacial layer caused by lower content of PE spherulites on PA6 fibrils surface. This hypothesis was confirmed by the finite element analysis (FEA) based on the model shown in Fig 3. Effect of the number of spherulites (volume fraction) in an 1 μm -thick interlayer on longitunoidal modus was analysed. 12 models (3 different fiber diameters and 4 volume fractions of spherulites) were created, to form a mesh, CPS4R elements were applied. The effect of varied spherulites content at the interface on MFC is demonstrated in Fig 3. This can explain differences in stiffness of the by polymeric fibers reinforced-system with comparable structure and crystallinity, as the contribution of reduced amount of spherulites in the thin interfacial layer has negligible effect on bulk crystallinity.

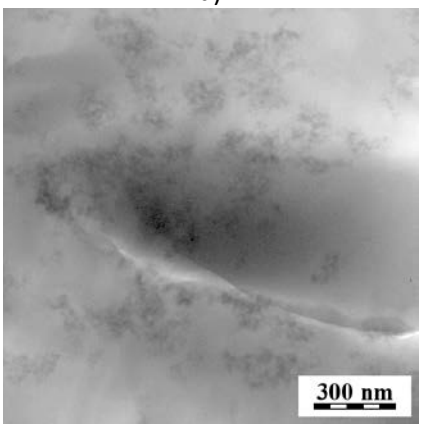


a) b) c)

Figure 1: SEM of a) undrawn and b) drawn HDPE/PA6/MMT 80/20/3 c) drawn HDPE/PA6/NS 80/20/2

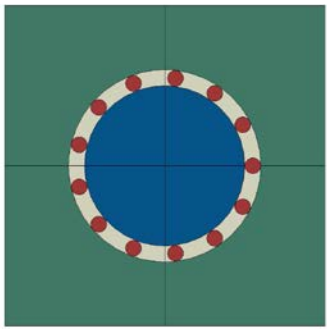


a)

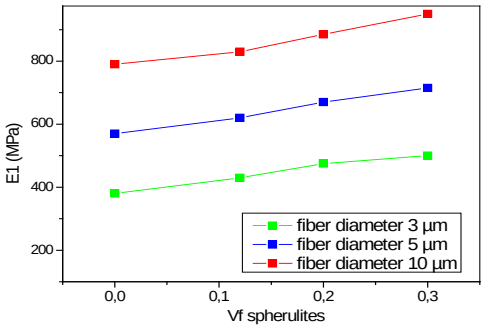


b)

Figure 2: TEM image of drawn a) HDPE/PA6/MMT 80/20/3, b) HDPE/PA6/NS 80/20/2



a)



b)

Figure 3: Proposed FE model (a) and effect of volume fraction of spherulites in the interfacial layer on composite modulus (b)

CONCLUSIONS

Results achieved indicate good potential of NF to upgrade MFC; the best efficiency was found with application of layered silicates. The antagonistic effects caused by drawing are explained using FEA as a consequence of reduced stiffness of the intefacial area. Understanding of the complex effect of NF and the interface parameters on MFC performance is also an important tool for designing of multicomponent-matrix polymer composites with improved balanced parameters.

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