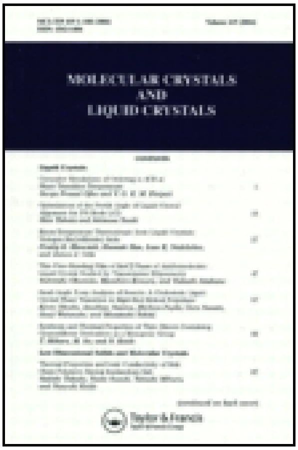

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Properties of Polymer Composites with Cellulose Microfibrils

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Polypropylene-based composites containing 10–30% by weight cellulose microfibrils were studied. Composites with polypropylene and cellulose microfibrils were characterised by MS-coupled simultaneous TGA-DSC and the reinforcing effect of cellulose microfibrils was emphasised by mechanical characterization. Experimental results are discussed in connection with the composite preparation method by mixing and extrusion. The effect of cellulose on the thermal stability and degradation behaviour of the polypropylene matrix is pointed out.

Keywords: cellulose microfibrils; polymer composites; polypropylene degradation; thermal analysis

INTRODUCTION

Recently eco-friendly polymer composites with cellulose microfibrils have received considerable attention because of the possibility of obtaining similar properties to silicate polymer nanocomposites [1–4]. The availability of the raw material as well as the well-known

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advantages of renewability, low-energy consumption, low density, high specific modulus and low abrasivity could explain the interest in these natural fillers [5–6]. Environmental policy and the increased pressure to use ecological technologies could also be considered strong arguments to use natural and renewable resources for composites preparation.

Cellulose microfibrils are crystalline entities with submicron dimensions resulting from linear association of cellulose macromolecules. They can be obtained from different sources (wood, plants, bacteria, sea animals) applying mechanical, mechano-chemical or enzyme-based treatments [2–6].

Composite preparation conditions, interface properties, cellulose microfibrils and matrix characteristics have a decisive influence on polymer composites properties [1–7]. Cellulose microfibrils with submicron diameters from cotton were used by William J. Orts *et al*. [4] for composites preparation by extrusion and caused an unexpected increase of mechanical properties of polymer matrix (starch): a six-fold increase of the modulus was observed at 5% microfibrils in starch. Nanocomposites from poly(lactic acid) and 5% by weight of cellulose microfibrils prepared by solution casting by L. Petersson and K. Oksman [1] showed no increase in the tensile modulus and only 12% increase in the yield strength compared to pure poly(lactic acid). Improved compatibility and interfacial adhesion between microfibbers and matrix were obtained by A. Amash and P. Zugenmaier [7] using maleic anhydride modified polypropylene as compatibilizing agent in a polypropylene–cellulose microfibbers composite showing improved mechanical properties. A stable suspension of cellulose crystals in dimethylformamide was prepared by N. E. Marcovich *et al.* [6] and incorporated into a polyurethane formulation to prepare crosslinked composite films with improved mechanical properties: the addition of 5% by weight cellulose nanocrystals produced a more than two-fold increase in the Young modulus with respect to the neat system.

In this brief report, we present some of our experimental results regarding polymer composites with cellulose microfibrils preparation and their thermal degradation studied by mass spectroscopy coupled TGA-DSC, reinforcing effect being pointed out by mechanical properties.

EXPERIMENTAL

Materials and Analytical Instruments

Polypropylene homopolymer HP 500 N ($\text{MFI} = 7.5\,\text{g}/10$ min: $\text{d} = 0.9\,\text{g/cm}^3$) supplied from Basell have been used as polymer matrix

(PP) for the preparation of the composites. Maleic anhydride modified PP (MA-PP; Polybond 3200; 2.2% maleic anhydride) used as compatibilizer was purchased from Uniroyal Chemical Co.

A Quanta Scanning Electron Microscope 200 served for microscopic investigations of cellulose microfibrils (accelerating voltage 15 kV, no coating).

Thermo-analysis with mass spectroscopy monitoring was performed with a simultaneous TGA-DSC system type STA 449 C Jupiter coupled with a mass detector QMS 403 C Aeolos from Netzsch, in helium atmosphere, at 5°C/min heating rate and using alumina crucibles. Mass spectra in scanning mode (0–300 Da) and in multi ion detection mode ($m/z = 15$; 18; 28; 41; 43; 44; 55; 57 and larger chain fragments) of the degradation fragments were recorded, thus monitoring the changes in the degradation mechanism of the composites.

Tensile properties of the composites were determined according to ISO 527 on specimens type IB (5 specimens for each test) with 50 mm/min for tensile strength and 2 mm/min for modulus of elasticity.

Cellulose Microfibrils Preparation

L type cellulose microfibrils were prepared by mechanical treatment of short dimension waste wood, a mixture of deciduous and resinous trees, from timber factories. Mechanical paste resulted after steam treatment at a pressure of 0.8–1.2 MPa and a temperature of 165–170°C was mechanical treated by repeated refining and grinding on a laboratory grinder. Cellulose microfibrils with 44.9% cellulose, 18.8% lignin and 7.5% extractible substances (the rest is ash) were obtained.

F type cellulose microfibrils were prepared by mechanical and chemical treatment. Microcrystalline cellulose with 96% α-cellulose from southern resinous trees was processed in the following manner: defibrated in a holender, swelled in an alkaline media at room temperature for 24 hours, washed and hydrolysed with diluted hydrochloric acid.

PP-Cellulose Microfibrils Composites Preparation

A Brabender Plasticorder was used for mixing and homogenizing each cellulose microfibril type (0.... 30 wt%) with the polymer matrix and the compatibilizing agent (10 wt%) in the following conditions: temperature 175–180°C, rotors speed 60 rpm/60 rpm. The mixture was blended for 10 min. The samples used for measurements were prepared by press moulding in an electrically heated press at 190°C for 10 min with a force of 50 kN. After moulding, the samples were cooled at room temperature under pressure.

Polypropylene, L type microfibrils sample (10 wt%) and the compatibilizing agent were mixed and homogenized with a Leistritz L.S.M. 30–34 double screw extruder at a temperature of 180–190°C and screws rate of 100 $\mathrm{min.}^{-1}$/100 $\mathrm{min.}^{-1}$.

RESULTS AND DISCUSSION

SEM Examination of Cellulose Microfibrils

Cellulose microfibrils with diameters from tenth of nm to a couple of microns were realized using the two low cost disintegration methods: a mechanical method applied to wood pulp and a mechano-chemical one applied to cellulose. Purely mechanical processing produces microfibrils between 800 nm and 14 μm in diameter as it can be seen in Figure 1. Combined chemical and mechanical processes produce microfibrils, 1–8 μm in diameter (Fig. 2).

Thermal Degradation of PP-Cellulose Microfibrils Composites

Calorimetric Evaluation

Melting temperature (T_m) of PP is not significantly changed when cellulose microfibrils are added but a slight decrease from 167.3°C

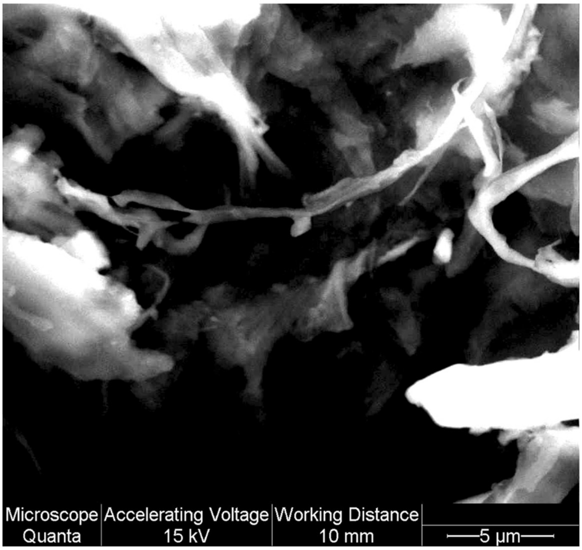

FIGURE 1 SEM image of L type cellulose microfibrils (magnification ×4000).

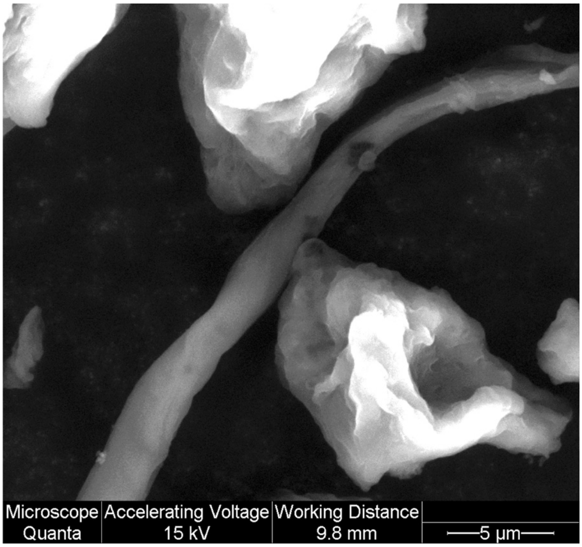

FIGURE 2 SEM image of F type cellulose microfibrils (magnification ×4000).

for neat PP to 166.5°C for PP composite with 10 wt% F and 165.5°C for PP composite with 30 wt% F is observed, as shown in Table 1. No correlation of T_m with the concentration of cellulose microfibrils could be established. Melting behaviour expressed by the heat of fusion was changed when cellulose microfibrils were added. A comparison of samples is possible calculating the crystallinity for PP component in the composites and correlating with the crystallinity of neat PP (Table 1). The crystallinity of PP (C) was calculated according to the equation:

$$C = (\Delta H/\Delta H^0) * (100/w) \tag{1}$$

where ΔH is the heat of fusion for the composite, ΔH^0 is the heat of fusion for 100% crystalline isotactic PP (190 J/g [7]) and w is the mass fraction of PP in the composite. The values of crystallinity for the composite samples were higher than for neat PP as shown in Table 1. An explanation for this behaviour could be the action of cellulose microfibrils surface as nucleation sites for the crystallization of PP, in agreement with previous observations [7–8]. MA-PP coupling agent, like other polar materials, is an effective nucleating agent [9] that further increases the nucleating ability of cellulose fibrils.

The melting behaviour of PP composites with 10% and 30% L type cellulose microfibrils (L) is similar to that of the previous samples: adding cellulose L microfibrils does not influence the melting

TABLE 1 Thermal Behaviour of PP - Cellulose Composites

Sample	Melting temperature, °C	Melting enthalpy, J/g	Crystallinity of the matrix, %	Onset degradation temperature (I), °C	Onset degradation temperature (II), °C	Residue at 700°C (coke), %
PP	167.3	33.89	17.8	–	428.6	0
PP/10%F	166.5	31.45	20.7	329.1	438.8	0
PP/30%F	165.5	27.24	24.0	326.1	417.4	< 0.1
PP/10%L	166.8	31.94	21.0	275.2	440.3	5.17
PP/30%L	166.3	25.46	22.3	274.9	443.1	10.7
PP/10%L (extrusion)	166.6	32.04	21.1	273.2	441.7	1

temperature of PP (only 1°C shift was observed). The values of crystallinity for the composite samples were higher then for neat PP as shown in Table 1, but the effect was lower in the case of high concentration of L. The presence of lignin and other substances on the surface of L type cellulose microfibrils and, especially, the lower specific surface of L microfibrils, because of higher diameters, could explain the lower efficiency of L microfibrils in generation of nucleating sites.

No significant changes were observed in the case of PP composite with 10% by weight L type cellulose microfibrils obtained by extrusion. The same melting temperature, melting enthalpy and crystallinity could be observed, as presented in Table 1.

Thermo-Gravimetric Analysis

The degradation onset temperature (Table 1) for PP is about 429°C, the degradation taking place in only one-step (Fig. 3, up).

When cellulose microfibrils were added, two degradation steps were observed (Fig. 3, up). The degradation onset temperature for the first step was relatively low ($\sim$329°C for the composite with 10% by weight cellulose microfibrils and 326°C for the composite with 30% by weight microfibrils) regardless the concentration of cellulose microfibrils (Table 1). The degradation onset temperature for the second step was shifted toward lower temperatures ($\sim$417°C) in the case of high cellulose microfibrils concentration in composite (Table 1) but was 10°C higher in the case of low microfibrils concentration ($\sim$439°C). A plausible explanation for this behaviour could be the free radical "scavenger" effect of the cellulose at low concentration.

The degradation behaviour of PP composites with 10% and 30% L microfibrils is different (Fig. 4, up) by comparing with the previous samples. The degradation process is again a two step one but the degradation onset temperature for the first step was about 50°C lower (Table 1) than in the case of F microfibrils (over 96% α cellulose), indicating the negative influence of the other components present in L microfibrils (lignin, extractible substances) on the degradation process. Another difference is the presence of a coke residue in relative high concentration (5–10%) in both composites after decomposition. Again, the presence of lignin and other components from wood are the cause of the coke formation in the process of degradation.

No significant changes in the degradation pattern were observed in the case of PP composite with 10 wt% L type cellulose microfibrils obtained by extrusion (Fig. 4, up). The only difference is the absence, practically, of coke (Table 1). It can be attributed to a better dispersion of the fibrils in the PP matrix that hampers graphitization of the filler during thermal decomposition.

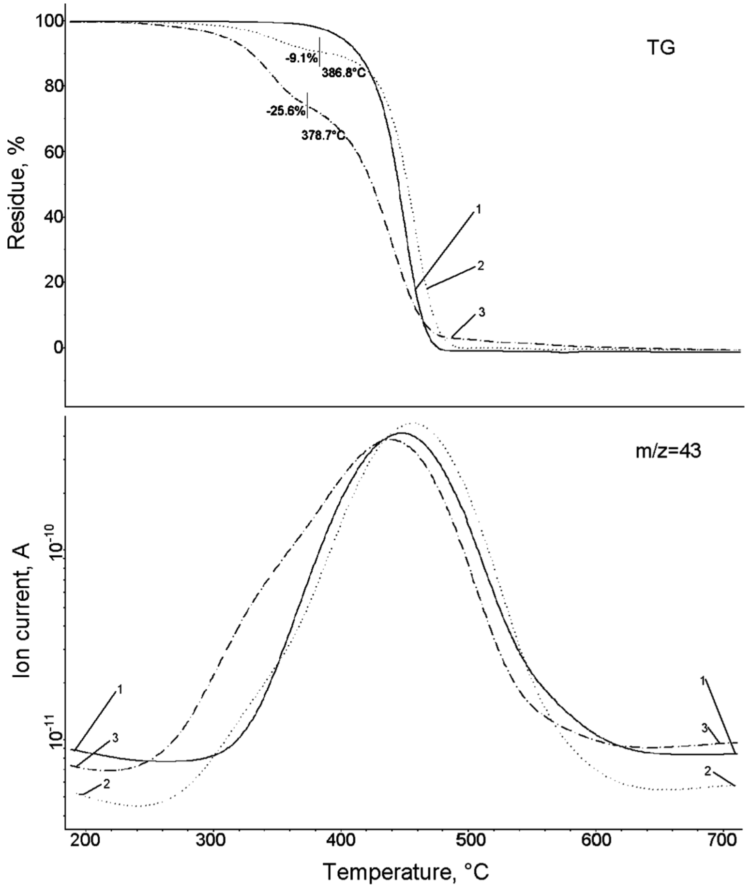

FIGURE 3 Thermal degradation of PP/F type fibber composites (up) and matrix characteristic fragment (down); 1 – neat PP; 2 – PP/10% F type fibber composite; 3 – PP/30% F type fibber composite.

Decomposition Site Assessment by MS

Reference samples analysed by TGA-MS in scanning mode showed that at least two fragments are characteristic for the polypropylene matrix, $m/z = 43$ and $m/z = 57$ and other two, $m/z = 41$ and $m/z = 55$, are characteristic for both the F and L cellulose fillers. None of the two characteristic fragments for one component was present in the degradation pattern of the other component. This allowed monitoring the PP matrix decomposition in multi-ion detection mode by the evolution of the fragment having $m/z = 43$.

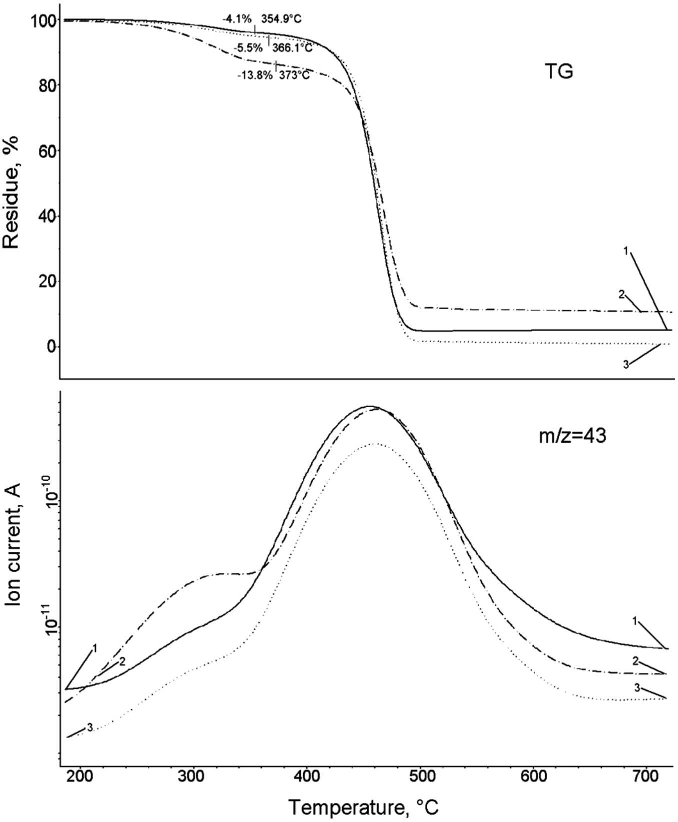

FIGURE 4 Thermal degradation of PP/L type fibber composites (up) and matrix characteristic fragment (down); 1 – PP/10% L type fibber composite; 2 – PP/30% L type fibber composite; 3 – PP/10% L type fibber composite, extruded.

The composite containing 10% cellulose F shows similar evolution to the neat PP (Fig. 3, trace 2 compared to 1), slightly shifted towards higher temperature, in agreement with the assumption that cellulose has radical “scavenger” effect in low concentrations. In the 30% cellulose F containing composite, a degradation of the matrix is induced in the second part of the first degradation step. The height of the first degradation step is (Fig. 3, up) very close to the initial cellulose content in both samples with cellulose type F, therefore it may be assumed that purified cellulose degrades individually, only slight effect on the matrix being revealed.

The evolution of the matrix-originating fragment for the L type cellulose containing composites is different (Fig. 4, down). In all samples evolution of m/z = 43 fragment is present from the beginning of the first degradation step. The first degradation step represents only half of the initial content of L type fibrils (Fig.4, up) while degradation of the matrix is important. We can assume that in this case the matrix and the filler degrade together. The inclusion of the L fibrils in the matrix delays their degradation and induces a premature degradation of PP.

Extrusion processed composite shows identical decomposition pattern as the sample processed on the mixer.

Mechanical Characterization of PP-Cellulose Microfibrils Composites

In the case of PP composites with F cellulose microfibrils (0....30% by weight), the relative tensile strength (σ/σ_0, σ-tensile strength of PP composite and σ_0-the corresponding value for PP) and the relative tensile modulus of elasticity (E/E_0, E – tensile modulus of PP composite and E_0 – the value for the neat PP) versus composition are presented in Figure 5. From the standpoint of relative tensile strength, the effect of addition of cellulose microfibrils in PP shows a slow increase and

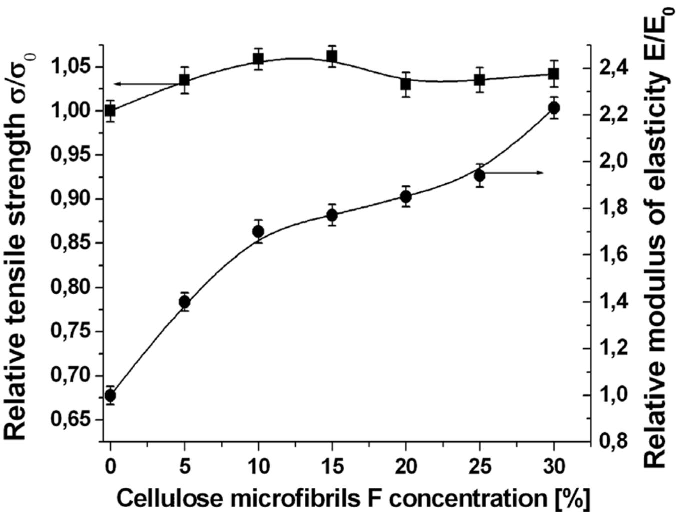

FIGURE 5 Tensile properties of PP and PP composites with F type cellulose microfibrils.

then an approximately constant value as the amount of the disperse phase increases. On the other hand, from the viewpoint of relative tensile modulus, there is a monotone increase with the raise of the F microfibrils concentration, up to a net increase of 2.2 fold, at 30% by weight F, compared with the unfilled PP. However, a decrease of the rate of variation of the tensile modulus with the increase of F microfibrils is also apparent.

Relative tensile strength and relative tensile modulus of PP composites with L microfibrils (0....30% by weight) are presented in Figure 6. The effect of L microfibrils consists in a slow increase and then a decrease, with constant rate, of the value of relative strength as the concentration of disperse phase is greater then 10%, while an increase of two fold at 30% L is also evidenced for the tensile modulus. The dissimilarities in the mechanical strength of the PP with F and L microfibrils could be both the result of the lack of lignin and other compounds in the former case of F microfibrils, as well as of the smaller values of the fibril diameter and narrower distribution of microfibrils dimensions.

Mechanical properties of the PP composite with 10 wt% L microfibrils obtained in a Leistritz twin screw extrusion installation are presented in Table 2 in comparison with mechanical properties of neat PP (the samples for mechanical characterization were prepared by

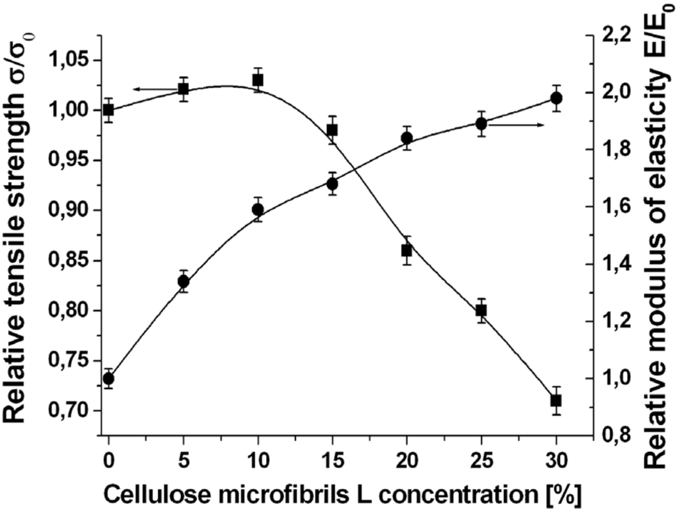

FIGURE 6 Tensile properties of PP and PP composites with L type cellulose microfibrils.

TABLE 2 Mechanical Properties of PP Composite with L Microfibrils Obtained by Extrusion

Sample code	Tensile strength [MPa]	Elongation at break [%]	Impact strength, KJ/cm^2	Relative modulus of elasticity
PP/10 wt% L – extrusion	36.2 ± 0.6	12 ± 1.5	6.5 ± 0.8	1.38 ± 0.04
PP – extrusion	30.1 ± 0.4	35 ± 1.2	2.2 ± 0.5	1.00 ± 0.03

injection molding). An increase from 30 to 36 MPa is observed for the tensile strength as well as a decrease of 3 times of the elongation at break and an increase of 3 times of the impact strength. Relative modulus of elasticity is slowly increased. All these results indicate a strong effect of reinforcing and stiffening of cellulose microfibrils on the PP matrix.

Consequently, there is a similar trend of increase of tensile modulus of elasticity of PP composites with cellulose microfibrils when the amount of microfibrils increases, although, on the other hand, in the range 0.... 30% by weight, the tensile strength shows approximately constant value in the case of F microfibrils and an important decrease in the case of L microfibrils.

CONCLUSIONS

Cellulose microfibrils with diameters from tenth of nm to a couple of microns were realized using two low cost disintegration methods: a mechanical method applied to wood pulp (L microfibrils) and a mechano-chemical one applied to cellulose (F microfibrils).

Melting temperature of PP is not significantly changed when cellulose microfibrils are added but a slight decrease is observed. An increase of the crystallinity of PP in composite samples is signalled demonstrating the effect of cellulose microfibrils surface as nucleation sites for the crystallization of PP and the action of MA-PP coupling agent in increasing the nucleating ability of cellulose microfibrils.

Disregard PP degradation, a one step process, the degradation of PP composites is a two step process, the degradation of cellulose taking place before PP degradation in the case of small concentration of cellulose microfibrils. At higher concentration, the degradation of cellulose and that of PP overlap, influencing reciprocally. Because of the presence of cellulose microfibrils, PP composites degradation begins at much lower temperatures (~320°C instead of ~430°C). The presence of lignin and other substances on the surface of L microfibrils and their lower specific surface determine some differences in the process of PP composites degradation process. The degradation of cellulose microfibrils and PP is simultaneous even from the first step, the degradation onset temperature for the first step is with almost 50°C lower then in the case of F microfibrils, relative high coke residue (up to 10%) is obtained after decomposition.

No significant changes were observed in the case of PP composite with 10 wt% L type cellulose microfibrils obtained by extrusion in comparison with the same composite prepared by melt mixing, indicating that the degradation process is the same for the both composites prepared by the two processing methods and allowing the scale-up of the process.

Mechanical characterization indicated an increase of tensile modulus of elasticity of PP composites with F and L cellulose microfibrils when the amount of microfibrils increases, in the range 0....30% by weight. The tensile strength shows approximately constant value in the case of F microfibrils and an important decrease in the case of L microfibrils.

Mechanical characterization of the PP composite with 10% by weight L microfibrils obtained by extrusion pointed out a strong effect of reinforcing and stiffening of cellulose microfibrils on the PP matrix. This effect, corroborated with the absence of coke, indicates that extrusion allows a better dispersion of the filler in the matrix.

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