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Rheological Study on Polypropylene/Cycloolefin Copolymer Blends

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Summary: Polypropylene, cycloolefin copolymer and their blends were characterized by means of melt flow analysis and capillary rheometry at temperatures between 190 and 230 °C in order to shed more light on COC fiber formation obtained in injection molding process. Melt viscosity and its activation energy as functions of blend composition show negative deviation from the expected additivity (Negative Deviating Blends). The COC/PP viscosity ratio increases with shear rate, but decreases with temperature. High temperature, low viscosity ratio and high shear rate seem to be favorable for fiber formation. Glass transition (from the reversible heat flow curve of modulated DSC) of dumbbell specimens produced by injection molding at 230 °C with COC minor component was 2–4 °C higher than that of grinded pellets obtained from mixing at 190 °C.

Keywords: activation energy; blending; blends; rheology

Introduction

In previous papers[1–4] we have shown that polypropylene/cycloolefin copolymers (PP/COC) blends may assume a rather rare phase structure, where COC forms short "reinforcing" fibers in PP matrix. As injection molding was used for the preparation of test specimens, COC fibers were uniaxially oriented in the direction of injection. Microscopy study[1] using scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) has revealed that the average fiber diameter rose from 0.25 μm for the 90/10 blend up to 2.6 μm for the 60/40 blend. The average aspect ratio of COC fibers was estimated to exceed 20, which was documented by the fact that tensile modulus of the blends obeyed the rule of mixtures valid for fiber composites with high aspect ratio fibers. Interestingly enough, the 50/50 blend was formed by COC cocontinuous phase with PP fibers and PP cocontinuous phase with COC fibers. In the 25/75 blend, PP fibers were embedded in COC matrix. Detailed analysis[2] of nonlinear creep of the PP/COC blends showed that the creep resistance in the fiber direction markedly rose with the COC fraction. A predictive format was developed in order to predict the nonlinear creep for any stress lower than the yield stress. In general, the creep resistance of blends with spontaneously formed fibers was found much higher than creep resistance of the blends with dispersed (discontinuous) components. Examination of tensile properties[3] brought evidence that modulus and yield strength of the blends in the direction of COC fibers much better follow the mixing rules for fiber composites than the predictions provided by the equivalent box models for isotropic blends. Tensile strength passed through a minimum at the fiber volume fraction $v_2 = 0.14$ thus indicating the critical concentration of COC short fibers.

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Annealing of the samples (75 °C for 45 days or 120 °C for 3 hours) did not markedly affect the tensile modulus, yield strength and stress at break. However, the annealing had an adversary effect on strain at break. Impact strength[4] was found to decrease with COC content with a minimum at about $v_2 = 0.15$ of COC and a relative maximum for blend 25/75 PP/COC.

Recent literature[5,6] reports that concentrated polymer blends may have fibrillar or various cocontinuous morphologies. The generated structures are viewed as transient (rather than steady state) occurring at short processing times and variable kinematic conditions. Fiber formation from drop-fibril transition was reported to be favored at higher concentration of the minor phase, at high draw ratio and shear stress in dependence on the relative viscosity ratio.[7–9] Uniaxial elongation of PS-PE blends was found effective to fibril formation even at low concentration[10] On the other hand, the effect of the highly viscous matrix on the droplet break-up of dispersed phase in PP/(PS-PPE) blends prepared in twin screw extruder at relative low shear rate was also reported.[11] We presume that the fiber-like structure of the PP/COC blend was formed and oriented in the process of injection molding. For instance, analogous HDPE/COC blends[12] processed by compression molding showed cocontinous phase structures without any formation of COC fibers.

The objective of this contribution was to analyze the effects of temperature and shear rate on the viscosity ratio of components, which ranks among the factors controlling the formation of fiber-like structures in the course of injection molding. As the formation of the fiber-reinforced blends was rather unexpected and perhaps fortuitous, our *a posteriori* analysis is mainly concentrated on the rheological properties of the parent polymers and of selected fibrous blends. However, we could not fully reconstruct the previous production process because we did not have access to the machinery originally used for preparation of the studied blends.

Experimental Part

Polypropylene Moplen C30G was a product of Basell (Italy): melt flow index MFI (210 °C, 2.16 kg) = 3.8 g/10 min; density: 0.90 g/cm^3; crystallinity: 45%. An amorphous cycloolefin copolymer produced under the trade name Topas 8007 was a product of Ticona, Celanese (Germany), consisting of 30% of bicyclo(2.2.1)hept-2-ene (norbornene) units and 70% of ethylene units: MFI (210 °C, 2.16 kg) = 4.8 g/10 min; density: 1.01 g/cm^3; $T_g = 75$ °C.

A series of PP/COC blends was prepared with 5, 10, 15, 20, 25, 30, 40, 50, 75 weight % of COC, by mixing polymers in a Banbury mixer (chamber 4.3 liters; 164 rpm) at 190 °C for 3.5 min. Dumbell test ISO 527 specimens (170 mm length, 4 mm thickness, gauge width 10 mm) were produced with a Negri-Bossi injection moulding machine (melt temperature 230 °C, barrel temperature 215 °C, mold temperature 50 °C, injection pressure 30 MPa, post-pressure 3 MPa, cycle time 40 s).

Melt flow analysis was performed by means of Melt Flow Index LMI 4000 (Dynisco), according to ASTM D1238–98 with the standard capillary (diameter 2.096 ± 0.005 mm and length 8.000 ± 0.025 mm) at various temperatures (190, 210 and 230 °C), and loads (2.16, 5.0 and 10 Kg). The Melt Volume Rate was measured by Digital Encoder (Kayeness Polymer Test Systems) following Method B of ASTM D1238-98, and the melt density was consequently evaluated as ratio of the Melt Volume Rate and the Melt Flow Rate at 230 °C and 2.16 Kg. Results were expressed as average value of three different measurements.

Steady shearing flow properties of single polymers and selected blends were measured with a Goettfert Capillary Rheometer (Model Rheograph 2001) at three temperatures (190, 210 and 230 °C) in the shear rate interval between 5 and 10000 s^{-1}. The diameter of capillary is D = 1 mm, and the ratio length to diameter is L/D 30 (Rabinowitsch-Weissenberg correction was applied).

Modulated differential scanning calorimetry, MDSC, was performed with about

Table 1.
MDSC data in the COC glass transition zone of pellets after mixing (left) and dumbbell samples after injection moulding (right) as function of blend composition.

PP/COC	glass	transition[a)]	glass	transition[b)]	endo	peak[a,c)]
composition	Tg (°C)	ΔCp (J/gK)	Tg_R (°C)	ΔCp_R (J/gK)	Ta (°C)	ΔHa (J/g)
80/20	73/73	0.08/0.10	78/80	0.02/0.02	75/79	0.34/0.19
75/25	72/71	0.09/0.10	76/79	0.05/0.06	75/75	0.52/0.23
60/40	73/72	0.15/0.13	77/80	0.07/0.08	70/69	0.98/0.72
25/75	73/74	0.25/0.20	78/82	0.11/0.11	70/71	1.78/1.65

[a] measured from the heat flow curve.
[b] measured from the reversible heat flow curve.
[b] measured from the non reversible heat flow curve.

5 mg of selected blend in flushing nitrogen at 100 ml/min in the range 0–100 °C with a heating rate of 2 °C/min, and modulation amplitude of ±0.3 °C and period of 60 s by using a TA2920 calorimeter (TA Instrument). The glass transition temperature, Tg, of COC and the variation of the specific heat at Tg (ΔCp) were measured from both the heat flow and the reversible heat flow curve, whereas the enthalpy (ΔHa) and the temperature (Ta) of the endothermic-aging peak at Tg was evaluated from the non reversible heat flow curve (Table 1).

Rheological Analysis

Preliminary rheological measurements regarding MF analysis of single polymers at various temperature in different load condition are shown in Figure 1. It is evident that the inversion of the viscosity ratio takes place, i.e. COC becomes less viscous than PP at higher temperatures, specifically at 195 °C for 2.16 Kg, and at 220 °C for 5 Kg.

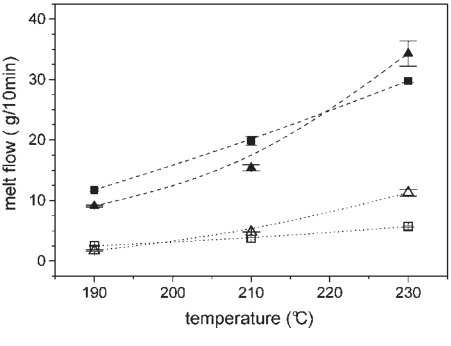

Figure 1.
Melt flow index of PP (□, ■) and COC (△, ▲) at loads of 2.16 Kg (empty symbols) and 5.0 Kg (full symbols) as function of temperature.

These data document that viscosity of COC is more sensitive to temperature than that of PP. For this reason, a simplified rheological evaluation was done by means of melt flow analysis following the approach proposed by Shenoy.[13] Melt flow index (MFI) at different temperatures and loads was used to evaluate the flow activation energy, E_{act}, according to eq. (1)

$$\log \mathrm{MFI} = \mathrm{M} - E_{act}/(2.303 \times R) \times 1/T \qquad (1)$$

where $R = 8.314$ J/(mol K) and M formally represents the log MFI at infinite temperature. Both M and E_{act} depend on the polymer, its molecular weight, and the applied load.

Fitting the experimental data reported in Figure 1 by eq. (1), activation energies of 40 ± 1 and 37 ± 4 kJ/mol for PP, in agreement with literature data,[14] and 97 ± 3 and 52 ± 6 kJ/mol for COC were evaluated for loads of 2.16 and 5.0 Kg, respectively. The higher the load, the higher the shear stress, and the lower the activation energy of the chain mobility in the flow. However, almost negligible variation of the PP activation energy was found in the two loading conditions. On the other hand, high sensitivity of COC to the stress/shear rate ratio can be attributed to pronounced shear thinning due to higher chain rigidity.

Another series of melt flow analyses concentrated on the effect of load for various blend composition (Figure 2). The relative viscosity of neat polymers COC/PP at 230 °C, evaluated as $\eta_{COC}/\eta_{PP} \approx \mathrm{MFI}_{PP}/\mathrm{MFI}_{COC}$, the inverse of MFI, increases with the

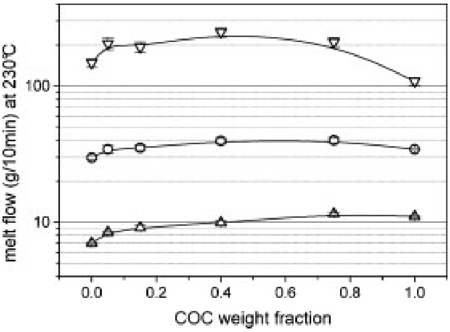

Figure 2.
Melt flow of PP, COC and selected blends at 230 °C at various load: 2.16 (△), 5.0 (○) and 10 (▽) Kg.

applied load, from about 0.6 at 2.16 Kg, to 0.8 at 5 Kg and 1.4 at 10 Kg. Moreover, it is worth to underline that melt flow index of blends in all loading conditions was higher than that of constituent polymers, or in other terms the viscosity of this immiscible blends exhibit a negative deviation from linearity.

The melt density at 230 °C reported in Figure 3 suggests a similar tendency for the COC volume fractions between 0 and 0.55, which evidences higher free volumes and hence higher molecular mobility in the molten blends. From these experimental findings, the sigmoidal curve can be related to the phase inversion, as documented from micrographs in our previous paper.[1]

Previous findings show that the investigation of rheological behavior is crucial at high shear rates For this reason, capillary rheometry of parent polymers and their blends was studied and compared between 190 and 230 °C, i.e. between the temperature of blending and that of injection molding (Figures 4a, b and c). At 190 °C, the melt viscosity of either COC or PP regularly decreased with shear rate, whereas at higher

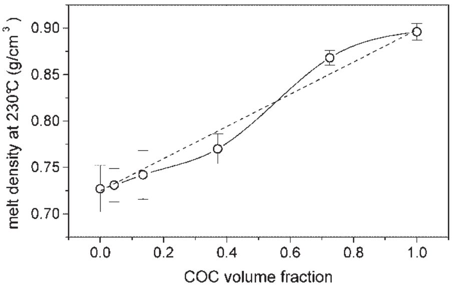

Figure 3.
Melt density of PP, COC and their blends from MF analysis at 230 °C (2.16 Kg).

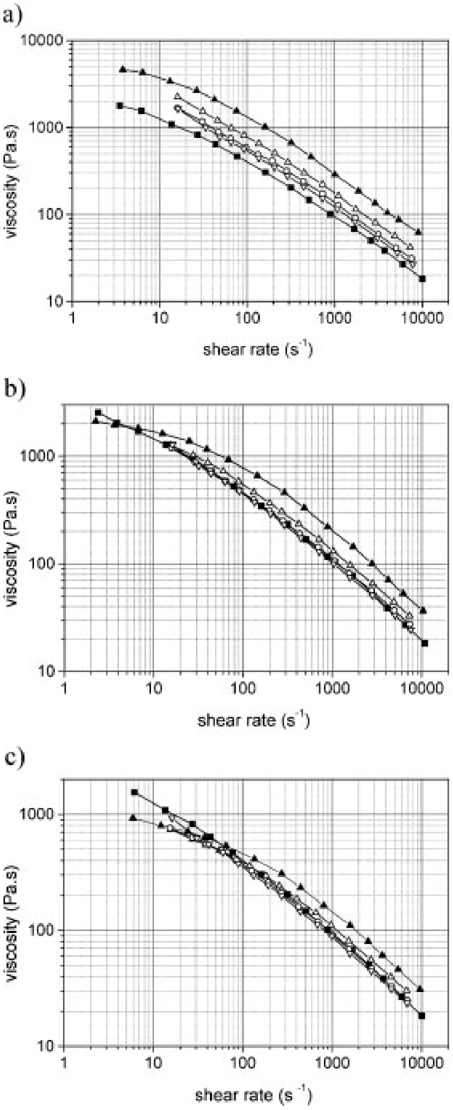

Figure 4.
a). Melt viscosity of 100/0 (■), 75/25 (▽), 50/50 (○), 25/75 (△) and 0/100 (▲) PP/COC blends as function of shear rate at 190 °C. b). Melt viscosity of 100/0 (■), 75/25 (▽), 50/50 (○), 25/75 (△) and 0/100 (▲) PP/COC blends as function of shear rate at 210 °C. c). Melt viscosity of 100/0 (■), 75/25 (▽), 50/50 (○), 25/75 (△) and 0/100 (▲) PP/COC blends as function of shear rate at 230 °C.

temperature a cross-over shear rate at about 5 and 50 s^{-1} at 210 °C and 230 °C can be observed, respectively.

In particular, the viscosity ratio λ (T) of the parent polymer varied with temperature and with shear rate (sr):

$$\lambda(\mathrm{T,sr}) = \eta_d(\mathrm{T,sr})/\eta_m(\mathrm{T,sr}) \qquad (2)$$

where η_d(T) and η_m (T) are the viscosity of the disperse phase and of the matrix respectively.

At 190 °C, the viscosity ratio is almost constant with an average value of λ (190 °C) = 3.1 ± 0.3 in the range 10 and 10000 s^{-1}. At higher temperature, lower viscosity ratio were measured, with η_{COC}/η_{PP} between 0.6 and 1.5 at low shear rate, and almost constant values of about λ (210 °C) = 1.9 ± 0.1 and λ (230 °C) = 1.6 ± 0.1 above 100 s^{-1} and 200 s^{-1}, respectively.

Moreover the melt viscosity of blends at high shear rate showed a negative deviation form log linearity at all considered temperatures, as exemplified in Figure 5 for shear rate of 100 and 1000 s^{-1}. Hence these PP/COC blends can be considered as Negative Deviating Blends (NDB), as proposed by Utracki.[15] The author reported several immiscible blends showing NDB behaviour. Various NDB are constituted of semicrystalline polymer with low glass transition temperature and amorphous glassy polymer, such as polyethylene/polystyrene,[16–17] polypropylene/polystyrene,[16–17] polyoxymethylene/polystyrene,[18] nylon12/polymethylmethacrylate[19] blends, similarly to PP/COC blends reported in the present study. The activation energy of flow can be also evaluated from viscosities of polymers or blends, η, measured by capillary rheometry as a function of temperature for various shear rates, according to the Andrade/Arrhenius equation[13]

$$\log \eta = \mathrm{V} + \mathrm{E_{act}}/(2.303 \times R) \times 1/T \qquad (3)$$

where R = 8.314 J/(mol K) and V formally represents the log of viscosity at infinite temperature. Both V and E_{act} depend on the polymer, its molecular weight, and the shear rate. As previously found in melt flow experiments performed at low shear rate, the activation energy of neat polymer measured by means of capillary rheometry decreases with increasing shear rate. The values of about 30 and 10 kJ/mol were calculated for COC and PP at the highest shear rate respectively, as presented in Figure 6a. Higher stiffness of COC main chains is obviously more sensitive to the effect of shear thinning evidenced by both viscosity and activation energy decreases with shear rate. In any case, higher viscosity of COC suggests a more elastic and "rigid" structure in the molten state that inhibits the droplet break-up and favors the fiber formation in the PP matrix. Moreover, also the activation energy of the blends is lower than that expected from an additivity rule (Figure 6b). In particular the deviation from linearity is almost negligible at low shear rate (20 s^{-1}), but at high shear rates the activation energy of the PP/COC blends showed negative deviations of about 15–30%. This negative deviation observed for the blends seems to be consistent with the evidence of fiber formation that has been favoured by higher mobility and lower activation energy of the blends at high shear rate. Both high melt temperature and shear rate of injection molding favor the fiber formation of the minority component COC in the PP/COC blends. Probably, also the mold temperature of 50 °C allowed the solidification and quiescence of the oriented structure with both PP matrix crystallization and the rubbery-glassy transition of COC fiber.

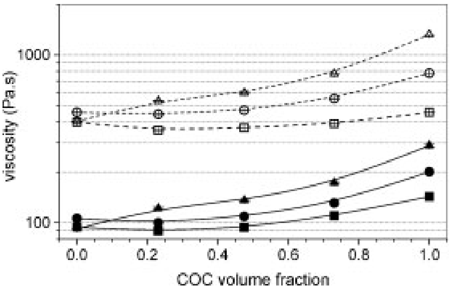

Figure 5.
Melt viscosity of PP/COC blends at temperature of 190 (△, ▲), 210 (○, ●) and 230 °C (□, ■), and shear rate of 100 s^{-1} (empty symbols) and 1000 s^{-1} (full symbols) as function of COC weight fraction.

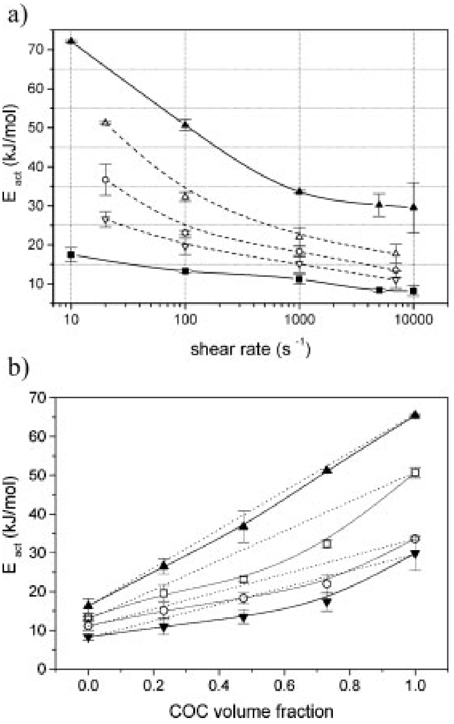

Figure 6.
a). Flow activation energy of 100/0 (■), 75/25 (▽), 50/50 (○), 25/75 (△) and 0/100(▲) PP/COC blends obtained from capillary rheometry at 190, 210 and 230 °C. b). Flow activation energy of as function of COC volume fraction at shear rate of 20 (▲), 100 (□), 1000(○) and 7000 (▼) s^{-1}, respectively. Continuous line represents the interpolation of experimental data, whereas dot line the additivity.

Figure 7 shows the surface fracture of PP/COC 75/25 ($\lambda = 1.6$ at 230 °C) where semicrystalline PP matrix contains some protruded amorphous COC fibers, which exhibited an aspect ratio higher than about 10, and diameter ranging between 0.2 and 1.0 micron.

Thermal Analysis

In order to shed more light on fibril formation, MDSC analysis was performed on selected blends by comparing the COC glass transition signals of both grinded pellets after mixing and injection molded ISO specimens (the samples were cut from the center of dumbbells). Glass transition data derived from the heat flow curve did not exhibit significant difference between the samples of blends after mixing and after injection moulding, except for a larger apparent ΔCp of pellets.

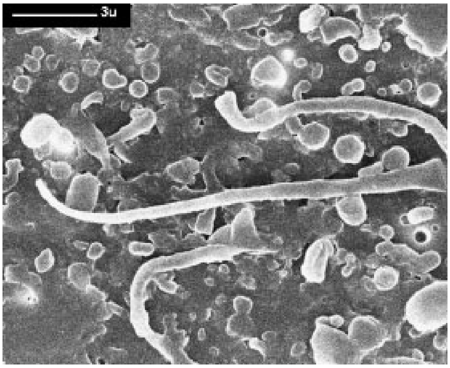

Figure 7.
Scanning electron micrograph of PP/COC 75/25 fracture surface obtained by Cambridge SEM Stereoscan at 20 kV.

On the other hand, the reversible heat flow curve evidenced the glass transition of dumbbell specimens about 2–4 °C above that of pellets, probably as consequence of the thermo-mechanical history in which the polymer orientation seemed to play the main role. Moreover, the endothermic peak observed in the non reversible heat flow curve at Ta, is related to the aging of amorphous phase. The higher the COC content and the longer the aging, the more intense the peak (integral ΔHa).

However, grinded pellets showed a higher enthalpy with respect to injection molded specimens, about two times in the case of 20–25% COC content. In particular the effect of aging appeared almost negligible for these injection molded PP/COC blends, for which the authors previously documented the presence of COC fibers with average diameter lower than 1 micron[1] and their reinforcing effect in the PP matrix.[3] These findings seem to confirm the absence of COC fibres in grinded pellets (obtained at 190 °C and at low shear rate).

Conclusion

The PP/COC blends exhibited a negative deviation from additivity of both the viscosity of blend and of the activation energy of melt. At higher shear rates activation energies of about 30 and 10 kJ/mol of COC and PP were determined, respectively. The higher the shear rate, the higher the relative negative deviation of the melt activation energy of the prepared blends. MDSC analysis evidenced a higher Tg of COC and a lower aging peak at Tg of the PP/COC specimens obtained by injection molding at 230 °C, with respect to grinded pellets obtained by mixing at 190 °C. The formation of COC fibers in PP matrix seemed to be preferentially obtained at 230 °C. This fiber formation from the COC minority component in the PP/COC blends appeared to depend on the specific conditions of injection molding, such as high shear rate, high viscosity ratio at the processing temperature, and a low mold temperature.

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