Synthesis and Characterization of Polypropylene Reinforced with Cellulose I and II Fibers

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ABSTRACT: Recently, cellulose fiber–thermoplastic composites have played an important role in some applications. Plastics reinforced with cellulose and natural fibers have been widely studied. However, composites with regenerated cellulose have rarely been investigated. In this study, the lyocell fiber of Lenzing AG (cellulose II) and its raw material a bleached hardwood pulp (cellulose I) were used as reinforcement materials. The mechanical and thermal properties of polypropylene (PP) reinforced with pulp and lyocell fibers were characterized and compared with regard to the content of the fiber and the addition of maleated polypropylene (MAPP). PPs with cellulose I or II as a reinforcement material had similar mechanical properties. However, when MAPP was used as coupling agent, the mechanical properties of the composites were different. The crystallinity of the composites were determined by differential scanning calorimetry. Cellulose I (pulp) promoted the crystallization of PP, whereas cellulose II did not. MAPP reduced this effect in cellulose I fibers, but it induced crystallization when cellulose II (lyocell) was used as a reinforcement material. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 364–369, 2006

Key words: extrusion; fibers; mechanical properties; poly(propylene) (PP); polysaccharides

INTRODUCTION

Recently, cellulose fiber–thermoplastic composites have played an important role in some applications, such as the fabrication of automobile interiors and building products, especially windows and door profiles.[1]

Cellulose fibers offer several advantages as reinforcers for thermoplastics that are related to low density, low abrasion, low processing temperatures, biodegradability, no health hazards, and the improvement of some mechanical properties of the composites.[1–6]

Polypropylene (PP) has been used as a matrix polymer for cellulose fibers in composite materials. Because of the poor adhesion between cellulose and PP,[2,4–15] several methods for the modification of cellulose and/or the polymer surface have been studied to improve fiber–matrix adhesion[4,10,11,16,17]; one of these methods is based on the addition of coupling agents that modify the interface between the matrix and the fiber. These coupling agents can react with the fiber and/or the thermoplastic matrix. Maleated polypropylene (MAPP) is commonly used as a coupling agent for cellulose–PP composites.

Plastics reinforced with cellulose and natural fibers have been widely studied. However, plastic composites with regenerated cellulose have rarely been investigated.

Cellulose I and II have the same chemical structure. However, the conformation of the C(6)-hydroxymethyl group differs in each chain. The chains of cellulose II are oriented antiparallel in the unit cell in opposition to the parallel arrangement of cellulose I.[18,19]

Cellulose II is produced by the precipitation of dissolved cellulose I into an aqueous medium; this is the typical process for the technical spinning of man-made cellulose fibers. It is also obtained by repeated mercerization, the swelling of cellulose I in a strong alkali (e.g., NaOH) followed by rinsing and drying.[18–20]

Lyocell, a new kind of regenerated cellulose (cellulose II), is produced from a solution of *N*-methylmorpholine-*N*-oxide/water on an industrial scale.[21,22] The price of lyocell is double the price of pulp.

The main objective of this study was the comparison of the properties of a PP composite reinforced with cellulose I (bleached hardwood pulp) and cellulose II (lyocell). The mechanical and calorimetric properties of the composites and the effects of MAPP as a chemical coupling agent were studied.

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TABLE I
Composite Composition

Composite	PP (wt %)	Pulp (wt %)	Lyocell (wt %)	MAPP (wt %)
1	90	10	0	0
2	80	20	0	0
3	70	30	0	0
4	88	10	0	2
5	76	20	0	4
6	64	30	0	6
7	90	0	10	0
8	80	0	20	0
9	70	0	30	0
10	88	0	10	2
11	76	0	20	4
12	64	0	30	6

EXPERIMENTAL

Materials

Lyocell and bleached pulp (a raw material of lyocell) were supplied by Lenzing AG (Lenzing, Upper Austria).

The used lyocell had 1.3 dtex and a fiber length of 6 mm. The bleached hardwood pulp (type KZO3) with a 0.5-mm fiber length was obtained by a sulfite process and was the raw material of lyocell. The pulp was disintegrated in water for 5 h and was then filtered and dried in an air oven at 60°C overnight.

Before compounding, the fibers (pulp and lyocell) were dried for 24 h at 60°C.

PP matrix was HE125MO supplied by Borealis GmbH (Linz, Austria).

Maleic anhydride and dicumyl peroxide from Fluka (Buchs, Switzerland) were used for the MAPP.

Preparation of MAPP

MAPP was prepared by reactive extrusion in a twin-screw extruder (ZSK 25 P 8.2 E; Werner & Pfleiderer, Stuttgart, Germany). Before extrusion, 1 wt % maleic anhydride and 0.05 wt % dicumyl peroxide were mixed with PP pellets. The temperature profile of the extruder was 185, 185, 180, 180, 175, and 175°C, and the speed was 150 min^{-1}.

Composite preparation

To evaluate the effects of the cellulose contents and MAPP, different composite compositions were compounded in the twin-screw extruder. PP and MAPP were manually mixed and put in the first extruder feeder, and dried pulp was placed in the second feeder. For the lyocell–PP compounding, the fiber was manually fed.

The temperature profile of the extruder was 205, 205, 200, 200, 195, and 195°C, and the speed was 150 min^{-1}.

The composition of the composites is presented in Table I.

Density and void determination

The density and void content (V) were determined according to DIN 53479 procedure A and ASTM D 2742-94 method A. An AG204 delta range balance (Mettler Toledo, Greifensee, Switzerland) was used. Before the test, the specimens were conditioned at least 16 h at 23°C and 50% relative humidity.

Mechanical testing

The specimens for tensile test (ISO 527-2/1B), Charpy impact, and flexural properties (width = 10 ± 0.2 mm, thickness = 4 ± 0.2 mm) were produced in an injection-molding machine (Engel 700/150 HL, Schwertberg, Austria).

The tensile and flexural tests were carried out according to ISO 527 and ISO 178 with a Kinston 4505 universal electromechanical testing machine (Kinston, High Wycombe, UK).

The Charpy impact tests were carried out with a Ceast Resil 25 (Ceast S.p.A., Turin, Italy) pendulum according to ISO 179.

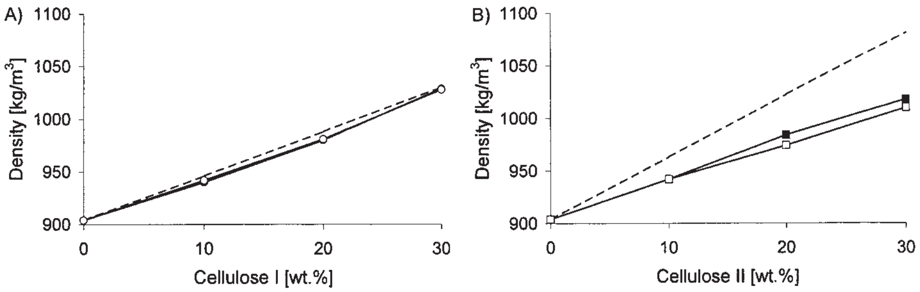

Figure 1 Variation of density as a function of the reinforcement weight concentration: (A) pulp (cellulose I)-reinforced PP (○) with MAPP and (●) without MAPP; (B) lyocell (cellulose II)-reinforced PP (□) with MAPP and (■) without MAPP. Dashed lines represent densities calculated according to eq. (1).

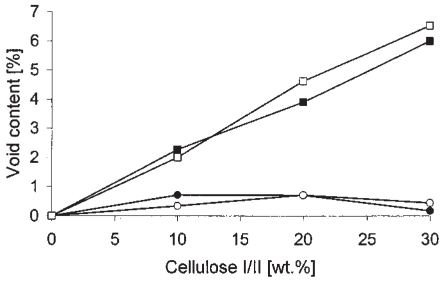

Figure 2 Variation of V in the composites: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

Before the test, the specimens were conditioned at least 16 h at 23°C and 50% relative humidity in accordance with ISO 291.

Calorimetric analysis

A differential scanning calorimeter (DSC-7; PerkinElmer, Boston, MA, USA) was used for calorimetric analysis. Composites samples of approximately 10 mg were heated up to 200°C at 20°C/min, and they were cooled to 30°C at a rate of 20°C/min. This program was repeated twice. At least two measurements for each composite were carried out. The analyses were performed under a nitrogen flow.

RESULTS AND DISCUSSION

The influence of the fiber and MAPP on different properties of the composites is presented. The variations between 0 and 30 wt % pulp and lyocell were analyzed. For the experiments with MAPP as a coupling agent, the weight relation of MAPP to cellulose was constant (1:5).

Density and V

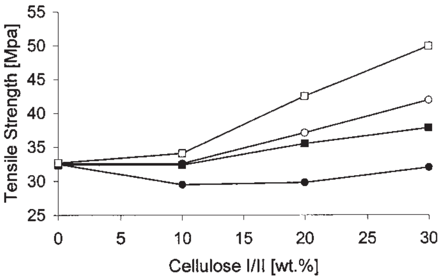

Figure 3 Variation of tensile strength as a function of fiber content: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

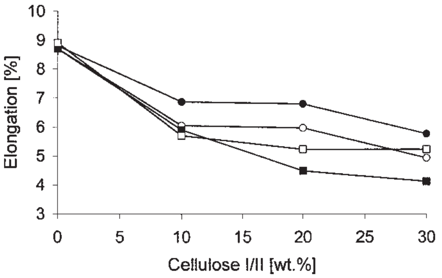

Figure 4 Variation of elongation as a function of fiber content: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

The densities of the composites were measured because voids should have been detected. The measured densities were compared to the calculated ones on the basis of the following relationship:

$$\rho_c = \rho_{PP} \times W_{PP} + \rho_R \times W_R \qquad (1)$$

where ρ_c is the calculated density of the compound (kg/m^3), ρ_{PP} is the density of polypropylene (904 kg/m^3), ρ_R is the density of the reinforcement material (1325 kg/m^3 for pulp and 1496 kg/m^3 for lyocell), w_{PP} is the weight fraction of polypropylene (wt %), and w_R is the weight fraction of the reinforcement material (wt %).

V (%) was obtained according to ASTM D 2734:

$$V = 100 \times \frac{\rho_c - \rho_m}{\rho_c} \qquad (2)$$

where ρ_m is the measured density of the compound (kg/m^3).

The experimental results (Fig. 1) show a linear correlation between the density and reinforcement content of the composites. For PP reinforced with pulp fiber, ρ_m with and without MAPP showed almost no difference. The experimental values agreed with ρ_c, as shown in Figure 1(A). On the other hand, according to Figure 1(B), the density of the lyocell-reinforced PP depended on the addition of the coupling agent

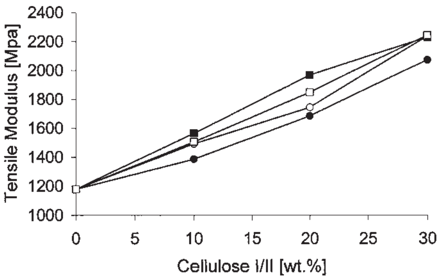

Figure 5 Variation of tensile modulus as a function of fiber content: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

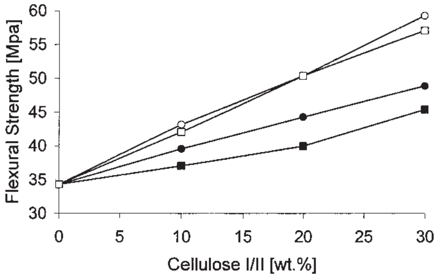

Figure 6 Variation of flexural strength as a function of fiber content: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

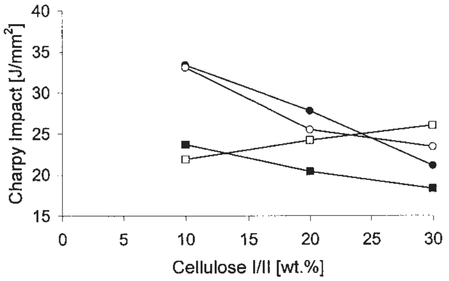

Figure 8 Effect of fiber content on the Charpy impact strength: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

MAPP. The experimental values were linear, but the slope was lower compared to ρ_c.

The V values of both kinds of composites were compared. As shown in Figure 2, the void volume of compounds with cellulose II (lyocell) as a reinforced material was proportional to the lyocell weight fraction up to about 6% voids for 30 wt % lyocell. The composites that used the cellulose I (pulp) as a reinforcing material always had under 1% voids.

Mechanical properties

Figures 3–7 show the influence of fibers and MAPP on the tensile, flexural, and impact properties.

As shown in Figure 3, there was an increase in tensile strength with the lyocell concentration, whereas almost no effect of the pulp concentration was registered on the tensile strength. In both cases, the use of MAPP increased the tensile strength. This improvement was attributed to the increase in the polarity of PP with the presence of MAPP, and therefore, a better adhesion between cellulose and PP occurred. This effect of MAPP in pulp-reinforced PP was also observed by others authors.[3,12]

Figure 4 shows that the pulp and lyocell content had a negative effect on the tensile elongation, and this effect increased with the concentration of the reinforcement fiber. The presence of MAPP affected the elongation of the composites in a different way. Although in the pulp-reinforced PP the elongation was diminished by MAPP, this property increased in the lyocell–PP composites.

As shown in Figure 5, the tensile modulus increased with the pulp and lyocell concentration. A superior tensile modulus was obtained with the use of lyocell as the reinforcement material of PP as compared to pulp. The effect of MAPP was different in both cases. Although the tensile modulus of pulp composites increased, for lyocell, this property was decreased.

As shown in Figure 6, the flexural strength of the pulp- and lyocell-fiber-reinforced PP increased with fiber content, and the flexural strength was higher when pulp was used as the reinforcement material. This indicated that the lyocell–PP composites were more flexible. When MAPP was used as the coupling agent, the flexural strength of both kinds of composites was improved because of better adhesion between the fiber and matrix.

Figure 7 shows how the flexural modulus increased with pulp and lyocell content in the composites. With MAPP used as a coupling agent, no effect was observed. Similar results were obtained by Rana et al.,[13] who worked with jute-fiber (another kind of cellulose I)-reinforced PP.

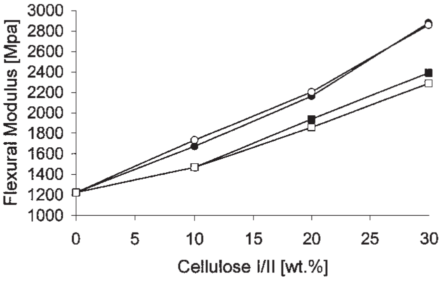

Figure 7 Effect of fiber content on the flexural modulus: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

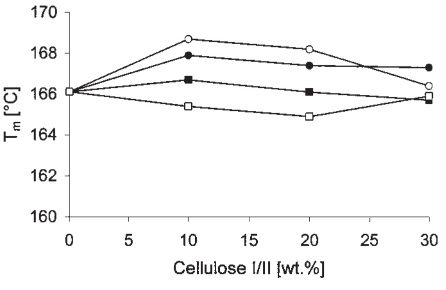

Figure 9 T_m as a function of fiber concentration: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

Figure 8 shows the behavior of the Charpy impact strength of the pulp- and lyocell-reinforced PP. The experimental Charpy impact strength of the used PP was 81 kJ/m^2. The presence of pulp and lyocell led to lower Charpy impact strengths. Further, the behavior of the Charpy impact strengths of the studied composites presented different tendencies depending on the kind of reinforcement fiber. In the case of pulp-reinforced PP, the Charpy impact strength decreased, and there was no effect of MAPP. Raj and Kokta[23] obtained similar results; they worked with wood fiber and polyethylene. When lyocell was used without a coupling agent, the Charpy impact strength decreased. It increased with the fiber concentration when MAPP was added.

Calorimetric analysis

The thermal parameters, melting temperature (T_m), crystallization temperature (T_c), melting heat (ΔH_m), and crystallization heat, were determined by differential scanning calorimetry (Figs. 9–11).

The T_m values of the composites were similar to the PP T_m, and almost no effect and no correlation with the pulp or lyocell content was obtained; this was also independent of the presence of MAPP (Fig. 9).

As shown in Figure 10, different responses on T_c were obtained for pulp- and lyocell-reinforced PP. Although a significant increase in T_c was observed with the pulp fiber content, the T_c value of lyocell-reinforced PP was constant at about 5°C higher than pure PP. For both kind of composites, no effects of MAPP were observed.

To evaluate the effect of the PP on ΔH_m, the crystallinity [x_c (%)] was determined by the following relationship[24,25]:

$$x_c\ (\%) = \frac{\Delta H_m}{\Delta H_m^{\phi}} \times \frac{100}{w} \tag{3}$$

where ΔH_m is the melting heat of the composite (J/g), ΔH_m^{o} is the melting heat of the 100% crystalline polypropylene [50 cal/g (209 J/g)],[9,26] and w is the mass fraction of polypropylene in the composite (wt %).

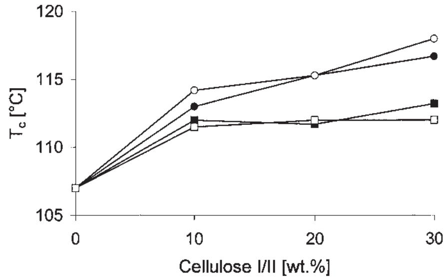

Figure 10 Effect of fiber content on T_c: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

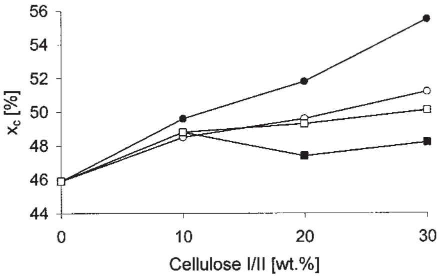

Figure 11 Variation of x_c of the composite as a function of fiber content: pulp (cellulose I) (○) with MAPP and (●) without MAPP and lyocell (cellulose II) (□) with MAPP and (■) without MAPP.

There was a linear increase in x_c with the cellulose content, and this increase was lower in the case of the composite with MAPP as the coupling agent (Fig. 11). As shown in Figure 11, with lyocell as the reinforcement material, x_c was higher than in pure PP. MAPP increased the x_c value of the composite compared to the composite without a coupling agent. These results could be explained by the assumption that the pulp fibers acted as a nucleating agent for the crystallization of PP and formed a transcrystalline layer around the fibers.[25] The lyocell fibers did not act as a nucleating agent.

CONCLUSIONS

According to the obtained results, both kinds of cellulose fiber studied as reinforcement materials of PP had a similar influence on the mechanical properties, but when MAPP was used as a coupling agent, the effect was not always the same. Although MAPP improved some mechanical properties of pulp–PP, they worsened when MAPP was used in lyocell-reinforced PP or the reverse.

T_c and x_c of the studied composites indicated that cellulose I promoted the crystallization of PP, whereas cellulose II did not. MAPP reduced this effect in the case of pulp fibers, but it induced crystallization when lyocell was used as a reinforcement material.

The mechanical properties of the composites demonstrated that pulp (cellulose I) was a better reinforcement material than lyocell (cellulose II). Further investigations are necessary with regard to the formation of voids in lyocell–PP composites and the behavior of crystallization in PP of both kinds of cellulose fibers.

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