The Influence of Draw Ratio on Morphology and Thermal Properties of MFCs Based on PP and PET

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ABSTRACT: The main goal of this study is to investigate the influence of draw ratio on morphology and properties in microfibrillar composites (MFCs). In situ MFCs based on polypropylene (PP) and poly(ethylene terephthalate) (PET) have been prepared at the weight ratio of 80/20 by twin-screw extrusion, followed by cold drawing and injection moulding. In order to study the differences in MFCs caused by draw ratio, the samples were prepared at different ratios and subjected to extensive characterization in each step of the MFC preparation process. The morphology of MFC and influence of draw ratio were investigated by using Scanning Electron Microscopy (SEM). The thermal decomposition of the polymers in MFCs was studied by Thermogravimetric Analysis (TGA), the melting and crystallization behaviour by Dynamic Scanning Calorimetry (DSC).

Keywords: microfibrillar reinforced composites, cold drawing, draw ratio, morphology, thermal properties

1 INTRODUCTION

Today, composite materials have found their place in numerous applications such as automotive industry, aerospace (Fakirov 2012), biomedicine (Wang et al. 2014), tissue engineering (Huang et al. 2007, Stribeck et al. 2013), food packaging (Shields et al. 2008), recyclability (Kayaisang et al. 2013) etc. Already is known, that blending of two or more polymers has an economical advantage for fabrication of new materials with good properties (Z-M. Li et al. 2002, Shields et al. 2008), but on the other hand a big problem is their immiscibility during processing (Friedrich et al. 2005, Jayanarayanan et al. 2011). Most of studies focusses on improvement of adhesion between two phases which is possible by addition of compatibilizing agents (CA) (Kayaisang et al. 2013).

However, the development of stretching an extruded blend was found as an interesting direction of preventing the immiscibility. Actually, the immiscibility goes in favour for making the micro- and nanofibrillar composites. Last decades, this concept was found as a new approach in the field of polymer-polymer composites (Fakirov 2008).

Microfibrillar composites (MFCs) are made of two polymers with different melting temperatures. The polymer with lower melting temperature plays a role of a matrix, and other polymer with higher melting temperature is a reinforcement component. The manufacturing of MFCs consists of three steps (Fakirov 2008): i) mixing step - melt blending (extrusion), ii) fibrillation step - stretching with orientation of both polymers and iii) isotropization step – thermal treatment at a temperature of lower melting component (injection moulding).

In the present work, we prepared microfibrillar composites based on PP and PET with different draw ratios. The development of morphology was studied in each step of their preparation, as well the thermal properties.

2 EXPERIMENTAL

2.1 *Materials*

The materials used in this study are polypropylene (PP), purchased from Sabic (Sabic 575P) with MFR of 11g/10min (2.16 kg, 230°C), and polyethylene terephthalate (PET) LIGHTER C93 (Equipolymers), a bottle-grade material with an intrinsic viscosity of 0.80 ± 0.02 dL/g. Before processing, PET was dried in a vacuum oven for 24h at 60°C, while PP was used as received.

2.2 *Preparation of MFCs*

Composites were mixed in a weight ratio of 80/20, where PP was used as a matrix and PET as a reinforcement. The melt blending of two polymers was done by twin-screw extruder (Coperion ZSK18), with two co-rotating screws with diameter of 18mm and opening die of 19x2mm. The rotation screw

speed was set at 125 rpm for all samples. The used temperature profile was set: 205°C – 245°C – 250°C – 250°C – 255°C – 255°C – 260°C – 260°C – 260°C. The received extrudate was passing through calander rolls which are cooled with water of ~15ºC and was obtained in the form of sheet with dimensions 25x1.5mm. Further, the cold drawing was done in the oven heated up to 200ºC stretched by a pair of rolls. The samples were obtained at three different draw ratios: DR4, DR8 and DR12.
Afterwards, the injection moulding by BOY22S was done at the temperature profile: 180°C – 190°C – 200°C – 210°C.

2.3 *Characterization*

Scanning Electron Microscopy (SEM) was used to study the morphology of MFCs and influence of draw ratio. The samples were sputtered with gold by a Baltec SCD005 sputter, and micrographs were obtained by FEG SEM JEOL JSM-7600F 202 instrument.

Thermal analysis was performed on a STA449 from Netzsch to study thermal decomposition of samples, and on a Netzsch DSC 204F1 to study the melting and crystallization behaviour.

3 RESULTS

3.1 *Morphology development*

The morphology development is of huge importance for a study about effect of draw ratio on properties (Z-M. Li et al. 2004, Fakirov et al. 2007, Xu et al. 20011, Shields et al. 2011). Figure 1 represents the SEM micrograph of blend PP/PET (80/20) after extrusion step. As can be seen from the observation, the blend shows a typical incompatible morphology with uniform dispersion of spherical PET particles in the PP matrix. The average size of PET particles is found to be 3μm.

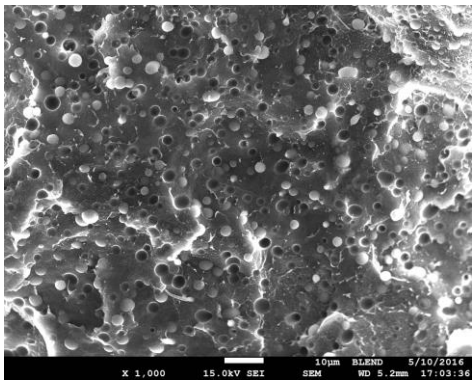

Figure 1. SEM micrograph of freeze-fracture surface under liquid nitrogen of the extruded blend 80PP/20PET.

Obviously, there is no adhesion between the two phases, which indicates a completely immiscible blend (Z-M. Li et al. 2004, Xu et al. 20011). This morphology is very convenient for drawing and making fibres, and later MFCs. The drawn blend is shown in the Figure 2a, and it is clearly indicated that both phases are in oriented state.

Further, the different morphologies were obtained for the samples DR4, DR8 and DR12 (Fig. 2b, c, d). From the images, can be seen the MFCs maintained the morphology made during cold drawing. The PET fibrils are present, more or less in all samples. The diameter of fibrils in samples DR4 and DR8 is found between 0.5-2μm, and they seem long even we could not measure the exact length as the matrix was not removed. Also, it can be seen in Figure 2d in the case of DR12, PET fibrils are stacked together. They are probably coalesced, due to the high shear stress which happens during injection moulding and such a very thin fibrils made by draw ratio 12, are not enough resistant, which causes their deformation and breaking up (Jayanarayanan et al. 2011).

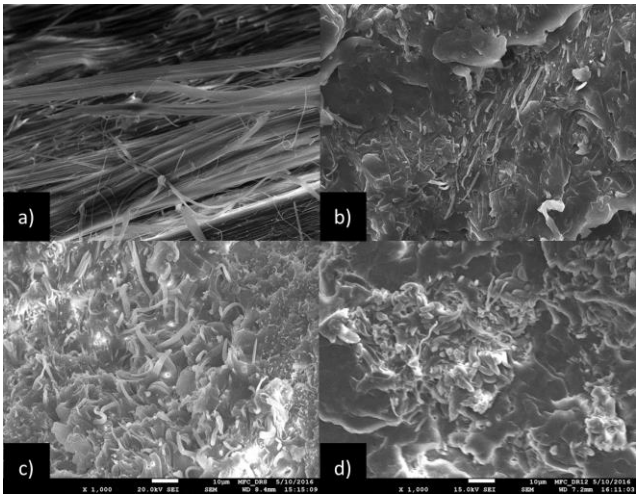

Figure 2. SEM micrograph of freeze-fracture surface under liquid nitrogen of a) drawn blend 80PP/20PET; b) DR4; c) DR8; d) DR12.

3.2 *Thermal decomposition*

To study degradation of samples thermogravimetric analyses (TGA) was used. The focus was on decomposition of MFCs with different draw ratios and effect of PET phase. The tests were done in the temperature range 30 - 600°C and corresponding TGA and dTGA profiles are given in Figures 3a and 3b. All samples have shown one step degradation. Already is known, that PP has a poor thermal stability in comparison with PET. The PP molecular structure consists of the carbon chain with methyl groups attached. Its decomposition starts with scission of C-C bonds, which are relatively easy to break comparing

with the scission of PET ester chain. From graphs can be seen that PP degradation has finished as the earliest (435.9ºC) and almost without any char yield (0.1%), while PET has left the highest amount of residue 14.5%.

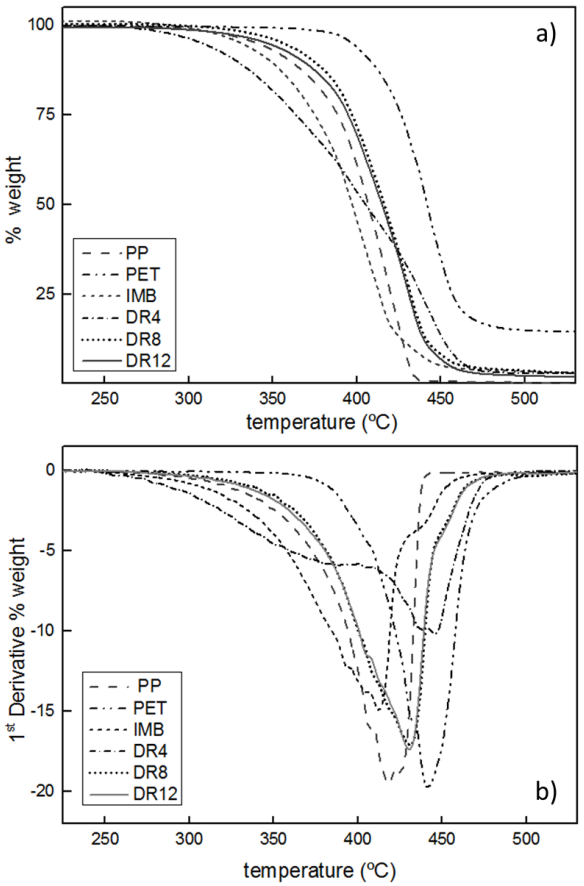

Figure 3. Thermal stability behaviour a) TGA b) dTGA curves of injection moulding PP, PET, IMBs and MFCs

In table 1 the temperatures (T^{onset}, T^{endset}) and char yield at 550ºC are listed of all samples. As, it can be seen, there is a delay in onset of degradation for the samples IMB, DR8 and DR12, while the decomposition of DR4 started a bit earlier, but it lasts longer.

Table 1. Non-isothermal decomposition characteristics of neat PP, PET, IMB and MFCs in nitrogen

Sample	T^{onset}	T^{endset}	Char yield at 550 ºC
	ºC	ºC	%
PP	320.7	435.9	0.1
PET	396.5	490.8	14.5
IMB	330.5	461.8	2.8
DR4	318.1	478.8	3.3
DR8	356.4	466.6	3.1
DR12	352.8	468.4	1.7

In the case of the IMB, it is obvious that PET phase has affected the degradation, as the char residue is 2.8%.

However, MFCs are prone to degrade slower compared with blends, due to the microfibrillar morphology (Jayanarayanan et al. 2011). Comparing the dTGA curves of MFCs with IMB can be noticed the shift of degradation peaks to 440ºC for DR4, 430ºC for DR8 and 430ºC for DR12. DR4 showed an additional shoulder peak at about 365ºC, which could mean a beginning of PP degradation and the main peak at 440ºC the maximum degradation temperature which corresponds to PET. Regardless to its early onset, it has finished at 478.8ºC with the longest degradation time (~19min). Also, the residue was the highest (3.3%) compared with other MFCs, which could be linked to its microstructure. It seems, the fibrils have been preserved and stayed oriented after injection moulding, so their decomposition was harder. Sample DR8 showed the highest temperature onset as can be seen from the graph. Its char yield (3.1%) follows the one of DR4. In both samples are present the microfibrils with high aspect ratio, hence there could be found the explanation for the higher residue. Looking into the degradation profile of DR12, it has left the lowest char yield of 1.7wt%, which is probably due to the breakage of fibrils and their coalescence, as proven by its microstructure (Fig 2d). The microfibrils with the aspect ratio 4 and 8 have the best degradation profile as can be concluded, which corresponds to the earlier studies done by Jayanarayanan et al. (2011).

3.3 *Crystallization behaviour*

The crystallization behaviour of the IMB and MFCs were studied by using Differential Scanning Calorimetry (DSC). It is widely known, under the term of crystallization is implied two different processes: nucleus formation and crystal growth (Xu et al. 2011). Several researchers (Jayanarayanan et al. 2011, Xu et al. 2011) have reported about the importance of morphology control, fibril diameter and aspect ratio on crystallization. PET fibrils can enhance the crystallization temperature of PP.

Table 2 represents the thermal properties of all samples: melting temperatures (T_m^{PP}, T_m^{PET}), crystallization temperature of PP (T_c^{PP}), heat of fusion ΔH_m^{PP} and percentage of crystallinity (χ_c), which was calculated for PP phase based on the theoretical enthalpy for 100% crystalline polymer and taking into account the mass percentage of the respective crystalline phase.

Table 2. Thermal properties of PP, PET, IMB and MFCs after the first heating

Sample	T_m^{PP}	T_m^{PET}	ΔH_m^{PP}	χ_c^{PP}	T_c^{PP}
	ºC	ºC	J/g	%	ºC
PP	171.1	-	73.74	35.6	114.0
PET	-	256.0	-	-	-
IMB	171.8	254.7	37.82	22.8	119.0
DR4	173.1	254.1	49.85	30.1	118.4
DR8	171.8	253.8	50.41	30.4	118.7
DR12	169.7	253.5	55.10	33.3	119.1

Comparing χ_c of PP phase in pure PP and IMB, was noticed that the crystallinity degree in IMB was significantly lower than in pure PP. Probably, due to low adhesion between two phases as they are completely immiscible. For MFCs can be seen the increase in crystallization degree with increasing the draw ratio.

In Figure 4 the DSC thermograms are represented of the PP, IMB and MFCs. It can be noticed that the crystallization temperature of PP phase in the IMB and MFCs was shifted to higher levels ~119°C. Due to the presence of PET phase, PP crystals become imperfect which causes an enhanced crystallization (Mirjalili et al. 2013, Jayanarayanan et al.2011, Zhu et al. 2014).

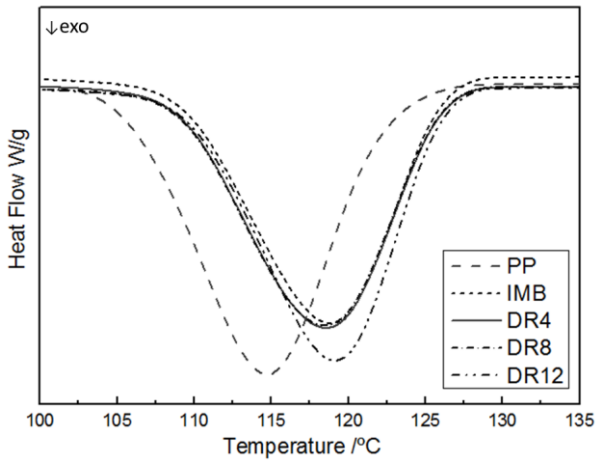

Figure 4. Thermogram of crystallization behaviour of neat PP, IMB and MFCs.

It seems, the PET fibrils could act as strong heterogeneous nucleating agents for PP (Xu et al. 2011). Hence, the increase in draw ratio should have a positive influence on the crystallinity of PP (Jayanarayanan et al. 2011).

4 CONCLUSIONS

The main goal of this study was the influence of draw ratio on morphology and thermal properties of MFCs. We have made successfully the MFCs with different draw ratios by three step processing: extrusion, cold drawing and injection moulding.

Morphology study confirmed the immiscibility of PP and PET in IMB, as well the existence of PET microfibrils in MFCs. It was found that an increased draw ratio leads to a decrease in fibril diameter, but for very high draw ratios such as ratio 12, it was not the case. There is a big possibility for deformation and break up of the thin fibrils, which causes an increase of fibril diameter due to the coalescence effect.

Thermogravimetric analysis showed for all samples one step degradation step. It was confirmed that PET has a much higher thermal stability than PP. As well, the analysis has shown that microfibrils are prone to degrade slower.

Furthermore, we saw that the PET phase has affected the crystallization behaviour of PP phase in PP/PET compositions, especially in the case of MFCs. Due to the presence of PET the crystallization of PP was enhanced. An increase in crystallization degree was found with increase in draw ratio, as thin fibrils act as a nucleating agents for PP. Blending and making MFCs of these two polymers have shown a strong influence of PET phase on thermal properties of PP in blends and composites.

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