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Morphology development and non isothermal crystallization behaviour of drawn blends and microfibrillar composites from PP and PET

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Summary

Microfibrillar composites (MFC) were prepared from the blends of polypropylene (PP) and poly (ethylene terephthalate) (PET) at a fixed weight ratio of 85/15. The blending of the mixture was carried out in a single screw extruder, followed by continuous drawing at a stretch (draw) ratio 5.The stretched blends were converted into MFC by injection moulding. Scanning electron microscopy (SEM) studies showed that the extruded blends were isotropic, but both phases possessed highly oriented fibrils in the stretched blends, which were generated insitu during drawing. The PET fibrils were found to be randomly distributed in the PP matrix after injection moulding. The non isothermal crystallization behaviour of the as extruded blend, stretched blend and MFC was compared. The analysis of the crystallization temperature and time characteristics revealed that the PET fibrils in the stretched blend had a greater nucleating effect for the crystallization of PP than the spherical PET particles in the as extruded blend and short PET fibrils in the MFC.

Keywords

microfibrillar composites; drawing; morphology; crystallization

Introduction

The processing of immiscible polymers in which the dispersed phase forms in situ reinforced fibers is an excellent route to achieve good mechanical properties for the resultant blend. This method was extensively used in the blending of homopolymers with liquid crystalline polymers (LCP s) [1, 2].The highly orientated nature of LCP leads to anisotropic physical property and makes thermotropic LCPs quite attractive as potential in-situ reinforcing materials. However LCPs are costly and cannot be used for many of the applications.

Evstatiev and Fakirov [3] introduced the concept of developing microfibrillar composites (MFC) from polymer blends. There are essentially three steps involved in the preparation of polymer/polymer MFCs, viz: a) blending of the polymers with wide difference in their melting temperatures (T_m) b) drawing or orientation and c) annealing or the isotropization step. In the first step, melt-blending of two or more immiscible thermoplastic polymers take place usually in an extruder. In the second step, the extruded blend is either cold drawn [4, 5] or hot drawn [6, 7] to achieve fibrillar morphology for the constituent polymers. In the third step, the drawn blends are annealed or isotropized which destroys the fibrillar morphology of the polymer with lower T_m.The fibrils of the polymer with higher T_m which are generated insitu are preserved and are randomly distributed in an isotropic matrix of the polymer with lower T_m. The sizes (diameter) of the fibrils generated are in the order of few microns and hence the name microfibrillar composites.

The polyolefinic materials were blended with polyamides and polyesters and were converted into MFCs [8-10]. Another method was employed by Li et al [6, 7] to produce PE/PET MFCs, where the blended extrudate in the form of a strip was stretched while they were still in the hot condition. The tensile strength and modulus increased with an increase in hot stretching ratio and beyond a critical value it reduced. Evstatiev et al [11] suggested a scheme for production of MFCs, which could be scaled up to industrial standards, using LDPE/PET blends. They made use of recycled PET obtained from bottles as reinforcement for LDPE, and thereby suggested the scheme as an efficient method for the recycling of PET.

The ultimate properties of fibre-reinforced composites based on crystallizable thermoplastics are determined by the crystalline morphology of the polymer matrix which in turn depends on the rates of nucleation and crystal growth that define the crystallization kinetics [12, 13]. In semi crystalline thermoplastic matrix composites, the nucleation and growth of a transcrystalline interface around the reinforcing fibre is thought to have a critical influence on the improvement of the stiffness and tensile strength.

In this work the morphology development of PP/PET blends during its conversion into MFCs is studied. We are also analyzing the non isothermal crystallization characteristics of this blend which is significant in understanding the thermal and mechanical behaviour of the resultant composite.

Experimental

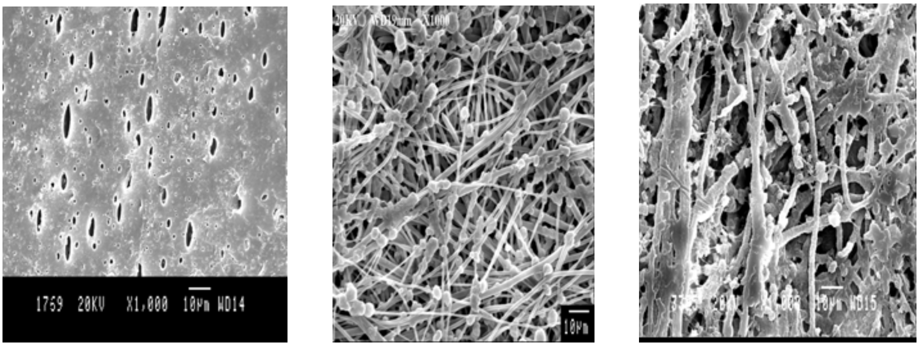
The polymers used were PP (Repol-H110MA, Reliance, India, Melting temperature-167°C, MFI-11.0g/10min) and PET (940400-B, Futura Polymers, India, Melting temperature-246°C, I.V.0.814dl/g). After drying PET for 12 hours at 100ºC it was tumble mixed with PP at a constant weight ratio of 15/85. The mixture was then melt blended in a single screw extruder (Screw diameter-20mm, L/D ratio-30) using a set temperature profile of 225,235,250,255,270ºC from the feed to the die zone and the screw rotating at 30rpm. The extrudate in the form of circular strands of approximate diameter 2mm were taken to a cooling water bath for solidification. Subsequently these strands were taken to a take up device for continuous drawing.

The take up device consists of a pair of nip rolls whose peripheral velocity (V_1) is maintained same as the velocity of the extrudate and a pair of stretch rolls whose speed (V_2) was maintained as $5V_1$. The diameter of the rolls was 50mm provided with variable speed drive. A hot air oven is located between the nip and stretch rolls to raise the temperature of the extruded strands to orientation temperature of 100°C. The diameter of the strands after stretching was in the range of 0.5 to 0.6mm.The stretched blends were injection moulded in a Ferromatik Milacron 50T machine at a set temperature profile of 160,170,190,205ºC, from the feed zone to the nozzle.

A JEOL JSM 840 SEM with an acceleration voltage of 20kV was used for studying the microstructure of the specimens. To extract the PET phase from the specimens, a mixture of phenol/1, 1, 2, 2, tetra chloroethane in 60/40 wt. % was used as the solvent. Similarly to extract PP, the specimens were treated with hot xylene. All specimens were coated with a thin gold layer prior to SEM analysis. DSC measurements of the samples were performed on Mettler Toledo DSC 822^e at a heating and cooling rate of 5°C/min. The samples were heated up to a maximum temperature of 200°C in the first scan, held there for 3 minutes and then allowed to cool to room temperature to record the crystallization behavior.

Results and discussion

As shown in Figure 1a, after extrusion, the blend indicates typical incompatible blend morphology with discrete domains of minor component dispersed in a continuous phase of the major component. The PET phase in the form of spherical and elliptical particles with sectional dimensions varying from 1to 6 µm is found to be distributed in the major phase PP. Large bunches of continuous fibres of PET are observed in the micrograph (Figure 1b) which are generated during drawing. After injection moulding, at a temperature between the T_m of the polymers, PET fibrils loose their orientation and are randomly distributed in the PP matrix (Figure 1c).



(a) (b) (c)

Figure 1. SEM images of a) as extruded blend with PET phase extracted, b) stretched blend with PP phase extracted and c) MFC with PP phase extracted

Based on the above studies a scheme for the morphology development of the blend during drawing and injection moulding is presented in Figure 2.After the melt extrusion at 270°C, the extrudate is cooled and then raised to the orientation temperature of 100°C for continuous drawing. The fibrils of PP and PET are highly oriented at this stage as represented in Figure 2b. In the next step, during injection moulding at 205°C, which is higher than the T_m of PP but lower than that of PET, PP phase melts and forms the isotropic matrix for the composite. The PET microfibrils which are highly oriented prior to injection moulding do not melt at this temperature. However, they loose their orientation to get randomly distributed in the PP matrix as represented in Figure 2c.

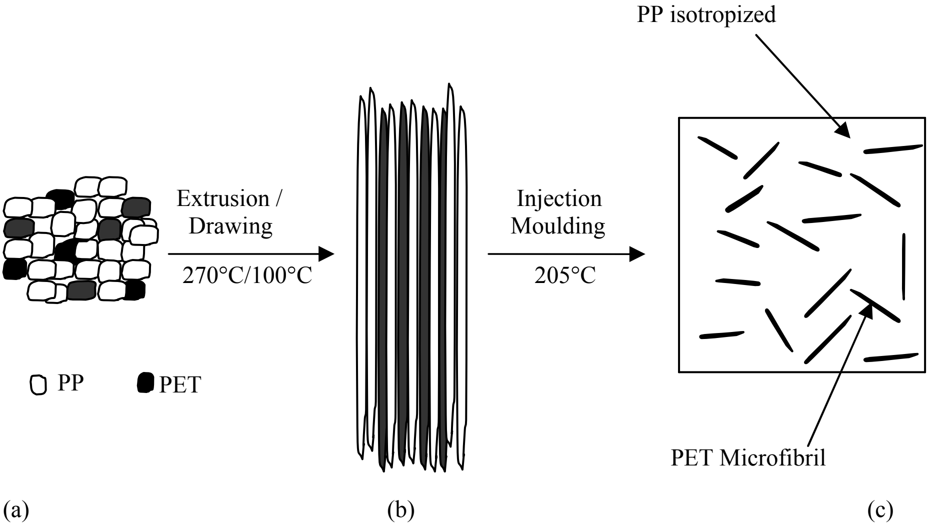


Figure 2. Morphology development scheme of the blend during extrusion and injection moulding

The melting and crystallization behaviour of PP, as extruded blend, stretched blend and MFC was studied. The thermal properties such as, melting temperature (T_m), heat of crystallization (ΔH_f),percentage of crystallinity (X_c), onset and peak crystallization rate temperatures (T_o and T_p, respectively), undercooling temperature (ΔT_c, difference between melting and crystallization temperature), maximum crystallization time (t_{max}, time required to crystallize from T_o to T_p) and half crystallization time ($t_{1/2}$) were obtained from the DSC scans for describing the non-isothermal crystallization behavior of these four samples.

The crystallinity of the PP component was determined using the relationship,

$$Xc = \left(\frac{\Delta H_f \times 100}{\Delta H_f^0 \times w} \right) \qquad (1)$$

The value of $\Delta H_f^{\,0}$ which is the heat of fusion of 100% crystalline PP was taken as 207J/g [14, 15] and w is the mass fraction of PP in the blend/composite.

As shown in Table 1, at a cooling rate of -5°C/min, T_o and T_p are the highest for the stretched blend, while t_{max} and $t_{1/2}$ are the lowest among four materials, and for the as extruded blend, T_o and T_p are higher, t_{max} and $t_{1/2}$ are lower than those for the neat PP. After injection moulding i.e. for the MFC, a slight decrease in T_o and T_p and a slight increase in t_{max} and $t_{1/2}$ in comparison with stretched blend is observed.

Table 1. Thermal properties of PP phase in neat PP, as extruded blend, stretched blend and MFC obtained from DSC studies

Sample	T_o	T_p	T_m	t_{max}	$t_{1/2}$	ΔT_c	X_c
	°C	°C	°C	s	s	°C	%
PP	126.9	114	167.1	152	200	53.1	58.6
Extruded blend	128.3	121.3	168	90	91	46.7	56.1
Stretched blend	129.3	122.7	166.2	77	80	43.6	68.7
MFC	128.5	122	166.1	85	86	44.1	60.2

The value of T_m of PP (Figure 3a) is found to be lower for the stretched blend and MFC which indicates that PP crystals become imperfect in the presence of PET fibrils. Further, X_c is the highest for the stretched blend, followed by MFC. This can be due to the effect of continuous PET fibrils available in the stretched blend causing transcrystallization of PP. The DSC cooling scans (Figure 3b) show sharp crystallization peaks with increased intensity for the stretched blends and MFC. Also, we [16] had reported that these peaks were found to advance to higher temperatures in comparison with neat PP.

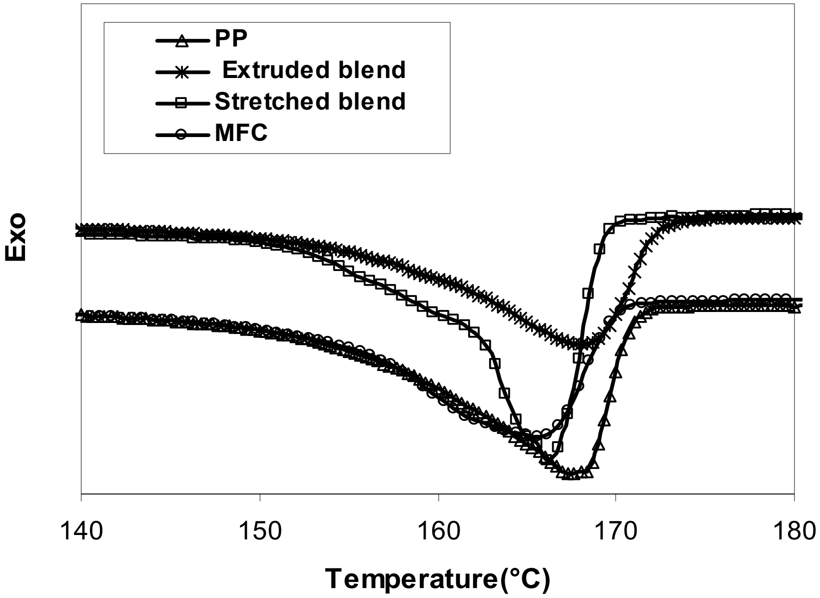
A relation to determine relative crystallinity was used by Wan et al [17], which is modified to obtain percentage relative crystallinity (X_T),

$$X_T = \left(\int_{T_o}^{T} \left(\frac{dH}{dt} \right) dt \Big/ \int_{T_o}^{T_e} \left(\frac{dH}{dt} \right) dt \right) \times 100 \qquad (2)$$

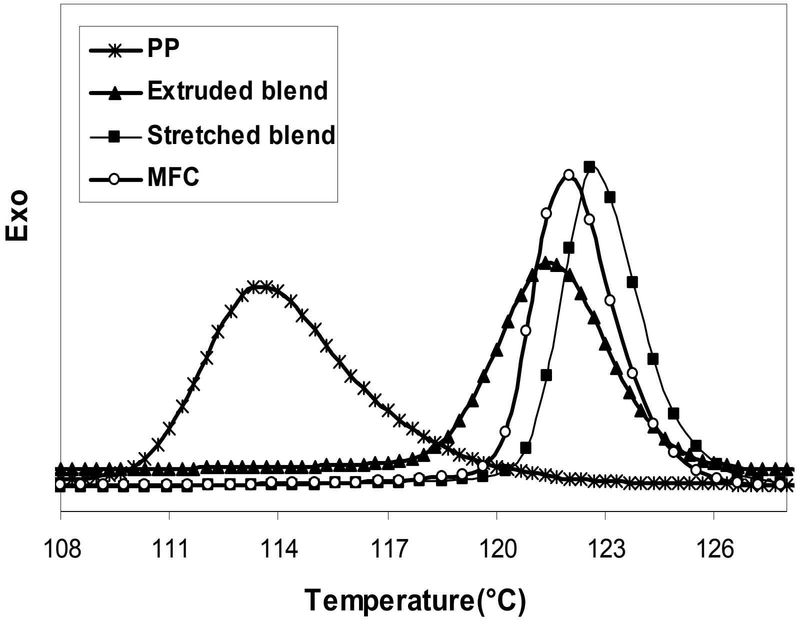
where, T_o and T_e are the onset and end of crystallization temperatures, respectively; dH/dt is the heat-evolution rate.

Figure 4 shows the percentage relative crystallinity, X_T, as a function of temperature for as extruded blend, stretched blend and MFC. At a given temperature in the crystallization range, the relative crystallinity of the stretched blend is the highest followed by MFC and as extruded blend.

Using the expression, $t = (T_o - T) / R$, where, T is the temperature at crystallization time t, and R is the cooling rate, the temperature in the X axis of Figure 4 can be converted into a time scale as shown in Figure 5. For the same crystallization time, stretched blends have the highest percentage relative crystallinity followed by MFC and as extruded blend.



(a)



(b)

Figure 3. DSC thermograms for a) heating of PP, extruded blend, stretched blend and MFC and b) crystallization of PP, extruded blend, stretched blend and MFC

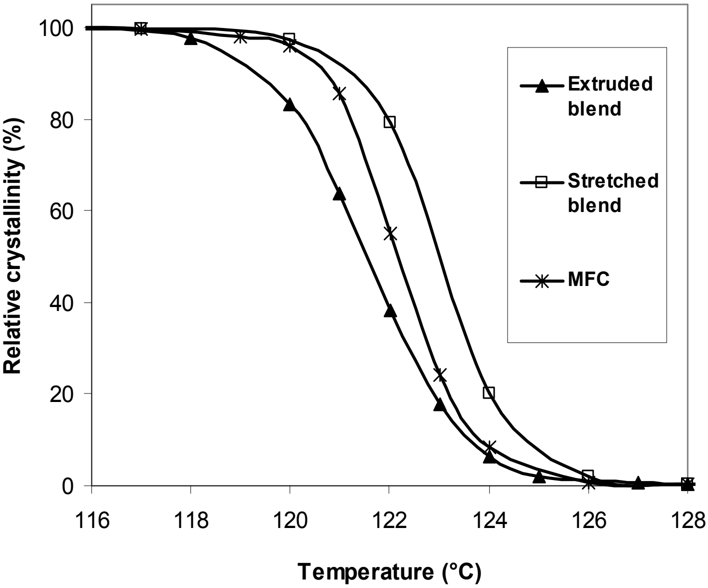


Figure 4. The variation of relative crystallinity of PP with temperature during crystallization for the extruded, stretched blends and MFC

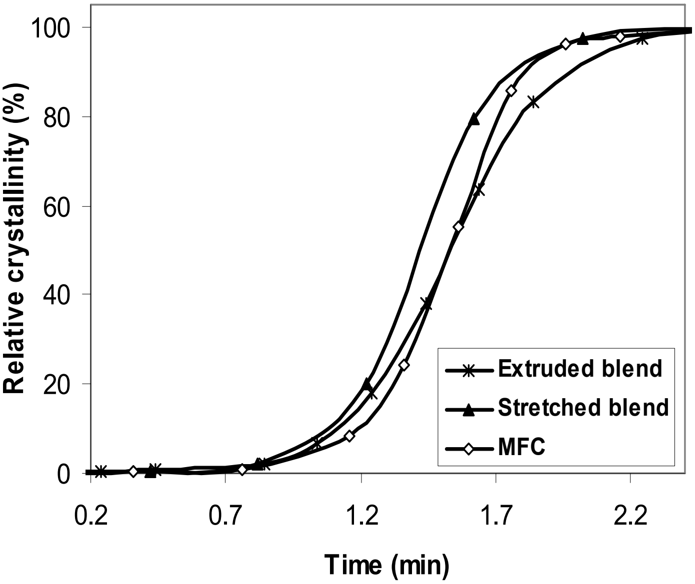


Figure 5. The variation of relative crystallinity of PP with time during crystallization for the extruded, stretched blends and MFC

The effectiveness of stretched blends for crystallization is consistent with an earlier study [17] using hot stretched PE/PET blends. However they did not report the crystallization characteristics of the MFCs. On the basis of the results obtained, it is found that the PP in the stretched blend crystallizes faster than that in MFC.

Conclusion

Microfibrillar composites were prepared by extrusion-stretching-isotropization method from the blends of PP and PET. After drawing (stretching) highly oriented PET fibrils of diameter 1 to 4 μm were obtained. After isotropization between the melting temperatures of the constituent polymers, PET fibrils were found to be distributed randomly in the PP matrix. The fibrillar morphology of the PET phase hastens the crystallization of PP. The long and oriented PET fibrils of the stretched blend have greater heterogeneous nucleating effect for the crystallization of PP than the short PET fibrils in the MFC.

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