

THE EFFECT OF EC ON ORIENTATION AND RELAXATION OF PP OBTAINED VIA DYNAMIC PACKING INJECTION MOLDING*

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Abstract As a long term project aiming at engineering plastics based on polypropylene (PP), in this work, we report the effect of ethylene-cellulose (EC) on the orientation and relaxation of PP obtained via dynamic packing injection molding (DPIM). 2 θ -WAXD results showed that PP with a highly oriented structure and a shish-kebab structure were achieved by DPIM, leading to an increase of tensile strength from 35.0 MPa to 48.6 MPa. The degree of orientation of PP was increased by adding only 1% of EC, resulting in a further increase of tensile strength from 48.6 MPa to 53.8 MPa. Shish was found to exist not only in the oriented layer but also in the core of the sample after adding EC, as evidenced by DSC result. This was understood as due to the overall decrease of viscosity by the addition of EC, thus an increasing of shear rate. Higher shear rate can favor the orientation of molecules and continuous growth of shish structure, resulting in a change of shish distribution along the sample thickness. On the other hand, the relaxation mode of shish in the melt re-crystallization of PP is also greatly affected by the presence of EC. A retarded relaxation of PP macromolecules was seen. Even more, SEM results showed that EC could form the short fibers in PP matrix along the shear flow direction. Compared with the morphology obtained by conventional injection molding, a much better dispersion and easy break-up of EC in PP matrix were observed for samples obtained by dynamic packing injection molding.

Keywords: PP/EC blends; Shear; Orientation; Re-crystallization and relaxation.

INTRODUCTION

Recently, the preparation of super polyolefin blends has been achieved in our laboratory by using dynamic packing injection molding (DPIM)^[1–6]. HDPE/EVA, PP/EPDM, PP/LLDPE, PP/HDPE and PP/PS blends with superior toughness and tensile strength have been obtained. For example, HDPE/EVA blends having high modulus (1.9–2.2 GPa), high tensile strength (100–120 MPa) and high impact strength (6 times as that of pure HDPE) have been prepared by controlling the phase separation, molecular orientation and crystal morphology of the blends. The phase inversion was also found to shift towards lower EVA content under shear stress. Extensive experiments have been carried out on the phase morphology, molecular orientation and peculiar structure of obtained samples to understand the reinforcing mechanism.

Due to the relative ease of orientation and the low viscosity of thermotropic liquid crystal polymers (TLCP), they have been frequently used in polymer blends as a reinforcement agent or processing aid^[7–9]. Under appropriate processing conditions, TLCP could form the fibril structure that serves as a reinforcing agent. Several factors^[10–14], such as the flow field and the type of flow field, the concentration of TLCP and the flow geometry, the processing temperature and so on, could influence the formation of fibril structure in liquid crystal and then finally influence the mechanical properties of the composites. On the other hand, the miscibility between

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liquid crystal and polymer can also affect fibril formation^[15–20]. It has been proved that the preferable compatibilizer could improve the adhesion between the phases and also lead to the formation of fibril morphology, resulting in an improvement of the mechanical properties. However, if the blends were completely compatible, the liquid crystal would form droplets, which were too finely dispersed to deform into fibrils. Furthermore, it was reported that droplets elongation was dependent on the viscosity ratio and droplet size under the condition of a given interfacial tension, matrix viscosity, and shear stress^[21–23]. A matrix viscosity higher than that of liquid crystal is required in order to achieve droplet deformation into fibril shape and smaller viscosity ratio favors droplets deformation and dispersion and thus improves the mechanical properties. The deformation rate must be faster than the relaxation rate or break up rate of the fiber from droplets.

As a long term project aimed at engineering plastics based on polypropylene (PP) via dynamic packing injection molding, in this work, ethylene-cellulose (EC) was added into PP as a modifier due to its liquid crystal property in nature and its processing temperature can match with PP^[24]. A much better dispersion of EC in PP matrix with fibril structure was observed for dynamic packing injection molded samples. On the other hand, a highly oriented PP with improved tensile strength was also obtained by adding liquid crystal EC with low viscosity. With the aid of 2d-WAXS, SEM and DSC, the orientation and re-crystallization behaviors of obtained samples have been investigated.

EXPERIMENTAL

Materials

Polypropylene (PP) and ethylene-cellulose(EC) used in the experiment were commercial products, PP (2401) was purchased from the Yan Shan Petrochemical, China (melt flow rate (MFR) was 2.5 g/10 min); EC was purchased from the Shanghai Refined Chemical Engineering and Science Institute, China, with a viscosity of about 0.04–0.1 Pa • s in 5% solution (ethanol/benzene = 1:4), an ethoxylate content of 46%. The melt temperature of EC from solid state to liquid crystal state is 180°C, and the temperature from liquid crystal state to isotropic liquid state is 215°C.

Samples Preparation

Various binary blends were prepared by varying the EC content (1 wt%, 3 wt%) in PP matrix. Melt blending of a pair of polymers was conducted using twin-screw extruder (TSSJ-25 co-rotating twin-screw extruder). After palletizing process, the blends were molded by dynamic packing injection molding technology which is shown schematically in Fig. 1, and the specimen is shown in Fig. 2. The dynamic packing injection molding technology relies on the application of shear stress fields to melt/solid interfaces during the packing stage by means of hydraulically actuated pistons. The main feature was that after the melt was injected into the mold the melts was forced to move reciprocally in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurred from the mold wall to the molding core part, and thus the samples formed a multi-layer structure including the skin, the shear layer and the core. The schematic representation of the typical multi-layer structure of dynamic samples is shown in Fig. 3. A sample with highly oriented structure was obtained in this way and called the dynamic sample. Which has a melt temperature of 180°C, a dynamic packing pressure of 35 MPa, and a packing frequency of 0.3 Hz, respectively. The detailed introduction and experimental procedure were described in Ref. [5].

Measurement of Mechanical Properties

A Shimadzu AG-10TA Universal Testing Machine was used to measure the tensile strength, at a moving speed of 50 mm/min. The measuring temperature was 20°C. The values of all the mechanical parameters were averaged over six to nine specimens for each composition.

Melt Flow Rate (MFR)

The MFR of pure PP and PP/EC blends was measured by using a XNR-400 Melt Flow Rate instrument, at 210°C, and the weight of poise was 3.375 kg.

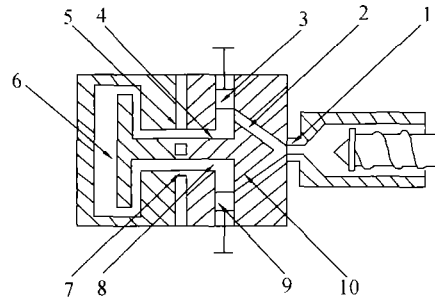


Fig. 1 Schematic representation of dynamic packing injection molding
1) Nozzle; 2) Sprue A; 3) Piston A; 4) Runner A; 5) Connector; 6) Specimen;
7) Connector; 8) Runner B; 9) Piston B; 10) Sprue B

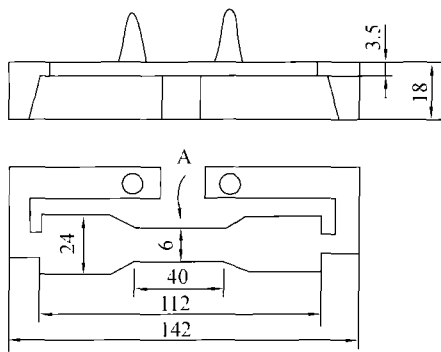


Fig. 2 A sketch of mechanical test specimen dimensions according to ASTM638 M standard

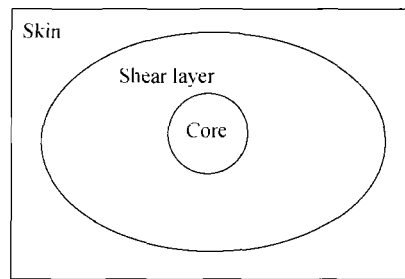


Fig. 3 Schematic diagram of the typical multi-layer structure of dynamic samples

Measurement of WAXD

The 2d-wide-angle X-ray scattering experiments (WAXD) were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromated X-ray from CuK α radiation was 0.154 nm and reflection mode was used. The samples were placed with the orientation (flow direction) perpendicular to the beams. The detector was placed about 15 cm away from the sample holder. The scattering angles were calibrated using a α -alumina NIST standard. All the 2d-WAXD patterns given in this article have been extracted from the background thus a qualitative comparison between the 2d-WAXD patterns became possible. The orientation parameter (S) was calculated as follows:

$$S = \frac{3(\cos^2 \theta) - 1}{2} \quad (1)$$

where

$$\cos^2 \theta = \frac{\int I \cos^2 \theta d \cos \theta}{\int I d \cos \theta} \quad (2)$$

and

$$\cos \theta = \cos \theta_{hkl} \cos \mu \quad (3)$$

In this equations, I is the scattering intensity, θ is the Bragg scattering angle, μ is the Debye angle and θ is the orientation angle of a lattice plane

SEM Observation

The samples were fractured along the shear direction (flow direction) in liquid nitrogen and their phase morphology were observed with a SEM instrument, JSM-5900LV, operating at 20 kV.

DSC Determination

The melting and crystallizing behaviors of the dynamic samples were studied by DSC using Perkin-Elmer DSC pyris-1. The instrument was calibrated using indium as standard. The crystallization behavior was conducted as follows: the samples were quickly heated to a definite temperature (180°C and 200°C) at a speed of 50°C/min, and stayed at this temperature for different period of time and then lowered the temperature at a speed of 20°C/min.

RESULTS AND DISCUSSION

Orientation of PP

As mentioned before, for a dynamic sample, shear induced morphology with a core in the center and an oriented zone surrounding the core was observed through the cross-sectional areas of the sample. One would expect a highly oriented structure in the oriented layer and a less oriented structure in the core. As an example, Fig. 4 shows the 2d-WAXD patterns of different sections of an oriented PP in the direction perpendicular to the shear flow. For pure PP, an intensity distribution observable in the skin section, which has five circles in WAXD patterns associated with different lattice planes of PP and there are some spots on the circle indicating the existence of some orientation of PP. The lattice planes observed are 110, 040, 130, $\bar{1}31$, and 111, from inner to outside circles, respectively. In the section of oriented layer, the circles are weakened and five very sharp dark spots are evident, indicating the presence of a highly oriented structure of PP chain along the shear flow direction. In the core section of the sample, only weak four-point arcs of (110) and two points of (040) lattice plane along the meridian can be observed, suggesting that there are much less oriented structures in the section of oriented layer and the skin. On the other hand, the four-point arcs of (110) at the equatorial plane are due to the orientation of daughter lamellar that epitaxially grew on the kebab structure. One of the interesting results evidenced in 2d-WAXD is the change of orientation of PP through the addition of EC into matrix PP, and this is shown in Fig. 5. One observes a dramatic enhancement of PP orientation by adding only 1 wt% of EC. The intensity of five distinct reflections becomes much stronger for the oriented layer (Fig. 5a) and improved reflection spots in the center core can also be seen (Fig. 5b), indicating that the addition of EC will indeed promote the orientation of PP. The average degree of PP orientation can be calculated from 2d-WAXS result by the equation mentioned in experimental part and a comparison of the degree of orientation between pure PP and PP/EC is listed in Table 1. One observes an increase of orientation parameter from 0.135 to 0.190 in the oriented layer and 0.08 from 0.112 in the core. The enhanced degree of PP orientation can be also evidenced by tensile test and this is listed in Table 2. A slightly increase of tensile strength is observed from 37.8 MPa for conventional injection molding samples to 39.1 MPa by adding 3 wt% of EC. However, an obvious increase of tensile strength is seen from 37.8 MPa to 48.6 MPa for dynamic packing injection molding samples. A further increase of tensile strength from 48.6 to 53.8 MPa is achieved by adding only 1% of EC.

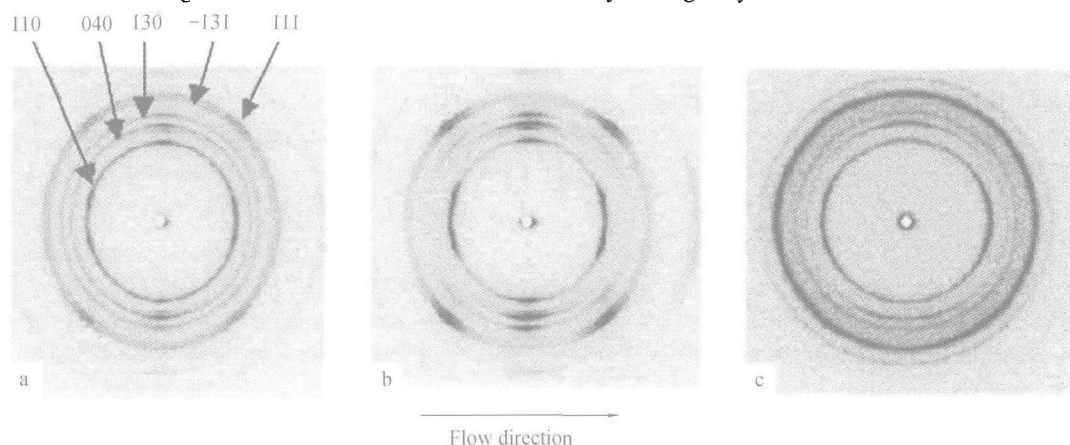


Fig. 4 2D-WAXD patterns of pure PP obtained via shear stress field
a) The skin section; b) The shear layer section; c) The core section

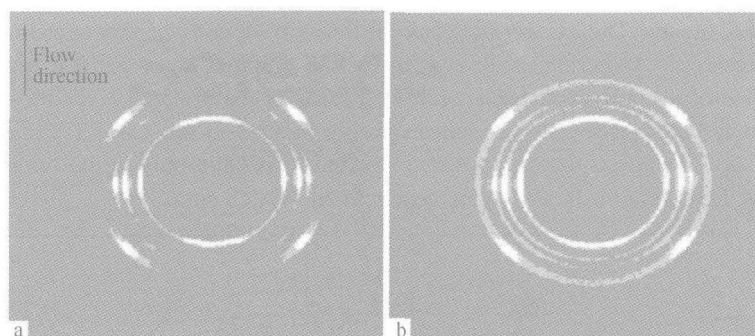


Fig. 5 2D-WAXD patterns of PP/EC blends obtained via shear stress field
a) The oriented layer; b) The core section

Table 1. The orientation parameter of PP and PP/PE blends from the different sections of the dynamic samples

	Skin	Shear layer	Core
PP	0.06	0.136	0.08
PP/EC (1%)	0.08	0.191	0.112
PP/EC (3%)	0.07	0.189	0.125

Table 2. The tensile strength of PP/EC blends obtained via different molding ways

Content of EC (wt%)		0	1	3
Tensile strength (MPa)	Static samples	37.8 ± 0.2	38.7 ± 0.5	39.1 ± 0.3
	Dynamic samples	48.6 ± 0.3	53.8 ± 0.2	51.6 ± 0.5

The orientation of PP was improved by adding certain amount of EC into the blends, which could be ascribed to the improvement of fluidity of PP in the shear stress. The melt flow rate (MFR) could be used to describe the fluidity of the blends. The MFR of pure PP and its blends was shown in Table 3. Obviously, the MFR value was increased when EC was added into the blends, it increased from 3.26 g/10 min for pure PP to 4.1 g/10 min and 5.08 g/10 min for blends which contained 1 wt%EC and 3 wt%EC, respectively. The improvement of fluidity of PP can lead to give more PP molecular oriented in the shear stress, and then improved the degree of orientation of PP as a whole.

Table 3. The MFR of pure PP and PP/EC blends

Samples	Pure PP	Content of EC in PP/EC blends (wt%)		
		1	3	5
MFR (g/10 min)	3.26 ± 0.03	4.1 ± 0.02	4.56 ± 0.02	5.08 ± 0.03

Melt Recrystallization

In order to understand the effect of orientation of PP on its crystallization, melt re-crystallization by DSC was carried out with melting of dynamic samples at 180°C for 2 min, provided that the oriented structure generated in dynamic packing injection molding would be kept unchanged. The exothermic curves of non-isothermal re-crystallization, shown in Fig. 6(a), are recorded for dynamic samples of PP of different sections and the exothermic curves of PP/EC (3wt%) are also included in Fig. 6(b) for comparison. Only one exothermic peak around 110 °C is observed for the skin and the core section of PP, which is understood as due to the crystallization via heterogeneous nucleation. Unexpectedly, for the oriented layer of PP, there exist two exothermic peaks. One is located at around 120°C and the other at around 110°C. These two exothermic peaks are produced by different type of nucleation. The crystallization at higher temperature is self-nucleation resulted from un-relaxed oriented (shish) structure at lower supercooling. This memory effect is caused by the persistence of nuclei in the melt, as expressed by self-seeding^[25, 26]. While that at lower temperature could be attributed to the heterogeneous nucleation at bigger supercooling. The shish-kebab structure of PP had been proved in our previous work^[27]. Interestingly, there is only one peak is observed at the skin and the oriented

layer sections for PP/EC blends. The exothermic peak for the skin section remains unchanged as in the case for PP. However, an increase of exothermic peak is seen for the oriented layer section, indicating an improved orientation. The absence of a lower exothermic peak for PP/EC in the oriented layer section indicates that the crystallization of PP may take place only via self-nucleation process in this case. Two peaks exhibited by the core section at 126°C again suggests that the oriented structure exists not only in the oriented layer section but also in the core section. DSC result is in well agreement with 2d-WAXS data.

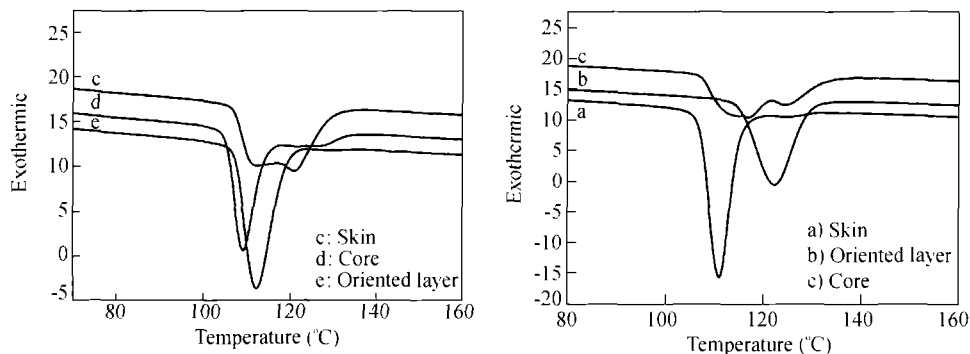


Fig. 6 Exothermic curves of non-isothermal re-crystallization of PP and PP/EC (3 wt%) blends
a) PP; b) PP/EC blends

Relaxation of Oriented PP

It is well known that the lifetime of oriented structure in the melt is dependent on its melt temperature and duration time. More thermodynamically stable oriented/shish structure can survive longer in the melt and thus accelerate nucleation rate^[28]. To identify the thermal stability of oriented structure formed in the virgin samples, annealing experiments at 180°C and various duration times have been devised. Fig 7 is the selective non-isothermal exothermic traces of dynamic packing injection molded PP with a temperature lowering rate of -20°C/min after annealed at 180°C for a certain time. One can observe a gradually shift of the higher exothermic peak to lower temperature as increasing of annealing time. Two peaks merge into one around 110°C after annealing time reaches 10 min, indicating that the oriented structure is destroyed completely and transformed into random coil. However, for PP/EC (Fig. 8), nearly no obvious change of exothermic peak can be observed at different annealing time, even annealed for 20 min, indicating that oriented structure in this sample is more thermally stable. To understand the relaxation of oriented structure of PP/EC in detail, a higher annealing temperature of 200°C was used. Figure 9 is the non-isothermal re-crystallization traces of PP sample after it is annealed at 200°C for a certain time. At this temperature, the oriented structure cannot survive thus the exothermic traces immediately return to 110°C.

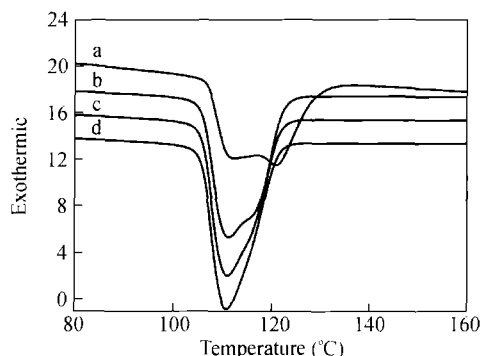


Fig. 7 Selective non-isothermal exothermic traces of dynamic packing injection molded PP at a temperature lowering rate of -20 K/min after annealed at 180°C for a certain time
a) 0 min; b) 5min; c) 10min; d) 20min

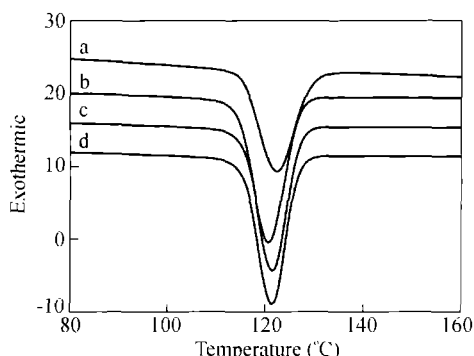


Fig. 8 Selective non-isothermal exothermic traces of dynamic packing injection molded PP/EC (3 wt%) at a temperature lowering rate of -20 K/min after annealed at 180°C for a definite time
a) 0 min; b) 5min; c) 10min; d) 20min

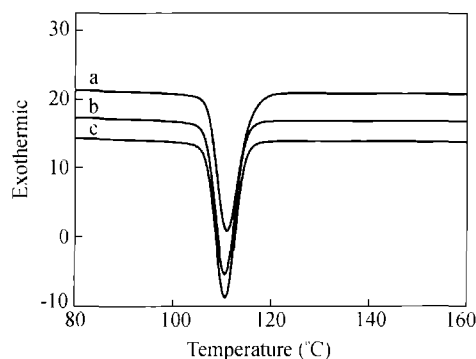


Fig. 9 Non-isothermal re-crystallization traces of dynamic packing injection molded PP/EC after annealed at 200°C for a definite time
a) 0 min; b) 1 min; c) 2 min

It is well known that nucleation is an activated process and crystallization can only proceed when a fluctuation leads to the formation of a nucleus with a size that exceeds a threshold. The probability of forming such a critical nucleus is determined by its excess free energy^[29]. The critical free energy and critical size are proportional to the reciprocal of the supercooling, expressed by $l^* = \frac{4\sigma_e T_m}{\Delta h_f \Delta T}$, where Δh_f is the free enthalpy of

fusion per cm^3 , σ_e is the interfacial free energy and $\Delta T = T_m^0 - T_c$ is supercooling. As the supercooling is increased, the critical free energy required for the formation of nuclei decreases and thus leads to the faster nucleation rate. Therefore, lower supercooling (*i.e.* higher crystallization temperature T_c) corresponds to larger critical size of nuclei. In our work, 2d-WAXS shows an increase of PP orientation by adding EC. Only those oriented structures with larger size can overcome the energy barrier, become stable and induce overgrowth of lamellae on them. In other words, the effect of oriented structure on self-seeding in melt re-crystallization of PP is dependent on the size of oriented structure formed in the virgin samples obtained by dynamic packing injection molding. Therefore, the growth of primary nuclei (shish) is mainly dependent on the shear rate encountered in the virgin samples prepared by dynamic packing injection molding. Since the shear stress τ , keeps unchanged, shear rate is related to the viscosity η of blends, expressed by $\dot{\gamma} = \frac{\tau}{\eta}$. It is clear that shear rate is inversely proportional

to the viscosity. Addition of low viscosity EC will obviously decrease the viscosity of PP, thus a higher shear rate is obtained. Moreover, higher shear rate can also be effective to shift the critical molecular weight to lower value and cause more molecules to orient, resulting in larger number of oriented structures^[30].

Dispersion of EC in PP Matrix

The dispersion of EC in the blends was investigated from the shear layer of dynamic samples by SEM, and the result is shown in Fig. 10. For the static sample (without shear stress), EC is dispersed in PP as short fibers with a diameter of 2–3 micron and a length of 8–10 micron. A much better dispersion of EC is seen with the help of shear stress for dynamic sample. In this case, one can only observe very tiny EC needle with a size of roughly 0.5–1 micron in both diameter and length. SEM result clearly indicates a better dispersion and easy break-up of EC under shear stress. In the flow field, the droplets suspended in the matrix can be deformed to some extent, depending on the competition between shear stress and interfacial stress. The deformation of droplets can be understood from the Taylor^[31] and Cox^[32] models. The deformation of droplet (its aspect ratio and its eventual break up) is controlled by two dimensionless parameters, namely the viscosity ratio of the dispersed phase and the matrix

$$\lambda = \eta_d / \eta_m \quad (4)$$

and the capillary number

$$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma} \quad (5)$$

which represents the ratio between viscous stresses (shear or elongation), $\eta_m \dot{\gamma}$, that tend to deform the droplets and interfacial stresses, and R/σ , that resist to the deformation and tend to restore the initial shape of the drop, R being the drop radius and σ the interfacial tension. The analysis of Taylor and Cox is restricted to the case of small deformations. So the better dispersion of EC in PP matrix in our work can be understood to be due to two reasons. The one is the shear stress provided by dynamic packing injection molding, which is helpful for the dispersion of EC in PP. The other is the orientation tendency of EC under shear stress, due to its liquid crystal property.

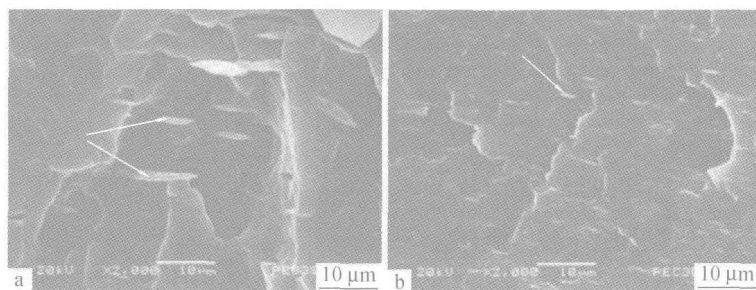


Fig. 10 Dispersion of EC in the blends observed via SEM, the morphology of EC was labeled by arrow (a) from static sample and (b) from shear layer of dynamic sample

CONCLUSION

In this work, the effect of EC on the orientation and relaxation of PP obtained via dynamic packing injection molding was investigated. The enhanced orientation of PP by adding EC was identified by 2d-WAXD and tensile strength results. A change of shish distribution along the sample thickness was also evident by DSC result. This is understood as due to the overall decrease of viscosity by the addition of EC, thus increasing the shear rate. On the other hand, the relaxation mode of shish in the melt during the re-crystallization of PP is also greatly affected by the presence of EC. A retarded relaxation of PP macromolecules was seen, probably due to the increased degree of orientation, leading to a more thermal stable oriented structure. SEM shows a better dispersion and easy break-up of EC in PP matrix under the effect of shear stress.

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