

Study on cellulose and xylan filled polypropylene composites

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Summary

The thermal and viscoelastic properties of polypropylene (PP)/cellulose as well as PP/Xylan composites were investigated by differential scanning calorimetry (DSC) and dynamic mechanical thermoanalysis (DMTA). Morphological aspects were available by using polarizing light microscopy and scanning electron microscopy (SEM). Three types of fillers were incorporated in PP: xylan fillers (XL), cellulose microfibers (CM) and short fibers of spun cellulose (CS). The compatibilizer maleic anhydride modified PP (MAPP) was added to the composites. The crystallization temperature and crystallinity of PP apparently increased in the presence of all fiber types. The cellulose fiber surfaces act as nucleating agents for PP, resulting in the formation of transcrystalline regions around the fibers. The DMTA spectra of PP/filler composites revealed a significant increase in the stiffness and a remarkable decrease of the damping values. This effect was stronger for PP/CS than for the other composites. The results verify that improved compatibility and interfacial adhesion between fiber and matrix markedly contribute to an improvement of the mechanical properties.

Introduction

In the last years a significantly rapid growth and high consumption rates were predicted for various polypropylene composites, due to the favorable price-performance relationship of this thermoplastic polymer and of the reinforced materials yielded by incorporating different kinds of fillers in PP. At the same time, the recent trend in environmental awareness has contributed to a still great interest in the development, improvement and use of polymeric composites with reinforcing natural fibers such as wood, cellulose and jute. In comparison to conventional mineral fillers, the cellulosic renewable materials from biological sources offer attractive advantages including low density, high stiffness, easy processing and low price [1]. However, the main disadvantage in reinforcing thermoplastics (particularly in polyolefines) with cellulose fibers is the significantly limited compatibility and interfacial adhesion between the hydrophilic fillers and the hydrophobic polymer matrix [2, 3].

With regard to the mentioned fundamental problem, numerous research efforts have been made in the area of cellulose and wood reinforced PP composites using different chemical

additives for fiber surface treatment in order to find suitable coupling agents for improving filler dispersion, compatibility and corresponding mechanical properties [1-9]. However, this important class of composites is still only partly investigated, since there is a wide range of possibilities for varying filler types, methods of incorporation, coupling agents and processing conditions. For instance, in addition to the normal wood cellulose and in dependence of the required composite properties for technical applications, the hemicellulose by-product (xylan) and the high modulus viscose fibers (spun cellulose) can serve as a good alternative for certain mineral fillers. In the literature no noticeable effort has been devoted to an extensive investigation of such PP composites.

The aim of this work is the study of morphology, dynamic-mechanical and thermal behavior of PP reinforced with three different types of fillers: xylan fillers (hemicellulose), wood cellulose microfibers and short fibers of spun cellulose (viscose fibers). For compatibilizing purpose a small content of maleic anhydride grafted PP was added during processing in all composites.

Experimental

Isotactic polypropylene (PP; P 5000; MFI=1.5 g/min; $\rho=0.902$ g/cm³; $M_w=263 \cdot 10^3$ g/mol) supplied from the Hüls AG served as polymer matrix for the preparation of the composites. Maleic anhydride modified PP-homopolymer (MAPP; Polybond; 1.3 wt% maleic anhydride) used as compatibilizing agent was obtained from Vestolen GmbH (Gelsenkirchen). Chopped strands of spun cellulose fibers (CS; Cordenka RT; $\rho=1.4$ g/cm³; length 6 mm) were supplied by Akzo Faser AG (Obernburg). Wood cellulose microfibers (CM; Arbocel BE; $\rho=1.5$ g/cm³; 40×20 μm^2) from leafwood and containing >98% cellulose, were obtained from Rettenmaier GmbH (Ellwangen). Xylan fillers (XL, not characterized) from birch wood were obtained from Dr. Puls (Bundesforschungsanstalt für Forst- und Holzwirtschaft, Hamburg).

A Haake twin-screw extruder TW100 model (length x diameter: 75 cm x 24 cm) was used for mixing and homogenizing each fiber type with the polymer matrix and a small content (ca. 7 wt%) of the coupling agent MAPP. The temperatures of the four zones of the extruder were 180, 185, 190 and 190°C, respectively. The screw speed was adjusted to 40 rpm. The samples used for the measurements were prepared by hot pressing the extruded granules in a hydraulic electrically heated press at 190°C for 10 min with a force of 50 kN. After pressing, the samples (about 0.3 mm in thickness) were cooled (20°C/min) to room temperature under pressure.

A DSC-7 (Perkin Elmer) served for calorimetric studies. The samples (each ca. 10 mg) were heated to 180°C and maintained at this temperature for 5 min. Then they were cooled from 180°C to 25°C at a rate of 10°C/min (cooling cycle), held for 5 min at this temperature and then heated again to 180°C at a rate of 10°C/min (heating cycle). From the thermograms, transition temperatures and enthalpies were determined. The crystallinity (X_c) of the PP component was obtained by using the relationship:

$$X_c = (\Delta H / \Delta H^\circ) \cdot (100/w) \quad (1)$$

where for 100% crystalline isotactic polypropylene the heat of fusion $\Delta H^\circ=190$ J/g was taken, and w is the mass fraction of PP in the composite.

The morphology of the composites was investigated by optical micrographs of thin specimens (~50 μm) using a BH-2 Olympus polarizing microscope. The films were prepared by the pressing procedure stated above. Fractured surfaces of composite specimens were studied by using a Hitachi S-800 scanning electron microscope operated at 25 kV.

Stress-strain oscillation measurements were performed with a dynamic-mechanical thermo-analyzer, Eplexor of Gabo Qualimeter (Ahlden, Germany), at a frequency of 10 Hz. The samples of 30 x 5 mm² area and 0.3 mm thickness were cooled to ca. -125°C and heated under a strain-controlled sinusoidal tensile loading to 170°C with a heating rate of 2°C/min. The static and dynamic strains amount to 0.15% and $\pm 0.05\%$, respectively. The viscoelastic properties, i.e. the complex dynamic modulus (E^*) and the mechanical loss factor (damping) $\tan\delta = E''/E'$ (E'' and E' loss and storage modulus, respectively), were recorded as a function of temperature.

Results and Discussion

Polymer composites with a polypropylene matrix and cellulose fibers up to 50 wt% have been obtained and studied in DSC and DMTA experiments. *Figure 1* shows, as an example, thermograms for the melting and crystallization of neat PP and the three composite types (PP+30 wt% fillers). In the temperature range considered, cellulose and xylan do not show a thermal transition. The DSC curves clearly demonstrate that the addition of cellulose and xylan fibers (CS, CM and XL) to PP results in a remarkable increase of the crystallization temperature (T_c) of the polymer matrix. In the presence of 30% incorporated fillers, the T_c of neat PP increased from ca. 112°C to 120°C. This effect can be explained by the assumption that the cellulose fibers act as efficient nucleating agents for the crystallization of PP and consequently increase its crystallization growth rate during the cooling from the molten state. With regard to the melting temperature of the different samples, the addition of the three fiber types in the PP matrix causes only a marginal effect ($\pm 1^\circ\text{C}$), and no essential correlation of the results with the fiber content can be established. However, a comparison of crystallinity X_c of neat PP, calculated according to *equation (1)* for the PP component in the composites, yielded higher values for the composite samples than for unfilled PP (neat PP: $X_c = 51\%$, all composites of PP+30% fillers: $X_c \approx 56\%$). This observation can again be explained by the fact that the surface of the cellulose fiber acts as nucleation sites for the crystallization and partial crystalline growth in PP. It may be assumed that the nucleating effect of the fiber surfaces considerably contributes to the occurrence of transcrystalline layers around the fibers resulting in an increase of the achieved percentage of crystallinity as shown in *Figure 2(a-b)* which represents optical micrographs for the composite samples, PP/xylan and PP/spun cellulose. It is apparent that somewhat dense transcrystalline regions (i.e. oriented aggregations of lamellae) have developed on the surfaces of the fibers.

In the literature, the ability of cotton and wood cellulose fibers to induce transcrystallinity has been reported [10]. An extensive review about transcrystallization in fiber reinforced polypropylene composites can be found in [11]. The transcrystalline morphology is characterized by a high density of nucleating crystallites which grow perpendicular to the surface responsible for nucleation. However, the occurrence of transcrystalline phases in different polymer composites is believed to improve the shear transfer and adhesion at the fiber/matrix interface resulting in a stiff transcrystalline layer around the fiber and strong interfacial adhesion which

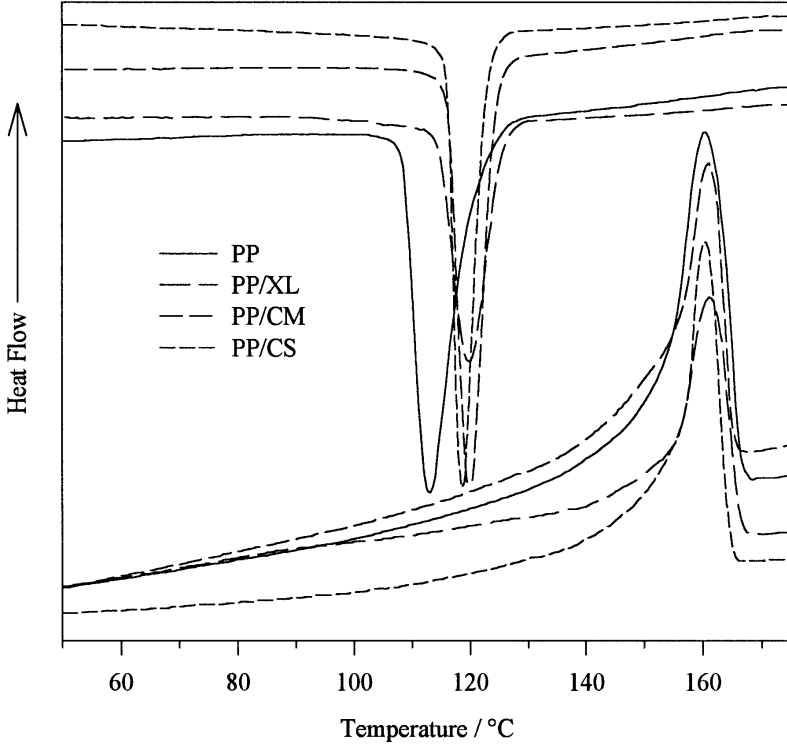


Figure 1: DSC curves for crystallization and melting behavior of neat PP and samples of PP+30 wt.% fiber composites (XL: xylan fillers, CM: wood cellulose microfibers, CS: short-fibers of spun cellulose).

contributes to an improvement in the final mechanical properties of the composites. The effects observed in this work under the conditions mentioned above and by using the compatibilizer MAPP apparently indicate that the addition of cellulose fibers to PP promotes thermodynamic conditions, which are favorable for the nucleation and certain growth of the crystalline morphology of the semicrystalline PP.

Figure 3 depicts the dynamic mechanical spectra (E' and $\tan\delta$ as a function of temperature) for neat PP and the composites investigated, PP+30wt% fillers. On the $\tan\delta$ curve of PP, three relaxations can be observed in the vicinity of -80°C (γ), 8°C (β) and at 100°C (α). The weak γ -dispersion is due to the motion of few chain segments in the amorphous regions, while the shallow α -relaxation shoulder is attributed to a lamellar slip mechanism and rotation in the crystalline phase [12]. The dominant β -peak represents the glass-rubber transition of the amorphous portions in PP, and the temperature of the loss-peak maximum is assigned to the glass temperature (T_g). This transition corresponds to a significant decrease of the E' -modulus curve, which exhibits a slight rubber plateau between T_g and T_m .

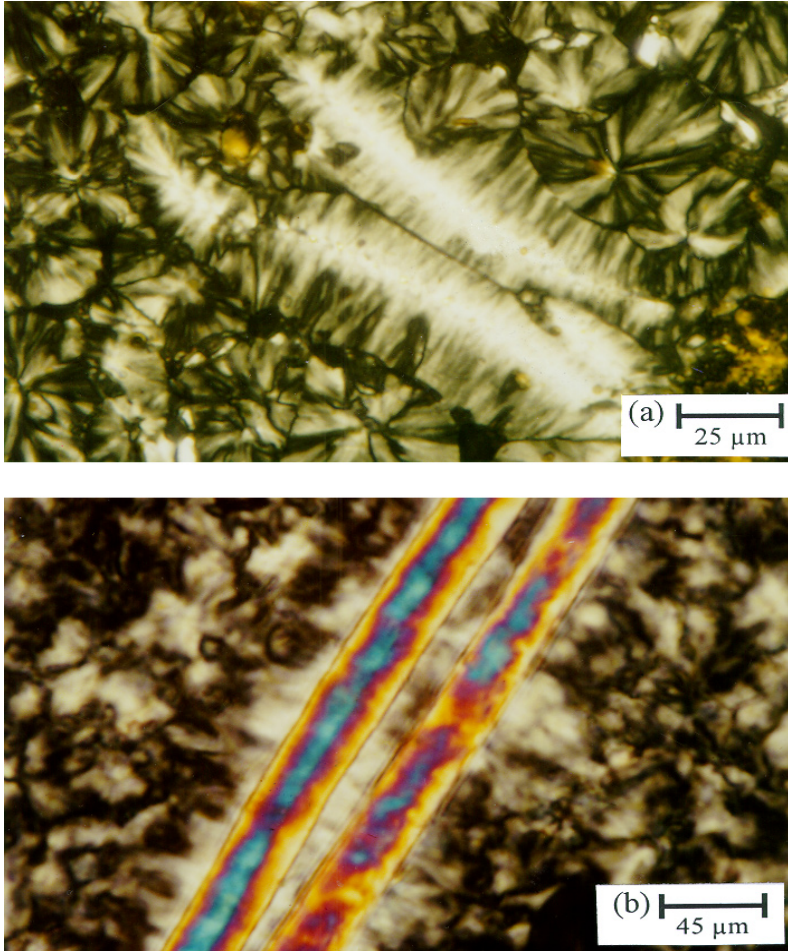


Figure 2: Optical micrographs showing the transcrystalline morphologies of selected samples of (a) PP/xylan and (b) PP/spun cellulose composites.

Comparing the DMTA spectra of neat polypropylene and PP/cellulose composites, it becomes obvious that the addition of the three types of fillers used in PP results in an increase of the stiffness and reduces the $\tan\delta$ values of the material. While a significant decrease is detected for the intensity and magnitude of both α - and β -relaxations, only a slight change can be observed for their shape and position. However, the E' -curves display an improved rubber plateau above T_g apparently indicating that the incorporation of cellulose fibers in PP induces reinforcement effects, which increase the heat resistance and mechanical stability of the material at high temperatures. However, comparing the stiffness increase in PP/CS samples to that detected for PP/CM composites and PP/XL samples, it becomes obvious that the E' -modulus increase in PP/spun cellulose composite is significantly higher than that of the other materials (at room temperature, PP/CS: $E' = 2530$ MPa, PP/CM: $E' = 2060$ MPa, PP/XL: $E' = 1890$ MPa, PP:

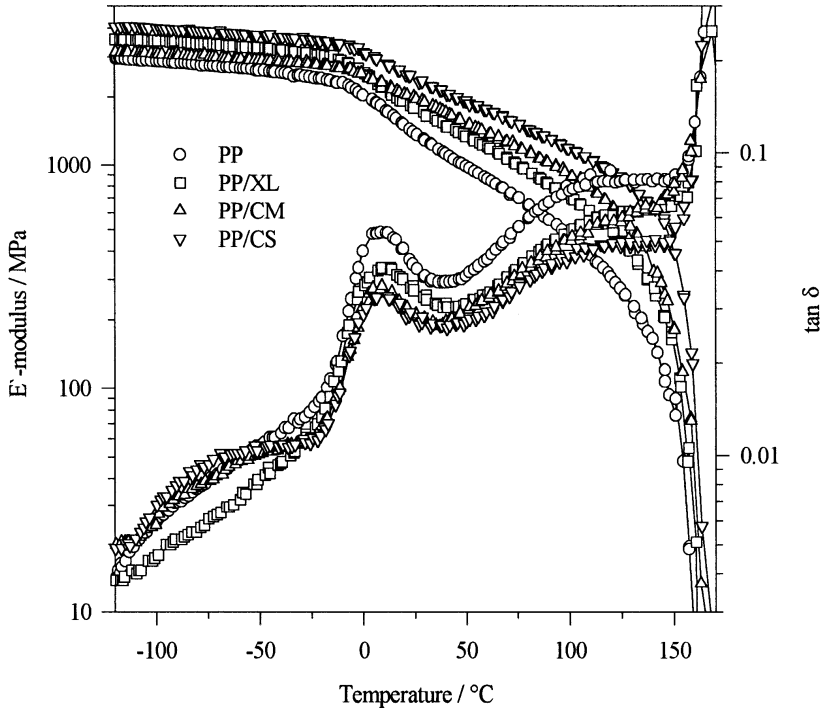


Figure 3: Storage modulus (E') and damping factor ($\tan\delta$) as a function of temperature for neat PP and PP+30% fiber composites (filler type as indicated).

$E'=1490$ MPa). On the corresponding $\tan\delta$ curves, it can be seen that the intensity of the β -relaxation of the amorphous polymer matrix in PP/CS composite is clearly lower than that of PP/CM and PP/XL composites, which also show a remarkable decrease in $\tan\delta$ values in comparison to neat polypropylene (at $T_g \approx 8$ °C, PP/CS: $\tan\delta=0.032$, PP/CM: $\tan\delta=0.035$, PP/XL: $\tan\delta=0.038$, PP: $\tan\delta=0.053$).

The reinforcement effects observed for the dynamic-mechanical properties of the composites investigated undoubtedly depend on their composition, i.e. volume fraction and individual component properties. The remarkable difference in the behavior mentioned for PP/CS samples and other composites can be particularly attributed to the big influence of the length (initially 6 mm) and high stiffness (E -modulus >30 GPa) of the spun cellulose fibers used. However, the improvement achieved in all materials investigated is also considerably affected by the strength and the efficiency of the interfacial adhesion and interaction balance on the interphase between the cellulose fibers and the bulk matrix. In the literature, several theories and mechanisms have been proposed and reviewed to explain the phenomenon of adhesion between phases [13].

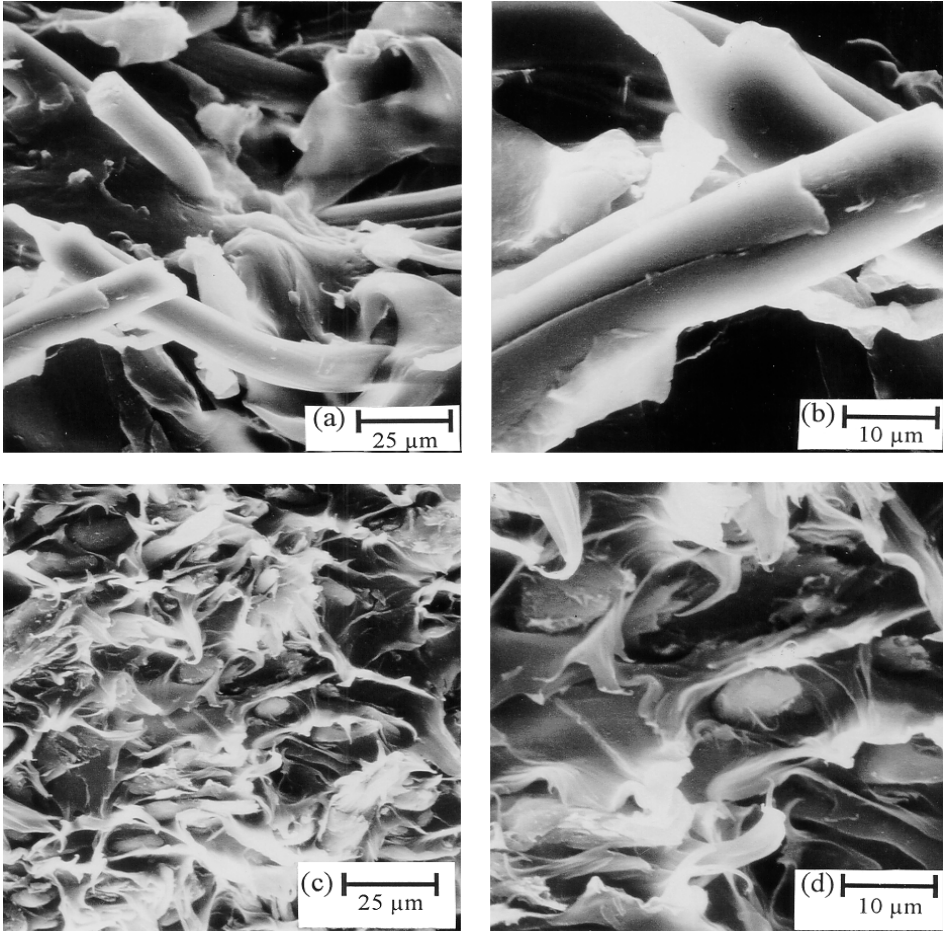


Figure 4: Scanning electron micrographs of the fracture surfaces of (a-b) PP/CS composite specimen and (c-d) PP/CM composite specimen (in both 7% content MAPP)

In general, the thermodynamic (or adsorption) theory is most widely used to explain the adhesion mechanism. It describes the achievement of intimate contact and the development of physical forces at the interface, a necessary step for the occurrence of other mechanisms to enhance the adhesive strength. An accepted adhesion mechanism for polymer systems is the model of interdiffusion, based on the occurrence of mutual diffusion of chains across the interface resulting in the creation of an interphase with entanglements which link the components. In comparison to these physical interactions, the formation of chemical bonds across the interface in multicomponent systems can significantly determine the level of interfacial adhesion and the interphase thickness resulting in great effects on the final materials properties. For the composites investigated in this work, the occurrence of chemical bonding during compounding can be assumed, since the functional group of the anhydride ring of the maleic

anhydride grafted PP is able to react chemically with the polar (OH) groups of cellulose at the fiber surfaces [7].

In addition to physical interactions, the resulting strong covalent bonds as well as hydrogen bonds considerably enhance the interfacial adhesion, stress transfer and the efficiency of interactions and improve the dispersion of the filler and the compatibility between the hydrophilic cellulose and the hydrophobic polypropylene matrix. It is assumed, that adhesion effects are crucial for the improvement of the dynamic mechanical properties. This is confirmed by an investigation of the fracture surfaces (at room temperature) of the composite samples. SEM micrographs of various magnifications are shown in *Figure 4 (a-d)* for the fracture surfaces of the composites PP+30% spun cellulose fibers (*Fig. 4a-b*) and PP+30% wood cellulose fillers (*Fig. 4c-d*). The SEM micrographs provide evidence of good filler dispersion in the matrix, effective wetting of fibers by the matrix and strong interfacial adhesion between the components. With the coupling agent MAPP, no regions of particle agglomeration were seen in any of the investigated composite specimens. For PP/CS composite the entire fibers are clearly covered by layers of the matrix material that have been pulled out together with the cellulose fibers. The surface appearance implies great ductility. Also for the PP/CM sample, it can be seen that the fracture leaves a significant amount of matrix adhering to filler surfaces. These observations are consistent with the assumption that the MAPP compatibilizer is covalently bound to both the PP matrix and the cellulose fibers.

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