

FIBRE-FORMING OF ETHYL CELLULOSE IN POLYPROPYLENE MELT

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ABSTRACT

Ethyl cellulose (EC), taken as a thermotropic liquid crystalline polymer, was blended with polypropylene (PP), followed by injection molding. Fibre-forming of EC in the PP matrix is analyzed, based on the rheological data, dynamic mechanical analysis and fracture micrographs of EC/PP blends. The addition of maleated PP, for the modification of the interphasial interaction between the PP matrix and the EC fibrils, did not impair the fiber formation substantially.

INTRODUCTION

About ten years ago, Suto, et al.^[1] found that ethyl cellulose (EC) is not only a lyotropic but also a thermotropic liquid crystalline polymer (TLCP) with the help of differential scanning calorimetry, polarized light microscopy and optical retardation variation. However, its thermotropic characteristics depend upon the degree of substitution (DS), molar substitution (MS) and distribution of ethyl groups. Recently, a route to reinforcing thermoplastics has been introduced by which the thermoplastic matrix is reinforced by TLCP fibrils formed in-situ in thermoplastic melt by shear or extension flow^[2-6]. In the present investigation, EC was taken as a thermotropic and melt blended with polypropylene followed by injection molding. Its fiber-forming in the PP melt has been studied through the rheology, morphology and modification of interphasial interaction of EC/PP blends.

EXPERIMENTAL

1. Materials

The EC resin in powder form, obtained from Shanghai First Preparation Factory, exhibits its fluidity and some birefringent structure in the quiescent state above 207 °C. Extruded strands of EC consist of fibrils aligning along the extrusion direction with diameters of 0.5 — 0.6 μm and an isotropic continuous phase. Polypropylene grafted with 0.4% maleic groups by a screw extruder was used as a compatibilizer.

2. Blending and injection molding

The blending of EC/PP was conducted on a single-screw extruder, equipped

with a screw having a diameter of 20 mm and a length to diameter ratio of 25. A screw speed of 90 rpm and a temperature profile of 165 — 185 — 210 — 185 °C (from inlet to die) were taken. Sample bars were injection molded at 205 °C with a 13.5 MPa pressure in an injection molding machine.

3. Rheological measurements

The shear viscosity was measured at 210 °C with an Italian CEAST 6742/060 capillary rheometer. A capillary die with a L/D ratio of 10 and diameter of 1 mm was used.

4. Morphology observation:

Injection molded bars were broken in liquid nitrogen and observed by using a HITACHI S-530 scanning electron microscope.

5. Dynamic mechanical analysis

Dynamic mechanical analysis was carried out on a Multifunctional Internal Friction Apparatus, in principle a torsion pendulum, manufactured by Scientific Instrumentation Factory, Academia Sinica. DMA spectra were recorded at testing frequencies of 1 Hz and 5 Hz at a heating rate of 2 °C/min.

RESULTS AND DISCUSSION

1. Formation of EC fibrils in PP matrix

Figure 1 shows the apparent viscosity of PP and EC/PP blends as a function

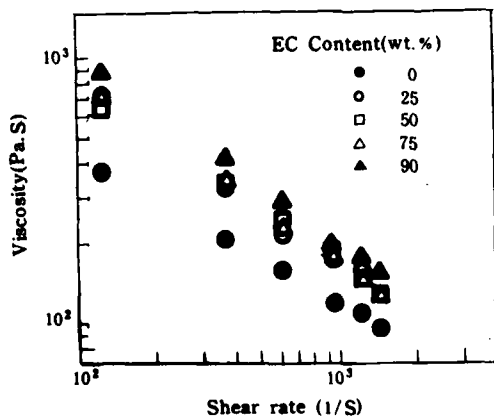


Fig. 1 Apparent viscosity of EC/PP blends as a function of apparent shear rate at 210 °C

of shear rate at 210 °C. It is noticed that the melt of PP and EC/PP blends exhibit non-Newtonian rheological behavior, i.e., the viscosity decreases with increasing shear rate. The viscosity of EC/PP blends increases with increasing EC concentration. It is difficult to get stable rheological data for EC due to the bubbling in EC melt, although it has been dried in vacuum. By supposing the curve of EC/PP 90/10 is close to the curve of pure EC, the viscosity of pure EC is double that of PP at the shear rate of 100 1/S, while the viscosity ratio of EC/PP is about 1.5 at 1000 1/S.

Deformation and breakup of dispersed phase exist in melt processing of polymer blends. Blizzard et al.^[7] established a physical model and defined a dimensionless parameter controlling deformation and breakup of a Newtonian droplet in a matrix:

$$K = \eta_d / \eta_m \quad (1)$$

$$W_e = \eta_m \dot{\gamma} r / \sigma \quad (2)$$

where η_d is the viscosity of the droplet, η_m is the matrix viscosity, $\dot{\gamma}$ is the droplet

radius, $\dot{\gamma}$ is the applied shear rate, and σ is the interfacial tension. For droplet deformation to occur in a Newtonian system, typically $0.01 < K < 2$, where K is the ratio of droplet to medium viscosity, defined above in Eq.1. Similarly, when the Weber number W_e is greater than unity, deformation is expected. The situation is more complicated for a viscoelastic system, and the fracture is easy to occur in shear and elongational flow. Importantly, the effect of the parameter K on the formation of a fibrillar morphology is applicable to non-isothermal cooling process of polymer melts. But when the value of K becomes significantly greater than unity, deformation of the dispersed phase will cease. Based on this model, the fiber-forming of TLCPs in thermoplastics has been discussed.

Figure 2 shows the scanning electron micrographs of fracture surfaces of EC/PP10/90 blends. It is seen that EC droplets have larger deformation in injection molded bar (Fig. 2, a), some of them are elongated into fibrils with diameters of $1\mu\text{m}$ and aspect ratios above 30, and dispersed uniformly in the PP matrix. However, SEM micrographs of fracture surfaces of extruded strands (Fig. 2b) show EC droplets elongated into short rods with diameters of $3 - 6\mu\text{m}$. These results indicate that the deformation of EC in injection molding is stronger than that in extrusion, and the degree of anisotropy of injection molded bars is higher than that of extruded strands. Combined with the viscosity ratio between the dispersed phase and the matrix, the fiber-forming of EC in the PP melt at different shear rates is in accordance with the physical model proposed by Blizard.

The authors consider that the fibrillation of EC with shear flow in the PP matrix is another proof of thermotropic characteristic of EC as a TLCP.



(a)

(b)

Fig. 2 SEM micrographs of fracture surfaces of EC/PP10/90 blends. (a) injection molded bar, (b) extruded strands

2. Effect of the compatibilization

Both EC and PP are crystallizable polymer, but EC is polar, PP nonpolar, so that EC/PP blends are multiphase immiscible systems. For effective stress transferring, strong interfacial interaction between EC fibrils and the PP matrix is needed. In order to investigate the effect of compatibilization on the fiber-forming,

a maleated PP was used as a compatibilizer. The DMA spectra of these blends are shown in Figure 3. Loss peaks of pure PP and pure EC are -2°C and 138°C , respectively, and the difference between two peaks is 140°C . For EC/PP10/90, loss peaks of EC and PP get 18.3°C closer, compared to those of the ingredients. With a maleated polypropylene (g-PP) as a compatibilizer to modify the interaction between EC and PP, the difference between EC and PP loss peaks in EC/g-PP/PP10/9/81 decreases 4.4°C more, compared to that of EC/PP.

Figure 4 shows the SEM micrographs of fractured surfaces of EC/PP and EC/g-PP/PP. It can be seen that EC/g-PP/PP has EC fibrils with diameters of $1\mu\text{m}$ dispersed uniformly in the matrix and having improved adhesion with the matrix. These results show that compatibility between EC and PP has been modified by the addition of a compatibilizer more or less, and this has not impaired the formation of EC fibers in the PP melt. The conclusion may be optimistic that for a multiphase polyblend containing a TLCP it is possible to optimize the processing to form a structure with reinforcing fibrils embedded and to have a strong interphasial interaction for effective stress transferring, at the same time.

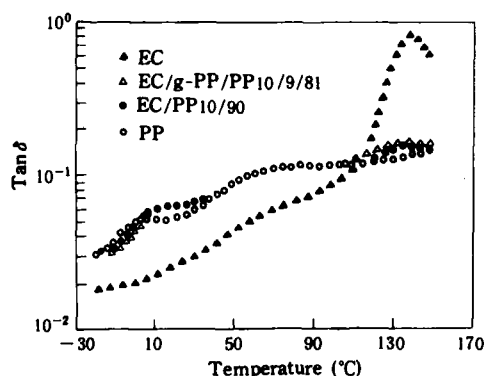


Fig. 3 DMA spectra of EC/PP blends

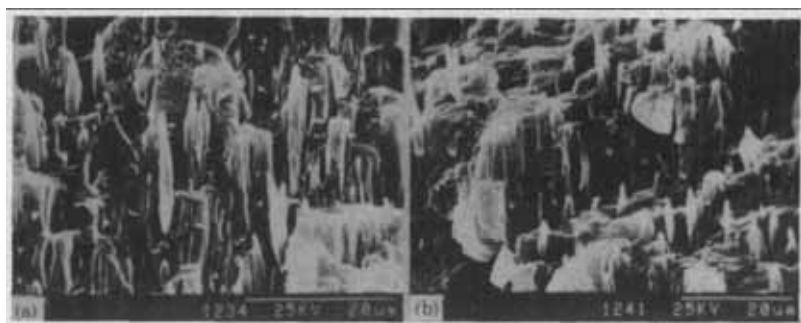


Fig. 4 SEM micrographs of fracture surfaces of EC/PP10/90 (a) and EC/g-PP/PP10/9/81 (b) injection molded bars.

Keywords:

Ethyl cellulose; Fiber-forming; Polyblends of polypropylene

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