# Processing-Improved Properties and Morphology of PP/COC Blends

**Taťana Vacková, Miroslav Šlouf, Martina Nevoralová, Ludmila Kaprálková**

*Institute of Macromolecular Chemistry, The Academy of Sciences of the Czech Republic, Heyrovsky, 16206 Prague 6, Czech Republic*

**ABSTRACT:** The aim of this study was to improve mechanical properties of polypropylene/cycloolefin copolymer (PP/COC) blends by processing-induced formation of long COC fibers. According to the available literature, the fibrous morphology in PP/COC blends was observed just once by coincidence. For this reason, we focused our attention on finding processing conditions yielding PP/COC fibrous morphology in a well-defined, reproducible way. A number of PP/COC blends were prepared by both compression molding and injection molding (IM). Neat polymers were characterized by rheological measurements, whereas phase morphology of the resulting PP/COC blends was characterized by means of scanning electron microscopy (SEM). The longest COC fibers were achieved in the injection molded PP/COC blends with compositions 75/25 and 70/30 wt %. Elastic modulus and yield strength of all blends were measured as functions of the blend composition using an Instron tensile tester; statistically significant improvement of the yield strength due to fibrous morphology was proved. Moreover, two different models were applied in the analysis of mechanical properties: (i) the equivalent box model for isotropic blends and (ii) the Halpin-Tsai model for long fiber composites. In all PP/COC blends prepared by IM, the COC fibers were oriented in the processing direction, as documented by SEM micrographs, and acted as a reinforcing component, as evidenced by stress–strain measurements. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1168–1175, 2011

**Key words:** polymer blend; phase morphology; fiber; mechanical properties; predictive models

## INTRODUCTION

Preparation of polymer blends is known as one way of upgrading the performance of existing polymers and much attention has been focused on their properties and phase morphology determined by many factors such as content ratios of the components, their viscoelasticity and the interfacial tension, shear stresses, flow-field, etc.[1–6] However, the basic constituents in most of the blends are immiscible and incompatible. As a result, during processing can be formed a large variety of shapes of the dispersed phase, e.g., spheres or ellipsoids or fibers.[7] The main mechanisms of polymer blend morphology changes are: (i) breakup of particles leading to a decrease in the average particle size and (ii) coalescence of particles leading to an increase in the average particle size. Both particle breakup and coalescence are well-known phenomena and have been widely studied.[6,8]

Despite the fact that the basic mechanisms are known, the control of morphology during the blending in extruders is difficult task due to the complex inside flow-field. If the flow field is simplified to shear flow, it is possible to predict the morphology based on breakups and deformability of the dispersed phase as a function of the viscosity ratio ($\lambda$) of components and the capillary number ($K$),[9] which is defined as the ratio between the viscous force and the interfacial force, where the former tends to break the droplet and the latter tends to keep it spherical. Under certain conditions, given by $\lambda$ and $K$, the dispersed phase may form nonspherical structures, such as fibers with high aspect ratio (i.e., ratio between the length and the diameter of the fibers).[5,9] If the fibrous morphology is formed, the polymer blend may be considered as a polymer composite system reinforced with dispersed fibers. It is known that the rheological behavior of fibers is different from that of the droplet, and it is also reported that the blends with fibrous structure have good mechanical properties.[5,7]

The processing and capabilities of binary immiscible polymer blends with fibrous structure of dispersed polymer seems to be very interesting. Such fibers reinforced composite systems may possess enhanced mechanical properties, e.g., modulus, yield,

*Correspondence to:* T. Vacková (vackova@imc.cas.cz).

or tensile strength. For this reason, it is desirable to anticipate these physical properties of intended blends and their phase structure too.[10,11] Polymer blends are generally considered isotropic heterogeneous materials with three-dimensional spatial continuity of one or more components.[11,12] And obviously important factors contributing to mechanical properties, typically for composite materials, are (i) aspect ratio of fibers and (ii) adhesion between the matrix and the reinforcement.[2–4,7]

Our intention was to prepare PP/COC blends with the fibrous "reinforcing" COC component. In the previous study[1] dealing with the phase structure of PP/COC blends, it was found that in the 90/10, 80/20, and 70/30 blends, the PP matrix contained some fibers of COC, but the impact of processing conditions on the blend morphology was not specified. Considering the above-mentioned study, preliminary experiments and theoretical predictions based on equivalent box model (EBM), we focused our attention on the controlled development of fibrous morphology in PP/COC blends with compositions 75/25 and 70/30 wt %, in which the COC component should have maximal positive impact on mechanical properties. Moreover, we also wanted to compare the experimental results for PP/COC blends with theoretical predictions given by two models: (i) the above-mentioned EBM model, which supposes isotropic, particulate morphology and (ii) Halpin-Tsai model, which is based on anisotropic, fibrous morphology. We expected that the results should approximate to the Halpin-Tsain model, on condition that the fibrous morphology was achieved in the real PP/COC blends.

## MODELS USED

### Equivalent box model for heterogeneous isotropic materials

Physical properties of blends with partially cocontinuous constituents can be calculated by means of a predictive and modified equations rendered by the percolation theory for two-component systems.[12,13] The scheme combines (i) an equivalent box model (EBM) and (ii) the concept of phase continuity that involves the critical volume fractions $v_{1cr}$ and $v_{2cr}$ at which blend constituents become partially continuous.[14] This combination is necessitated by the fact that the EBMs are not self-consistent models.

Application of the model for the prediction of physical properties of blends requires calculation of the volume fractions $v_{ij}$ (in case of two compounds subscripts 1 and 2) and derivation of equations for the properties. The EBM operates with partly parallel (subscript $p$) and partly serial (subscript $s$) couplings of components. This EBM is a two-parameter

model as of four volume fractions $v_{ij}$ only two are independent; its volume fractions are interrelated as follows:

$$v_p = v_{1p} + v_{2p}; \quad v_s = v_{1s} + v_{2s}; \quad v_1 = v_{1p} + v_{1s};$$
$$v_2 = v_{2p} + v_{2s}; \quad v_1 + v_2 = v_p + v_s = 1 \quad (1)$$

$$v_{1p} = [(v_1 - v_{1cr})/(1 - v_{1cr})]^q;$$
$$v_{2p} = [(v_2 - v_{2cr})/(1 - v_{2cr})]^q, \quad (2)$$

where $q$ is the critical exponent. In general, a universal prediction using theoretical values $v_{1cr} = v_{2cr} = 0.156$ and $q_1 = q_2 = 1.8$ should be viewed as a first approximation that we can obtain for any intended blend.[12–14]

The tensile modulus of parallel and series branches of the EBM[12] is following: $E_p = (E_1 v_{1p} + E_2 v_{2p})/v_p$; $E_s = v_s/[(v_{1s}/E_1) + (v_{2s}/E_2)]$. Resulting modulus of two-component system is given by summation of $(E_p v_p + E_s v_s)$:

$$E_b = E_1 v_{1_p} + E_2 v_{2p} + v_s^2/[(v_{1s}/E_1) + (v_{2s}/E_2)] \quad (3)$$

The yield strength in tension $\sigma_{yb}$ of the resulting blend obeys the following equation[12,13]:

$$\sigma_{yb} = \sigma_{y1} v_{1p} + \sigma_{y2} v_{2p} + A\sigma_{y1} v_s, \quad (4)$$

where $\sigma_{y1} < \sigma_{y2}$ characterize the parent polymers and $0 \leq A \leq 1$ the extent of interfacial debonding. Two limiting values of $\sigma_{yb}$, identified with the lower or upper bound, can be distinguished by means of eq. (4): (i) interfacial adhesion is so weak that complete debonding occurs before yielding between the fractions of constituents coupled in series ($A = 0$ at the yield stress); (ii) interfacial adhesion is strong enough to transmit the acting stress between constituents so that no debonding ($A = 1$) appears in the course of yielding.

### Halpin-Tsai model for fibrous structures

Longitudinal tensile modulus of aligned short fibers is routinely calculated by means of the Halpin-Tsai equation[15,16] that is usually expressed in the following form:

$$E_b = E_1(1 + ABv_2)/(1 - Bv_2) \quad (5)$$

where $A = 2L/d$ is given by the ratio of the fiber length $L$ and the fiber diameter $d$; while $B = [(E_2/E_1) - 1]/[(E_2/E_1) + A]$. Similarly enough, the tensile strength $\sigma_{ub}$ of a composite with uniaxially oriented short fibers reads[16]

$$\sigma_{ub} = \sigma_1' v_1 + \sigma_{u2} v_2 \quad (6)$$

where $\sigma_{u2}$ is the tensile strength of fibers, $\sigma_1'$ is the stress attained in the matrix when the strain-at-break of fibers is reached.

## EXPERIMENTAL

### Materials

Polymers used in this study were PP and amorphous COC. PP Moplen C30G was a product of Basell (Ferrara, Italy) [MFI = 6 mL/min (230°C, 2.16 kg); density 0.903 g/cm$^3$; $T_g = -10$°C]. The amorphous COC copolymer produced under the trade name Topas 8007 was a product of Ticona (Celanese, Frankfurt, Germany), consisting of 35% of norbornene and 65% of ethene units [MFI = 1.7 g/10 min (190°C, 2.16 kg); density 1.02 g/cm$^3$; $T_g = 75$°C].

### Blend preparation

Neat polymer materials and a series of PP/COC with 25 and 30 wt % of COC blends were prepared by compression or injection molding (IM). The COC was dried for 3 h at 60°C in vacuum. Polymers were mixed in the W50EHT mixer of a Brabender Plasti-Corder at 230°C and 60 rpm for 10 min. Specimens were molded or extruded.

To obtain plates 100mm × 100mm × 1.7 mm, the melt of blends was stand direct to the chamber of press Fontijne; initial temperature 230°C; pressure 3.1 MPa applied for 2 min; cooling time to room temperature ∼ 20 min. Dumb-bell test specimens were prepared from molded plates according to international standard,[17] which were machined for the measurements of stress–strain dependencies.

The blend extrudates were ground and then injection molded using an Arburg Allrounder 320C IM machine, equipped with an ASTM standard mold. All zones of the IM machine were maintained at the same temperature (temperature of the melt: 230°C; barrel temperature: 215°C; injection pressure: 30 MPa) and the mold was maintained at 40°C. Injected dumb-bell test specimens type 1A for the measurements of stress–strain dependencies were prepared according to standard.[18]

### Rheology

Melt flow studies of the neat polymers were carried out in a rotational rheometer Physica MCR 501 (Anton Paar, Austria) equipped with convection temperature device CTD 450 and parallel plate fixture of 25 mm diameter. The rheological behavior of the neat polymers was studied in the linear viscoelastic region, determinated from the dependence of the storage modulus on the amplitude of deformation. Linear viscoelastic characteristics were deter-

mined during frequency sweep in the frequency range (0.1–100) rad/s at 230°C (above $T_m$ the neat polymers). To ensure a uniform temperature profile, specimens were equilibrated for 10 min.

### Scanning electron microscopy

Scanning electron microscopes (SEM) JSM 6400 (Jeol) and Vega Plus TS 5135 (Tescan) were used for studying the phase morphology. The studied specimens were obtained by cryogenic fracturing in liquid nitrogen. The specimens were covered with platinum by using a vacuum sputter coater Bal-Tec SCD 050 (Balzers) before being examined in the electron microscope.

### Image analysis

In case of fibrous COC minority component formed in the PP matrix, the dimensions were estimated from the image analysis of SEM micrographs. For each system, several hundreds of fibers in SEM micrographs were measured. Therefore, it was possible to determine both the length and the aspect ratio of COC fibers, which were used as input parameters for modeling.

### Stress–strain measurements

An Instron tester, type 5800R, was used to measure tensile mechanical properties of studied blends according to ČSN EN ISO 527 at room temperature. Tensile modulus was determined by using a strain gauge extensometer on ASTM dumbbell-shaped specimens tested up to 0.45% strain at a crosshead speed of 1 mm/min. A speed of 50.0 mm/min was used to determine the ultimate properties. Five specimens were tested for each blend. To evaluate differences between compression molded and injection molded specimens, statistical analysis was performed using a Student's $t$-test for two-tailed distributions with unequal variance.

## RESULTS AND DISCUSSION

### Rheology

The objective of this study was to prepare the PP/COC polymer blends with a specific, fibrous morphology. As the final morphology of a polymer blend critically depends on rheological properties of its components, we preselected and tested three types of PP with high viscosities and one common, commercial type of COC with low viscosity. In such systems, where the matrix exhibits high viscosity and the minority component (COC) has lower viscosity, the probability of forming cocontinuous
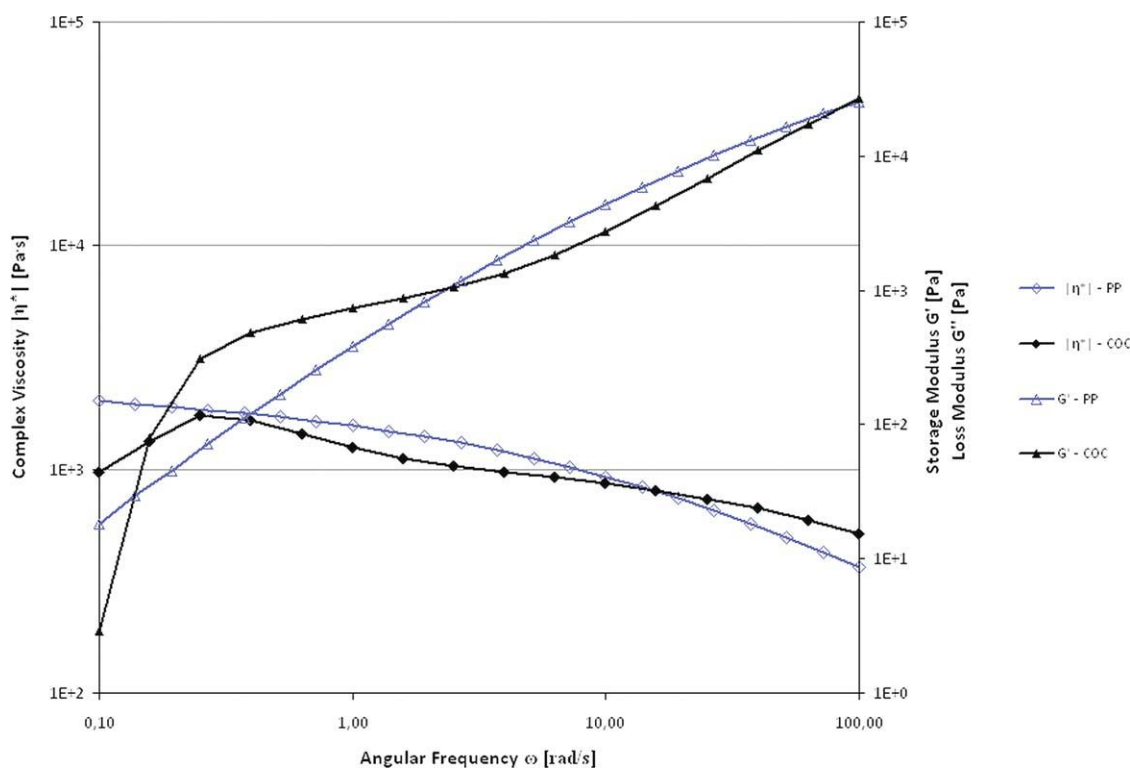
**Figure 1** Dependence of the absolute value of complex viscosity $|\eta^*|$ and storage modulus $G'$ on angular frequency ω. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and/or elongated fibrous morphology increases.[19] The finally selected PP and COC polymers were completely characterized by rheological measurements at processing temperature of blends (Fig. 1). The substantial differences in viscoelastic characteristics reflect the structural properties of used polymers. The curve of COC $|\eta^*|$ plainly rises in the range of low angular frequencies. Our tentative explanation is that COC undergoes to crosslinking during the time needed for stabilization of temperature measurements in the rheometer.

The value of viscosity ratio $\lambda = \eta_D/\eta_M$, as a quotient of dispersed phase and matrix viscosity measured at angular frequency 1 rad/s, is equal to 0.80. According to investigation of the deformability of a Newtonian droplet under shear flow,[20] the situation is usually as follows: (i) for $\lambda < 0.7$ deformations and small drops of the dispersed phase occur, (ii) for $0.7 < \lambda < 3.7$ the drops elongate and form fibers which may break up due to capillary instability mechanism and (iii) $\lambda > 3.7$ it is rarely form fibrous structures since the critical capillary number under shear deformation quickly increases to infinity in this region. This general theory was confirmed in our study, in which the suitable viscosity ratio resulted in the formation of fibrous morphologies for suitable compositions and well-defined processing conditions, as discussed below.

## Morphology

Morphology of both compression molded (CM) and injection molded (IM) PP/COC blends was conveniently visualized on fracture surfaces, prepared in liquid nitrogen. SEM micrograph of CM PP/COC blends [Figs. 2(a,b)] confirmed that this standard processing of the blends resulted in the common particulate morphology with spherical COC particles dispersed in PP matrix. The particles exhibited average diameter ∼ 2.0 μm in case of 75/25 blend composition and ca ∼ 2.2 μm in 70/30 composition.

Fibrous structure of COC phase in IM blends was formed throughout the whole specimen volume along the injection direction. Figure 3(a,b) show SEM micrographs of fracture surfaces of PP/COC blends perpendicular to the injection direction. Diameter of these fibers was ∼ 0.35 μm and slightly increased with increasing amount of the dispersed phase. Fiber lengths were estimated from SEM micrographs showing fracture surfaces parallel with injection direction [Fig. 3(c,d)]. As the fibers emerge, break, and immerge in the matrix, a single fiber is hardly observed along all its length. However, careful examination of SEM micrographs suggests that the length of the fibers is at least 7 μm in the case of 75/25 blends and > 11 μm in 70/30 blends. The aspect ratios range from 20 to 25.
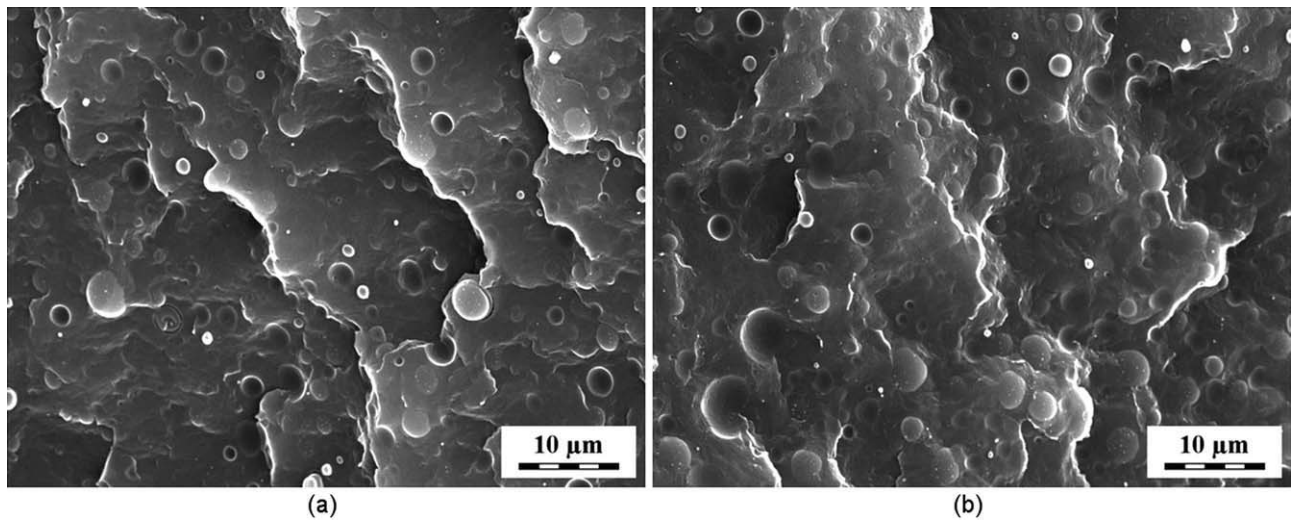
**Figure 2** SEM micrographs showing fracture surfaces of the compression molded PP/COC blends with compositions (a) 75/25 and (b) 70/30.
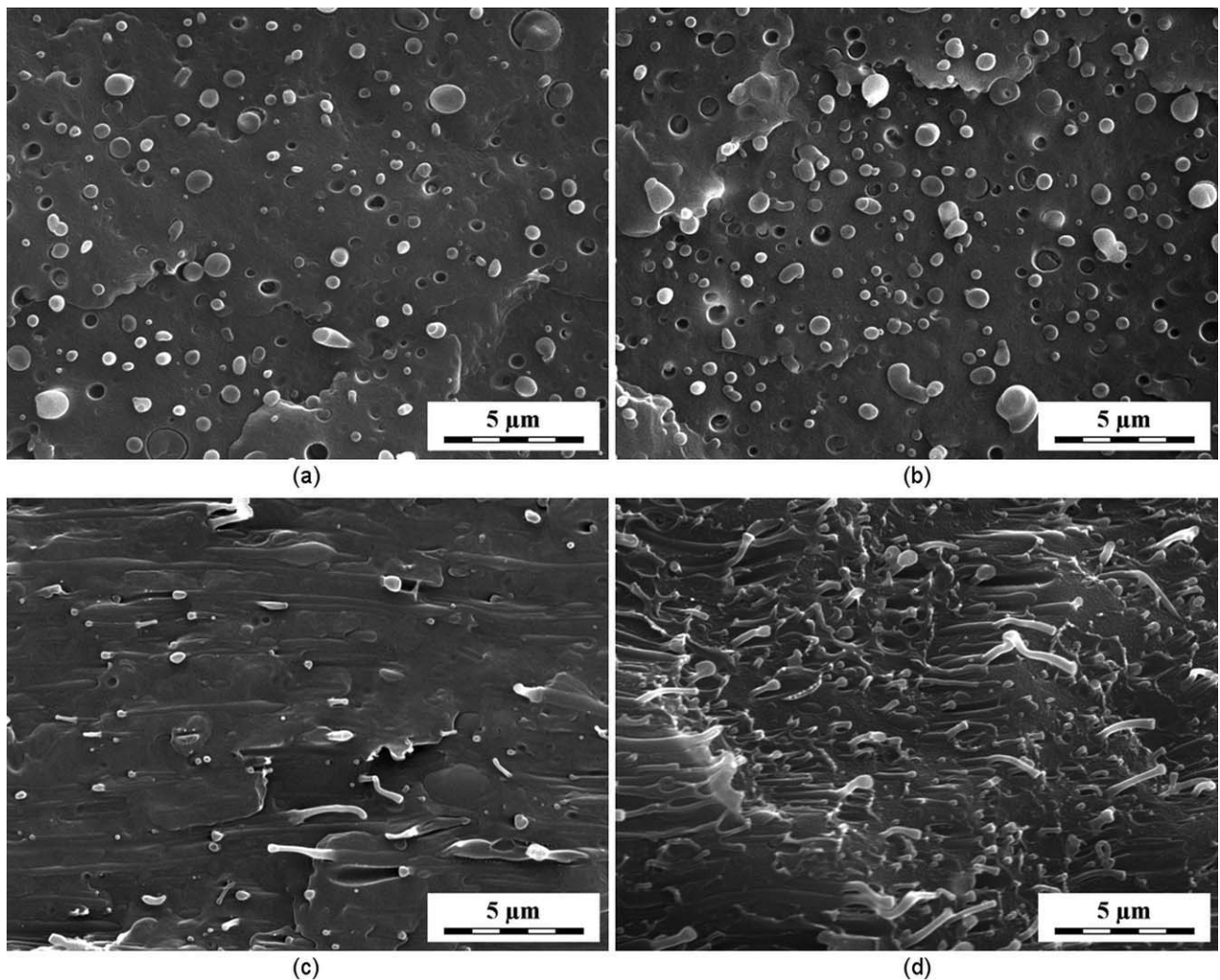


**Figure 3** SEM micrographs showing fracture surfaces of injection molded blends with compositions 75/25 (a,c) and 70/30 (b,d). The fracture surfaces are perpendicular (a,b) and parallel (c,d) to the injection direction.
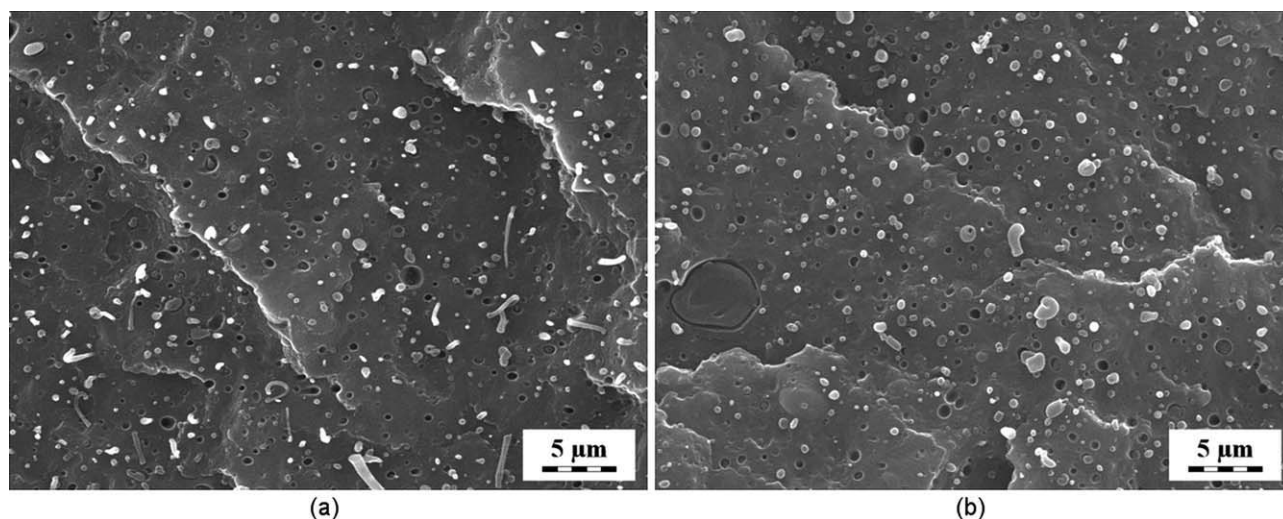
**Figure 4** SEM micrographs showing fracture surfaces of PP/COC blends with compositions (a) 75/25 and (b) 70/30; the fracture surfaces are perpendicular to the injection direction.

In selected SEM micrograph of fracture surfaces perpendicular to injection direction, COC single fibers showed partial pull-out as evidenced by Figure 4. However, major part of COC fibers is broken at the level of fracture surface. This indicated certain interfacial adhesion between PP and COC.

The evolution of polymer blend morphology under the normal extrusion conditions is generally accompanied by two processes. The first one is a reduction in the particle size of the dispersed phase from millimetre to micrometer scale. The second process is connected with particle breakup and coalescence, which are influenced by the viscosity ratio and the capillary number.[5,7] When droplets are subjected to a flow, the stressed medium tends to deform and orient them. If the effect of a hydrodynamic force on drop deformation is larger than that of the interfacial tension, the droplets can form anisotropic microstructures such as ellipsoids or fibrous structure assuming that they do not break up to the droplets during mixing.[5,7,9] Based on this, the polymer blends of different morphology can be developed depending on the viscosities of compounds as was proven.

## Mechanical properties

Moduli ($E$) and yield strengths ($\sigma_y$) of the blends were measured and/or calculated for volume fractions of the PP $v_1 = 0.80, 0.75, 0.70, 0.60$ and of the COC $v_2 = 0.20, 0.25, 0.30, 0.40$. Mechanical properties of the neat PP were: modulus $E_{PP} = 1.48 \pm 0.05$ GPa and yield strength $\sigma_{yPP} = 32.6 \pm 0.3$ MPa. Polymer COC as an embedded reinforcing component has this mechanical properties: $E_{COC} = 2.47 \pm 0.05$ GPa and $\sigma_{yCOC} = 61.7 \pm 1.2$ MPa.

Results from the tensile tests and the calculated values from the predictive models for $E$ and $\sigma_y$ of the blends are depicted in Figure 5. In comparison with the compression molded (CM) blends, the injection molded (IM) blends exhibited an improvement of both studied mechanical properties ($E$, $\sigma_y$) and in the case of $\sigma_y$ the increase was statistically significant. This reconfirms that the properties of polymer blends are strongly related with their morphology. It is worth emphasizing that the improvement occurs solely due to more favorable processing conditions. All measured values as a function of blend composition are close to those calculated from basic characteristics of the parent, neat polymers according to EBM and Halpin-Tsai models, respectively.

The IM blends [Fig. 5(b)] exhibited higher average values of elastic moduli $E$ than CM blends [Fig. 5(a)], although the final values were not statistically significant ($P = 0.19$ and $0.20$ for 75/25 and 70/30 blends, respectively). The low statistical significance resulted mostly from the higher scatter of the experimental data in case of CM blends, which manifested itself as a higher estimated standard deviations [Fig. 5(a)]. This suggested that the preparation by IM is more reliable and reproducible for the studied compositions of PP/COC blends. In both cases, the experimental $E$ values were slightly higher than those calculated from the theoretical models. The fibrous structure of the IM blends was so well formed, that the calculated values from the Halpin-Tsai model [black points in Fig. 5(b)] were close to the linear law of mixtures [dashed line in Fig. 5(b)].

The IM blends [Fig. 5(d)] had higher $\sigma_y$ in comparison with the CM specimens [Fig. 5(c)] and the differences were statistically significant ($P = 3.32 \times$
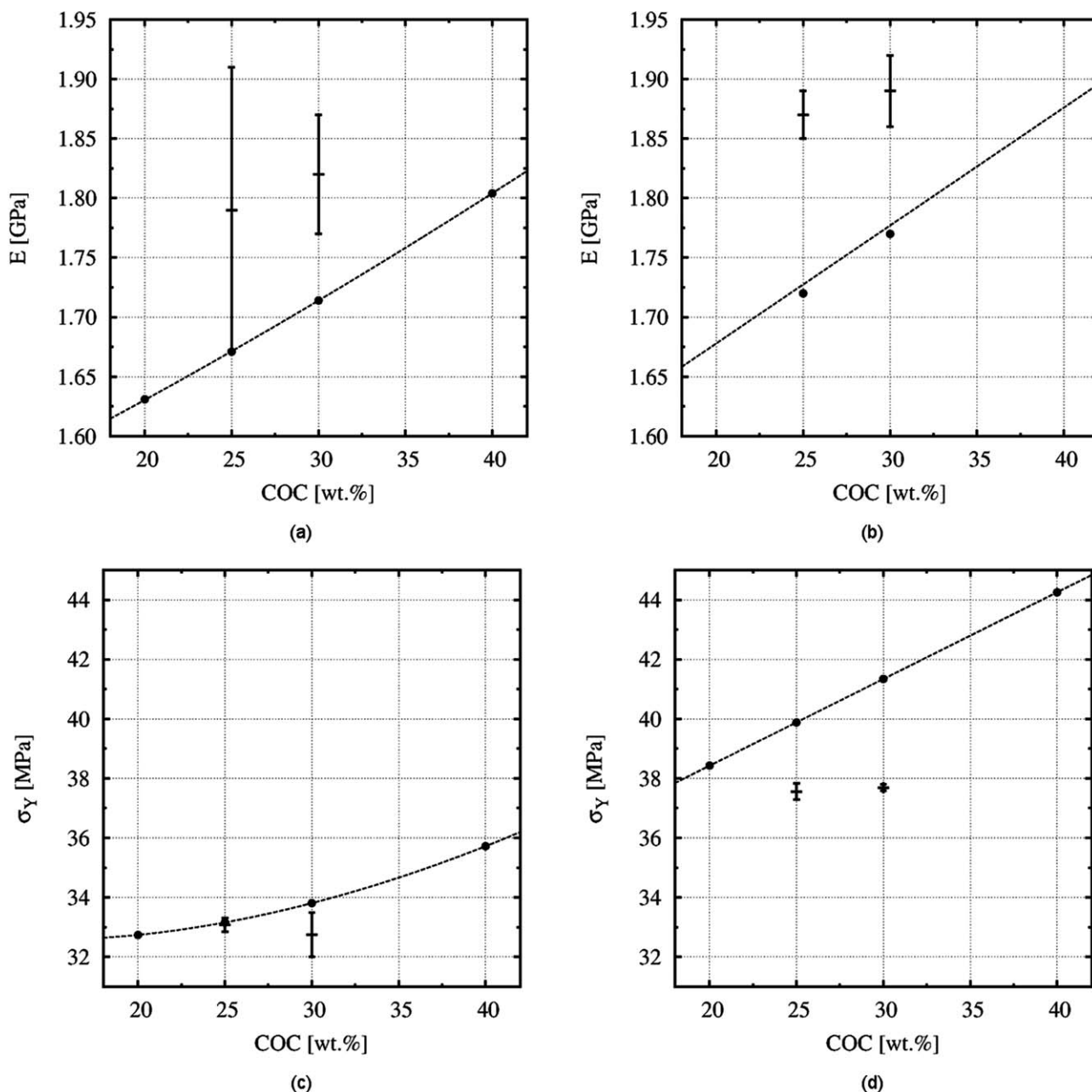
**Figure 5** Comparison of elastic modulus (a,b) and yield stress (c,d) of PP/COC blends. The blends were prepared by compression molding (a,c) and injection molding (b,d). The points with error bars denote experimentally determined values with estimated standard deviations. The dashed lines represent theoretical calculations based on equivalent box model (a,c) and linear rule of mixtures (b,d). The black points show calculated values for selected compositions: 80/20, 75/25, 70/30, and 60/40; in the case of injection molded blends the calculation of black points was based on Halpin-Tsai model, which took into account real aspect ratios of COC fibers obtained from image analysis.

$10^{-9}$ and $1.01 \times 10^{-4}$ for 75/25 and 70/30 blends, respectively). The predicted values of $\sigma_y$ for both CM blends and IM blends were slightly above the experimental values but the overall agreement between theory and experiment was reasonable. It is a strong indication that further improvement of $\sigma_y$ would have been possible with the interface adhesion decreased by a suitable coupling agent. As in the case of elastic modules [Fig. 5(a,b)], the lower estimated standard deviations of $\sigma_y$ [Fig. 5(c,d)] for

the IM blends indicated another advantage of injection molding in these systems—better reproducibility of the results.

## CONCLUSIONS

The aim of this study was to improve mechanical properties of PP/COC blends by processing-induced formation of long COC fibers. Under precisely defined conditions, the fibrous morphology of the

minority component was achieved and the main results can be summarized as follows:

1. Fibrous morphology of PP/COC blends was achieved by means of injection molding (melt temperature 230°C, barrel temperature 210°C, injection pressure 30 MPa) with components of viscosity ratio $\lambda = 0.80$ as documented by rheological measurements.

2. The longest COC fibers were obtained in the PP/COC blends with compositions 75/25 and 70/30 wt % as evidenced by SEM micrograph of fracture surfaces parallel and perpendicular to the injection direction. The control specimens with the same compositions, which were compression molded in a standard way, exhibited common particulate morphology.

3. The fibrous COC morphology of injection-molded blends resulted in statistically significant improvement of the yield strength in comparison with standard, control, compression molded specimens with particulate morphology.

4. Comparison of experimental results with theoretical models showed that the compression molded specimens yielded mechanical properties close to predictions based on equivalent box model,[14] whereas the injection molded specimens displayed mechanical properties closer to Halpin-Tsai model,[16] which reconfirmed the presence of long, reinforcing COC fibers in the blends.

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