

Recycling of lignocellulosics filled polypropylene composites. I. Analysis of thermal properties, morphology, and amount of free radicals

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ABSTRACT: Composites of isotactic polypropylene filled with comminuted rapeseed straw are studied. Improvement in interfacial adhesion is achieved by chemical modification of the lignocellulose filler. Composites were subjected to recycling by extrusion. The effect of multiple recycling of the composites on the process of nucleation and crystallization of polypropylene matrix, surface topography, and free radical generation was checked. On the basis of differential scanning calorimetry data, a significant influence of the recycling on nucleation activity of the lignocellulose filler was evidenced. A relation between the filler particle size and multiple recycling was established by observations under a polarization microscope, while scanning electron microscope analyses confirmed the positive effect of chemical modification of rapeseed straw on the interfacial adhesion. The composite structure changes forced by multiple recycling are discussed in the context of free radical generation. Concentration of free radicals in the rapeseed straw samples and composites was measured by the electron paramagnetic resonance spectroscopy to show that it was higher in the systems subjected to multiple recycling. Interestingly, the composites after multiple recycling showing elevated concentration of free radicals are also characterized by higher nucleation activity. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41693.

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INTRODUCTION

In line with the requirements of sustainable development, the design and production of materials to be used in different branches of economy should be accompanied by the design of methods for their recycling or recovery. Increasing interest in production of polymer composites filled or reinforced with lignocellulosic materials^{1–6} is prompted not only by the need to use biodegradable materials from renewable sources but also by their much easier recycling or much easier recovery of energy from them when compared to the materials reinforced by glass fibers.

A composite of prospective widespread application is that made of a thermoplastic matrix, for example, polypropylene matrix, filled with comminuted rapeseed straw. Rapeseed is grown in many countries, mostly in China, Canada, EU countries, and Australia. Rapeseed straw is a waste material and as the annual global production of rapeseed is over 50 million tons, including over 19 million tons in EU countries,⁷ the straw seems a very

attractive filler of polymers. The method for production of polymer–rapeseed straw composites and detail characterization of the composites, among others their attractive mechanical properties, have been described in earlier papers.^{8–10} In these papers, we have focused on processing and selected properties of polypropylene composites with rapeseed straw. Results of the hitherto studies on recycling of thermoplastic polymers with lignocellulose fillers have been described in many papers,^{11–20} but they have not concerned the systems of polypropylene–rapeseed straw. Much attention has been paid to studies on degradability of other composites.^{21,22} Thorough investigation of recycling of composites reinforced with sisal or hemp fibers has been made by Bourmaud and Baley, who have analyzed the topography of composites surface, their mechanical, rheological, and thermal properties.^{11,12} These authors have emphasized the role of crystallization of the polypropylene matrix and the nucleation effect of the filler on polypropylene crystallization. They have also reported a relation between selected mechanical properties on the number of reprocessing cycles. A significant

decrease in fiber length during reprocessing has been found to be induced by the injection and mechanical grinding process. According to the analysis of thermal properties, the presence of natural fibers has been found to increase X_c and T_c thanks to the nucleating properties of sisal and hemp fibers on polypropylene crystallization.¹¹

Physical and mechanical properties of polypropylene composites with wood have been studied by Beg and Pickering.¹³ According to them, material recycling of WPC composites was classified as thermomechanical as in particular cycles the composite properties were influenced by elevated temperature and mechanical comminution of the filler. For instance, for the composites containing 40% of wood fibers, the tensile strength and Young modulus were found to decrease with increased reprocessing number.¹³ Bakkal *et al.*¹⁴ have studied multiple processing of polyethylene composites filled with waste cotton fibers and as a result of structural, rheological and mechanical studies they have found that the tensile strength of the composites decreased as a consequence of the fiber damage.

Interesting comparative study on polypropylene-based eco-composites filled with kenaf or rice hulls has been carried out by Srebrnkoska *et al.*¹⁵ Mechanical properties of the composites with kenaf were found much better than those of the composites with rice hulls and the composites filled with kenaf seemed to be less sensitive to reprocessing as compared with polypropylene/rice hulls composites.¹⁵ However, it should be noted that according to Rowell *et al.*, kenaf fibers have been concluded to have excellent specific properties and have potential to be outstanding reinforcing filler of plastics.¹⁶

A comprehensive review of the studies on recycling of composites with polyolefin matrix filled with lignocellulose materials has been presented in Ref. 23. The practical aspect of the studies is to check the effect of multiple processing on the composite properties, especially on its mechanical performance, that must be kept at a certain level allowing its further use. The effect of recycling is also studied from the cognitive point of view, to bring the information on the effect of long-term exposure to high temperatures and sharing forces on the composite performance. Recycling of composites made of thermoplastic polymers filled with lignocellulosic materials is known to cause shortening of fiber length and exposure to high temperature can lead to fibers degradation. However, when a safe temperature of recycling is maintained, the recycling procedure can improve the distribution of the filler in the matrix, which has a beneficial effect on the composite properties.

The main aim of the study was to determine the effect of recycling and also chemical treatment of fillers on the structural properties of recycled composites, with particular emphasis on the nucleation activity of the polymer matrix. The results were interpreted taking into account the generation of free radicals in the composite, which had not been attempted earlier. Generation of free radicals in mechanically and thermally treated lignocellulosic materials and polypropylene has been studied in Refs. 24 and 25 by electron paramagnetic resonance (EPR) spectroscopy, which is useful for detecting a relatively small number of

unpaired electrons in materials containing transition metal ions, free radicals, and so forth.

For this reason, we used EPR method to study the influence of chemical modifications of rapeseed straw and recycling processes on generation of stable free radicals in the composites of polypropylene with rapeseed straw. We expected that the number of free radicals formed in the recycling processes may be related to the degree of degradation and properties of polypropylene matrix/straw interface of the composites studied.

EXPERIMENTAL

Materials

The matrix was isotactic polypropylene Moplen HP 500 J of melt flow index MFI 3.2 g/10 min (Basell Orlen Polyolefins Plock, Poland). The lignocellulosic filler was rapeseed straw from the experimental plots of the Institute of Plant Growth and Acclimatisation, branch in Poznan. The filler was prepared from a mixture of the same amounts of rapeseed straw of the following species of rapeseed winter crop: Bojan, Bries, Californium, Castille, Casek, Contact, Dogger, Elektra, Kaszub, Lisek, Lubomir, and Winner. The straw was mechanically comminuted to the size of 0.5–2.0 mm. The filler was the wooden tissue from the rapeseed straw, separated from the ground tissue by the pneumatic method.

Rapeseed Straw Modification

The first procedure was mercerization of the lignocellulosic filler. The rapeseed straw was immersed in sodium hydroxide solution of a concentration 17.5%, for 30 min.²⁶ Next the straw was washed several times with distilled water to remove the excess NaOH. A final pH of 7 was obtained. The rapeseed straw was dried in air at about 105°C until a constant mass was achieved.

At the next stage, the comminuted and mercerized rapeseed straw was subjected to chemical modification with acetic acid anhydride according to procedure described in Ref. 27.

Preparation of Composites

Composites containing 70% of polypropylene and 30% of lignocellulose filler were obtained by extrusion molding in a single screw extruding press, Fairex (Mc Nell Akron Repiquetn, France). Temperatures in subsequent zones were 150, 180, 195°C, while the temperature of the head was 200°C. The process was performed at the screw rotational speed 30 rpm.

The recycling process was modeled as follows. The granulate obtained in a given extrusion cycle and dried was subjected again to extrusion molding, this procedure was repeated six times. Recyclates of the composites in the form of granulates after each cycle were used for producing solid shapes by injection molding on a machine Engel ES 80/20 HLS (Engel, Austria GmbH). During injection molding, the processing parameters were: injection pressure of 65 MPa, injection speed of 100 mm/s, mold temperature of 20°C, cooling time of 35 s injection temperature of 190°C. These conditions were recognized as optimal after many tests.

It is evident from the data presented in the text, that the temperature of 200°C was exceeded neither in the extrusion or

Table I. Abbreviation of Investigated Samples

Abbreviation	Samples
PP	Nonfilled polypropylene
CN	Composite with native rapeseed straw
CN-1	Composite with native rapeseed straw after one recycling cycle
CN-3	Composite with native rapeseed straw after three recycling cycles
CN-6	Composite with native rapeseed straw after six recycling cycles
CM	Composite with modified rapeseed straw
CM-1	Composite with modified rapeseed straw after one recycling cycle
CM-3	Composite with modified rapeseed straw after three recycling cycles
CM-6	Composite with modified rapeseed straw after six recycling cycles

injection process. The samples of recyclates obtained as a result of extrusion are labeled as in Table I.

Differential Scanning Calorimetry

Thermal analysis was performed using a Netzsch Differential Scanning Calorimeter, model DSC 200, under argon atmosphere. The differential scanning calorimetry (DSC) equipment was calibrated with indium standard ($T_m = 156.6^\circ\text{C}$, $\Delta H_m = 28.4 \text{ kJ/kg}$) for temperature and enthalpy changes. For non-isothermal crystallization investigation, the samples were heated to 200°C (at a heating rate of 10°C/min) and kept at this temperature for 3 min to eliminate the previous thermal and/or mechanical history. Then, the samples were quenched to 40°C at the rate of 5°C/min (using argon flow). The procedure was repeated twice. The temperature program used in DSC study was the same as in our previous experiments.²⁸ DSC measurements provided the temperatures of phase transitions (melting and crystallization) and half-times of crystallization determined as the time when the conversion into crystal reached 50%, which was read off from the curves of crystal conversion versus time.²³

Optical Microscopy

Optical microscopic observations were made on a polarization microscope BX53P OLYMPUS equipped in a digital camera XC10 and controlled by Stream Motion software. Samples for microscopic observations were produced as thin foils obtained from the fragments of molded pieces heated between the microscope slides up to 210°C at which they were kept for 5 min to remove their thermal memory. Then the molten composite was cooled at the rate of 10°C/min to 130°C , at which isothermal crystallization took place.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) observations were made on a ZEISS EVO 40 microscope. Voltage between the electrodes was 17.2 kV. The samples were fractured cryogenically in dry nitrogen. Observations were performed of the cleavage surfaces

of the composite samples, coated with sputtered gold film to increase contrast.

EPR Investigations

EPR spectra were recorded at room temperature by a BRUKER ELEXSYS 500 in X-band. The samples of dry rapeseed straw and composites were weighted and placed in quartz tubes. A magnetic field modulation of 4 G and microwave power of 10 mW was used for all experiments to avoid resonance line saturation. To determine the number of free radicals in the samples, the intensity of radical spectra was compared to the intensity of the standard line of $\text{Al}_2\text{O}_3 : \text{Cr}^{3+}$ single crystal with a known spin concentration. EPR intensity data were recalculated per 1 g of straw in the composite.

The scheme presenting the subsequent procedures applied is given in Figure 1.

RESULTS

Thermal Analysis

DSC studies of polypropylene composites with lignocellulosic fillers have been reported in a number of papers,^{29–33} however, to the best of our knowledge, no analysis of phase transitions in

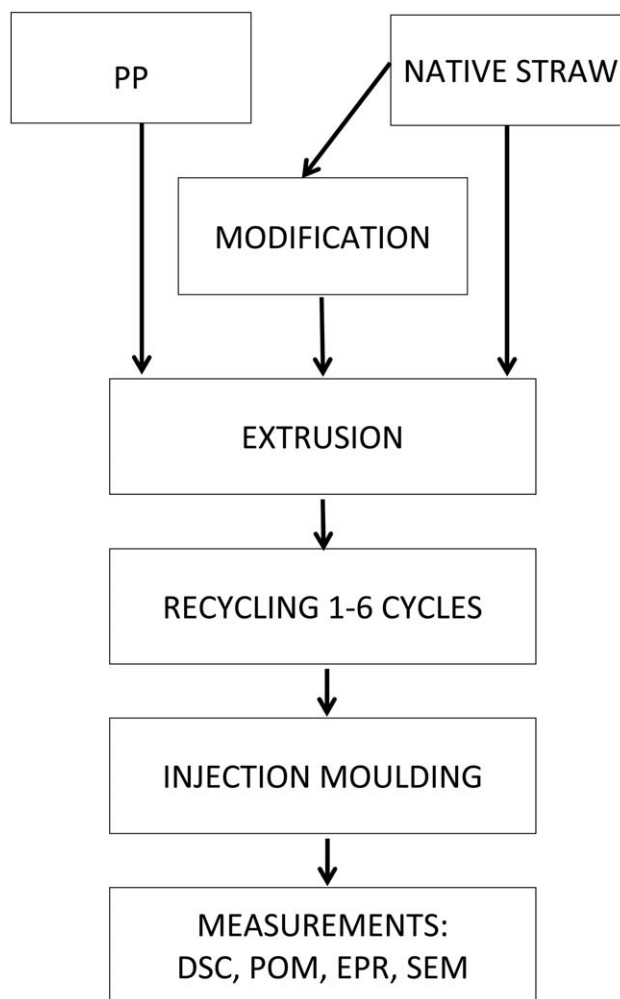


Figure 1. A scheme of subsequent procedures applied.

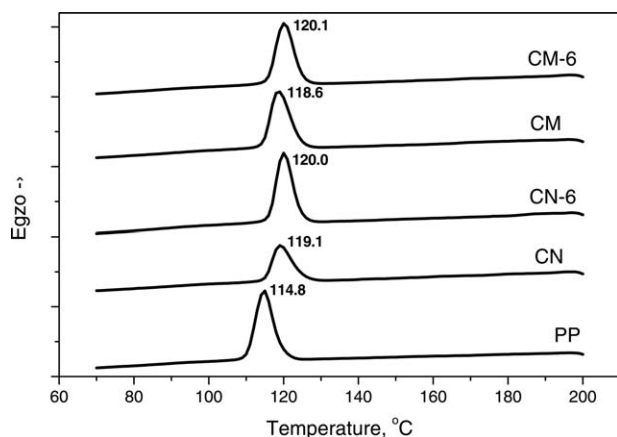
Table II. Thermal Parameters of Polypropylene and Composites

Sample	Melting temperature (°C)	Crystallization temperature (°C)	Half time of crystallization (s)
PP	167.0	114.8	160
CN	166.5	119.1	130
CN-6	167.1	120.0	102
CM	167.1	118.6	125
CM-6	167.2	120.1	107

such systems subjected to multiple reprocessing has been made. Table II presents the melting points, crystallization points, and half-times of PP crystallization measured for the composite materials subjected to multiple reprocessing and the polypropylene matrix.

The crystallization point of pure polypropylene is much different than that measured for a composite of polypropylene with a lignocellulose filler (Figure 2). Addition of a filler of any type is responsible for increase in the crystallization point.

It can suggest that rapeseed straw is an effective nucleant for polypropylene matrix, which would be in agreement with our earlier results²⁸ obtained in the study of crystallization of a few polypropylenes differing in rheological properties. An interesting observation was that modification of rapeseed straw did not cause significant changes in the crystallization point of PP. The crystallization points of the composites with rapeseed straw subjected to modification are comparable to those of the composites with native straw. These results are in contrast to those we reported earlier,³⁴ that is, to the observation that the addition of wood modified with organic acid anhydrides to polypropylene was responsible for an increase in T_c by about 4°C. The results of this study also showed that six times repeated processing of PP/rapeseed straw composites had no significant effect on the crystallization point of polymer matrix. According to DSC data, also the melting points of all samples studied were comparable and fell in the range 166–167°C.

**Figure 2.** Crystallization curves of samples.

Another parameter determined from DSC data and characterizing the kinetics of crystallization is the half-time of crystallization. For all composites, the half-times of crystallization $t_{0.5}$ were much shorter than that measured for unfilled polypropylene. This observation confirms the nucleating effect of rapeseed straw in the polymer matrix, suggested by the increase in the crystallization point. The half-times of crystallization determined for the composites of PP and modified rapeseed straw are similar to those of the composites with native rapeseed straw. It is an interesting result which is in contrast to that obtained for the systems of PP/wood.³⁴ For the latter composites, it was established that esterification of wood by a number of organic acid anhydrides led to a significant decrease in the nucleation ability of wood. The results obtained for the composites of PP with rapeseed straw are in excellent agreement with the findings reported on the nucleation abilities of fillers of semicrystalline polymers and confirm the complex character of crystallization processes in the composites with lignocellulose fillers. According to literature results, chemical modification of fillers can be responsible for reduction of the nucleation abilities as in Refs. 31,32,35–37 or quite the opposite for their increase as in Refs. 32 and 38.

Another interest in this study was the effect of the composites reprocessing on the process of PP crystallization. It was found that multiple reprocessing had a considerable influence on the kinetics of crystallization. After six times repeated processing, the half-times of crystallization were much smaller ($t_{0.5} = 102$ – 107 s) than that of the composite not subjected to reprocessing ($t_{0.5} = 125$ – 130 s). Similar half-times values were observed for the composites containing native rapeseed straw and chemically modified rapeseed straw. These results indicate that reprocessing is responsible for increased nucleating activity of the polypropylene matrix. An attempt to explain this interesting finding was made on the basis of microscopic observations and EPR results, discussed below.

Optical Microscopy Analysis

Figure 3(a–d) presents microscopic images of the composites studied. Optical microscopy observations were made to analyze the morphology of composites of polypropylene with rapeseed straw subjected to non-isothermal crystallization. The images reveal significant differences in the size of particles of the lignocellulose filler used between the composite subjected to multiple reprocessing [Figure 3(b,d)] and those subjected to single processing [Figure 3(a,c)].

In the samples subjected to six times repeated processing [Figure 3(b,d)], the particles of rapeseed straw are smaller and their content in a unit volume of the composite is much higher. The changes caused by multiple reprocessing are caused by the filler particles comminution under the effect of multiple application of shearing forces and plasticizing temperature. The arrows in the images point to the position of the filler in the matrix. The microscopic observations are in excellent correlation with the DSC results. An increase in the number of the filler particles as a result of the comminution of larger ones can be responsible for increased number of active centers, which affects the process of PP matrix crystallization. The composites with a larger

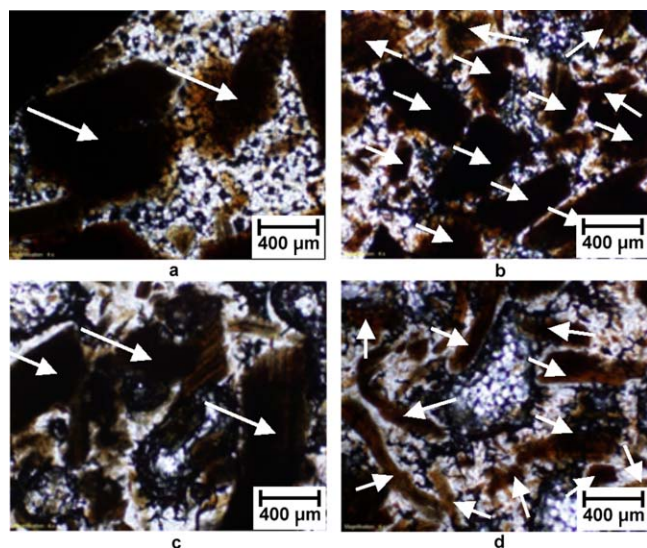


Figure 3. Optical microscopic images of the composites: (a)—CN-1, (b)—CN-6, (c)—CM-1, (d)—CM-6 (arrows indicate the filler distribution in the matrix), amplification— $\times 60$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

number of smaller size filler particles were found to show shorter half-times of PP crystallization, which testifies to an increased nucleating activity of the filler subjected to multiple reprocessing.

The influence of size of particles filler on the nucleation process was described by Deville *et al.*³⁹ They proposed that the nucleation stage is controlled by the particle size, the surface of the ceramic particles acting as nucleation sites. The smaller particles size leads to a larger surface area and a higher number of nucleation sites.

The results from this study are in agreement with those reported by Bourmaud and Baley,¹¹ who analyzed the effects of multiple processing of PP composites with hemp or sisal fibers. These authors based their conclusions on measurements of the temperature of crystallization and degree of crystallinity only. Addition of vegetal fibers to polypropylene resulted in an increase in T_c . This can be explained by the effect of the nucleating ability of lignocellulosic materials. Moreover, according to these authors, recycling had no particular effect on T_c as its value remained stable after a number of reprocessing cycles.

EPR Analysis

EPR study was undertaken to determine the number of free radicals in the composites studied and to compare the samples after single and multiple processing. The single EPR resonance line of $g = 2.004$ and the linewidth $\Delta B_{pp} = 9 \pm 0.5$ G was recorded for all samples studied. Additionally, broad unresolved and superimposed lines were observed for all samples (rather small for native), especially for the composites (Figure 4). Similarly as in the previous work⁴⁰ we assigned these lines to paramagnetic impurities (presumably Fe^{3+} , Mn^{2+} , Cu^{2+} , etc.) which entered the straw and the composites upon chemical treatment and/or recycling process.

In the EPR spectroscopy, the paramagnetic sites of transitions ions are described among others by the value of g -factor.^{41,42}

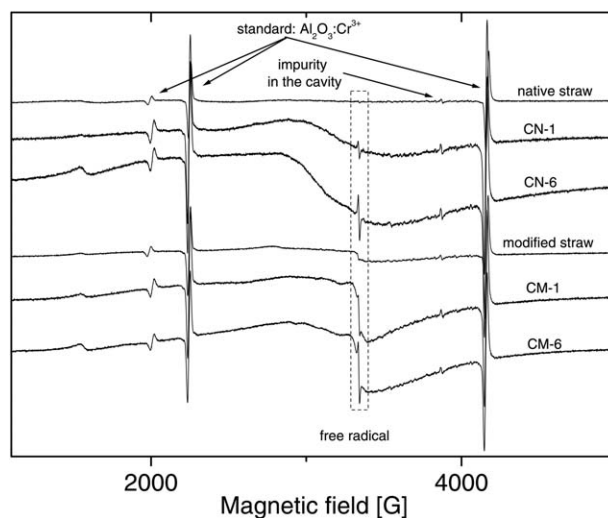


Figure 4. EPR spectra of native and modified rapeseed straws and composites CN-1, CN-6, CM-1, CM-6, respectively. It should be noted that the amplitude of the spectra is normalized because of differences in the mass of the samples.

The resonance line of $g \sim 4.26$ can be assigned to Fe^{3+} ions located in the low symmetry site but the resonance line of $g \sim 2$ is observed for the Fe^{3+} ions located in a site of higher symmetry. Similarly the resonance line with $g \sim 2$ can be assigned to the Mn^{2+} site. The additional unresolved and superimposed resonance lines $g > 2$ may indicate the presence of Cu^{2+} impurity. The concentration of paramagnetic ions was estimated to be in the range $10^{18} \div 10^{19}$ per 1 g.

Figure 5 presents the concentration of free radicals in the composites obtained from polypropylene and unmodified or modified rapeseed straw, before and during subsequent steps of recycling. Concentration of free radicals in the native sample of

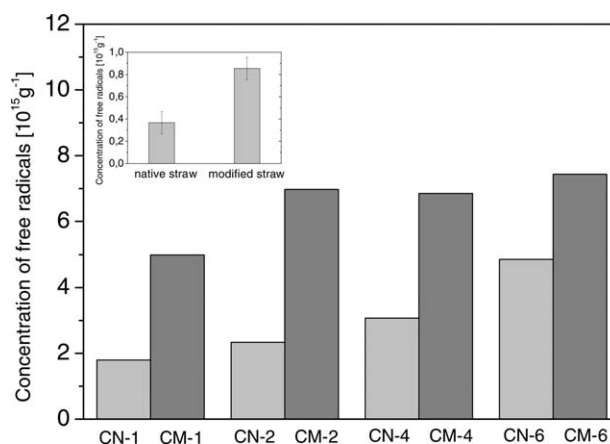


Figure 5. Concentration of free radicals in the composites obtained from polypropylene and unmodified or modified rapeseed straw recorded before and during subsequent steps of recycling process. The light gray and dark gray bars denote unmodified and modified filler, respectively. The insert shows the concentration of free radicals in the samples with native rapeseed straw (unmodified filler) and samples with rapeseed straw treated with acetic acid anhydride (modified filler). It should be noted that the number of free radicals refers to the mass of the rapeseed straw.

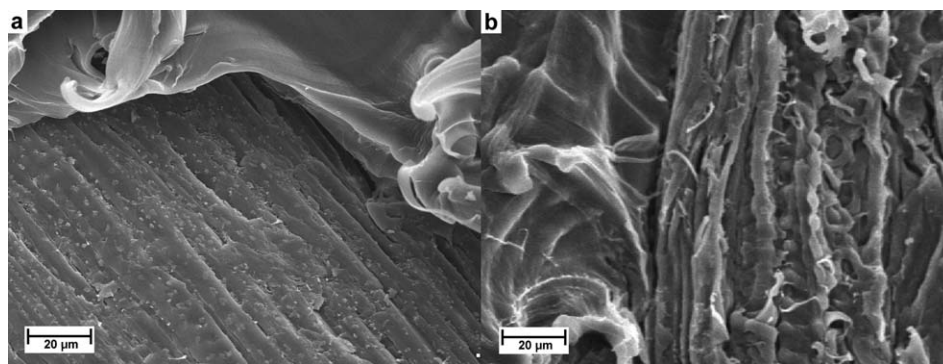


Figure 6. SEM images of composites of PP with unmodified (a), and modified (b) rapeseed straw, not subjected to reprocessing.

rapeseed straw (unmodified filler) and in the rapeseed straw treated with acetic acid anhydride (modified filler) was inserted in the same figure.

A certain amount of free radicals in the native rapeseed straw is frequently observed as a result of generation of radicals during the plant growth, which has been repeatedly reported.⁴³ After mercerization and chemical treatment, the number of free radicals increases, which has been also observed in our previous studies.⁴⁰

The number of free radicals in all composites is visibly greater with respect to their number in rapeseed straw, also before the recycling process. For the composites with modified filler, the number of free radicals reaches a maximal level already after the second cycle of reprocessing and further steps of recycling do not cause a further increase in their number. In the composites formed with unmodified filler, the number of free radicals is distinctly smaller in contrast to that in the samples with modified filler and gradually increases after subsequent reprocessing.

Upon mercerization, some extraction of lignocellulose materials and phase transition from cellulose I into cellulose II take place, so a weight loss and changes in the morphologies of fibers were observed.⁴⁴ Acetic anhydride treatment leads to further modification of fiber surface, which becomes hydrophobic so that the adhesion between the fibers and the polymer matrix increases.⁴⁵ Both modifications result in generation of free radicals.⁴⁶ Similarly, thermal and mechanical treatment of composites which contain lignocellulose materials may result in breaking of chemical bonds, filler, and polypropylene main-chain scissions and free radicals generation.^{26,47}

Mechanical properties of the composites largely depend on the interaction/adhesion between the fiber and the polypropylene matrix. One of the conditions favoring enhanced adhesion is the persistence of reactive species, such as free radicals.⁴⁸ In fact, besides chemical modifications, the radiation treatment of cellulose fibers and polypropylene produces the free radicals and peroxy groups in both components, stimulating crosslinking on the interface and consequently ensuring better adhesion. In the high temperature process of composite formation a large number of peroxy groups generate peroxy radicals and together with the trapped free radicals produced radical–radical crosslinking between polypropylene and fibers.

As a result, the adhesion increases and hence an improvement in mechanical properties is observed.⁴⁹

In our study, the number of recorded free radicals is much higher in the composites containing modified filler in contrast to those with unmodified one. Upon the chemical modification and recycling process, the free radicals may be generated in the bulk of straw and polypropylene matrix as well as on the surface, which leads to radical–radical crosslinking. In addition at high temperatures, part of free radicals may migrate to the surface; however, some amount of free radicals still remain trapped in the bulk of the filler and the crystalline regions of polypropylene. Taking this into account, we suppose that the number of stable free radicals in the composites studied recorded by EPR is associated with the interface properties and the degree of adhesion between straw and polypropylene matrix.

Conversely, the active species such as free radicals are responsible for degradation of the composites. In fact, during the recycling process, polypropylene is very sensitive to chain scission and oxidative degradation which can be competitive to crosslinking. The oxidation and degradation mechanism of polypropylene have been the subjects of many papers. It is well established that the radical chain reaction is initiated by the hydroperoxide group.^{50,51} The degradation of PP is preferentially performed by chain scission, resulting in the shift of the molecular weight distribution towards the low molecular weight side according to the type and extent of degradation.^{52–54} Also, Shengying *et al.* noted that in the process of polypropylene degradation, the chain scission is kinetically preferred.⁵⁵ Sequentially, the new carbon-centered radical can re-enter the oxidation cycles and lead to further chain scission, possibly involving the self-termination reaction to the extent causing severe degradation.⁵⁵ Moreover, the formation of short life time radical by the extruder action was experimentally observed.^{56–58}

As follows from EPR results, the composites subjected to multiple reprocessing contain much more free radicals than the systems not subjected to recycling. This observation suggested a relation between the number of free radicals and the process of crystallization in the polymer–filler composite. After reprocessing, the composite samples were found to show a higher number of free radicals and higher nucleating activity (shorter half-time of

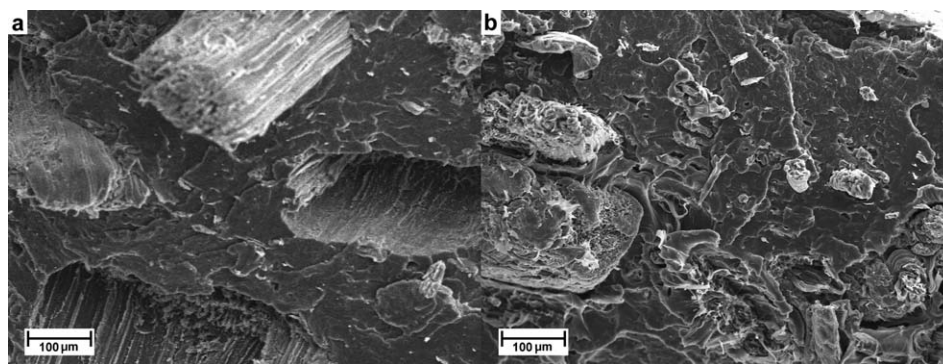


Figure 7. SEM images of composites of PP with unmodified (a), and modified (b) rapeseed straw, after multiple reprocessing.

crystallization). A reasonable explanation is that free radicals present in the polymer matrix and the filler can be responsible for increased mutual interactions thus increasing the process of crystallization. Moreover, the increased concentration of free radicals after reprocessing can indicate shortening of polymer chains, which may induce increased nucleating activity and rate of crystallization. Studies aimed at verification of this supposition are presently in progress and will be presented in a separate paper.

Morphology Analysis

Properties and performance of composites made of polymer matrices and fillers are to a substantial degree related to the interface adhesion between these two components. Figure 6(a,b) shows SEM images of composites of PP with unmodified and modified rapeseed straw, not subjected to reprocessing.

The effect of rapeseed straw modification on the composite structure is well seen; in Figure 6(a) the components show poor adhesion, while in Figure 6(b) their adhesion is much better. The images also reveal differences in the surface character of the modified and unmodified filler. After modification the filler surface is more rough and thus can increase the surface area and final mechanical properties of the composites. These changes are the subject of a separate paper concerned with macroscopic properties of reprocessed composites.

Figure 7 shows the SEM images of the composites studied after multiple reprocessing. Figure 7(a) shows a SEM image of a CN-6 composite; despite multiple reprocessing the matrix and the filler are easily distinguishable. The pores visible on the surface of cleavage indicate poor adhesion between the components.

The SEM image of CM-6 sample shown in Figure 7(b) indicates that in this sample the adhesion between the components is much better and the composite structure is more uniform. Results of this study are in agreement with literature data according to which chemical modification of the lignocellulose filler brings about an improvement in polymer–filler adhesion.^{59–61} Moreover, the SEM observations can be correlated with EPR results. The composites with modified rapeseed straw are characterized by better interface adhesion than those with unmodified straw. Because of this better adhesion, upon processing or reprocessing, the displacement of modified filler in the

molten polymer matrix can generate greater shearing forces between the composite and the wall of the mold or extruder's head, leading to generation of a higher number of free radicals.

The above supposition will be verified in the study on other composites with different fillers subjected or not to a number of chemical modifications. A continuation of this study will be concerned with dielectric and mechanical properties of the composites and their flammability.

CONCLUSIONS

Results obtained in this study revealed interesting relations between the composite properties and their recycling. Multiple reprocessing of the composite materials was found responsible for increased nucleating ability as indicated by shorter half-times of crystallization. These changes can be related, among others, to the size of the filler particles reduced as a consequence of multiple reprocessing, as illustrated by microscopic observations. The composite samples subjected to multiple reprocessing are characterized by much smaller filler particles which is explained by multiple action of shearing forces. Such a change can lead to a much greater nucleating activity. An interesting observation is that chemical modification of the filler improved the interface adhesion between the components but had no significant effect on the kinetic parameters of PP crystallization in the composite materials.

As follows from the EPR study, the composites subjected to multiple reprocessing show a greater content of free radicals. An important and hitherto not reported observation is a relation between the number of free radicals and in the process of PP crystallization in the polymer/filler composite. The composites subjected to reprocessing have higher content of free radicals and show higher nucleating activity manifested as a shorter half-time of crystallization. A possible explanation is that the increased number of free radicals in the polymer matrix and lignocellulose filler leads to their increased mutual interaction, which can contribute to increased rate of PP crystallization. Moreover, the EPR measurements revealed differences in the content of stable free radicals between modified rapeseed straw/polypropylene composite and native filler/PP one.

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