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Thermal and Dynamic-Mechanical Characterization of Rice-Husk Filled Polypropylene Composites

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Abstract: Natural fiber-filled polymer composites have attracted great interest due to increasing environmental concerns and their low costs. In this study, the properties of rice husk flour-filled polypropylene (PP) were analysed in view of the large quantities of this agricultural product available as residue in Brazil. The rice husk flour (RHF) was characterized by SEM and particle size distribution. The properties of the composites were studied by MFI, DMA, DSC and TGA analyses. A commercial PP modified with maleic anhydride (MAPP) was used as coupling agent. It was verified that RHF decreased the MFI of the composites and that the coupling agent decreased it even more. The efficiency of MAPP was confirmed by the high storage modulus and high loss factor of the coupled composites.

Keywords: rice husk, polypropylene, DMA, thermal properties, mechanical properties, thermal degradation.

Introduction

The incorporation of various types of fillers into polymer matrices is an interesting route to produce polymer composites with different properties. For example, the mechanical properties of PP can be improved by the addition of glass fibers.[1] Over the past two decades organic fillers have becoming strong competitors to this traditional inorganic filler due to their low densities, very low cost, non-abrasiveness, possibility of high filling levels, recyclability, biodegradability and renewable nature.[2] Since many polymer matrices (as is the case of polypropylene) as well as most natural fillers are low dense materials, composites based on them usually show excellent specific properties.[3] Various types of lignocellulosic fillers have been exploited including wood flour, henequen, kenaf, hemp, sisal, flax, rice husk, jute and others.[2,4,5]

Rice husk (RH) is one of the major agricultural residues produced as a byproduct during the rice milling process. Usually it has been a problem for rice farmers due to its resistance to decomposition in the ground, difficult digestion and low nutritional value for animals.[6] Most of the RH produced is either used as a bedding material for animals, burned or used for land filling. According to FAO statistical data the annual world rice production was approximately 600 million tons in 2000, of which 20% was wasted as RH.[7] The Brazilian rice production has been in the order of 10 million ton/year and Rio Grande do Sul (the southernmost state of Brazil) is responsible for ~50% of this production.[8] Therefore, the development of new polymer composites filled with RH turns out to be a very interesting approach.

Composites of natural fibers and thermoplastics are finding places in many industries, particularly in the automotive industry.[9] The automotive industry in Brazil is one of the largest of the world and it is continuously demanding for more and new materials that show low density and low cost, being environmentally friendly. In this sense the study of new polymer composites containing easily available and

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renewable natural fibers such as RH is highly desirable.

RH contains cellulose (35%), hemicellulose (25%) and lignin (20%). After thermal decomposition its ash content (~17%) is mainly composed by silica.[10] In this sense it is a special lignocellulosic material since its contents of lignin and hemicellulose are lower than those found in most similar natural fillers. For this reason, rice husk-filled polymers can be processed at higher temperatures than wood polymer composites, which have thermal stability problems at temperatures above 200 °C. RH is considered stable until 250 °C.[11]

However, PP chains are nonpolar and the RH filler is a polar material. So, for better interaction between both incompatible materials, the presence of a coupler is envisaged. Even though new alternatives are being currently studied maleic anhydride-grafted PP (MAPP) has been the most common coupling agent used to improve interfacial adhesion among bio-fillers and apolar thermoplastic matrices.[12,13]

The objectives of this study were to develop basic information on the influence of rice husk on the thermal and viscoelastic properties of PP composites and to evaluate the effect of the addition of a coupling agent on such properties. Because fiber-reinforced thermoplastic composite materials can undergo various types of dynamic stressing during service, mainly in automotive products, studies on the dynamic mechanical properties of these materials were also performed.

Experimental

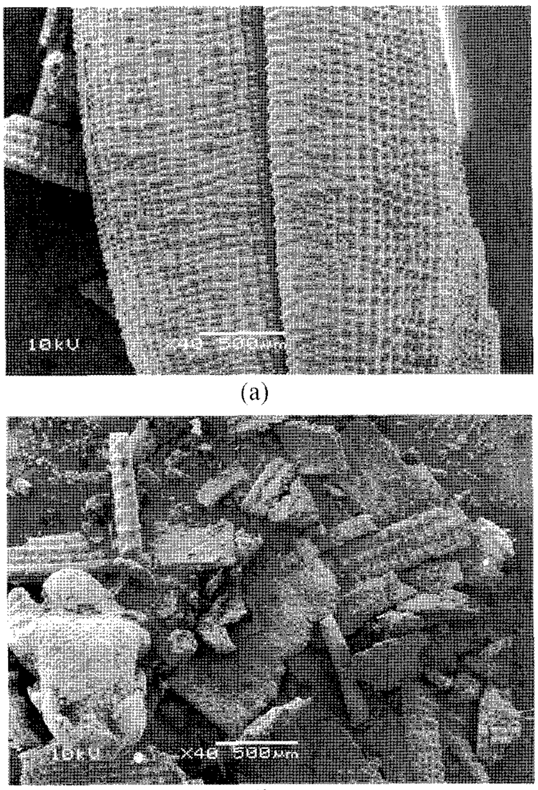
Materials. PP was supplied by BRASKEM (Triunfo, Brazil) in the form of pellets with a density of 0.91 g/cm^3 and a melt flow index of 3.5 g/10 min (230 °C/2,160 g). RH was supplied by Engenho Meirebe (Eldorado do Sul, Brazil). It was previously ground and screened. The rice husk flour obtained (RHF) was oven dried at 80 °C, for 24 h, at 30 mm Hg, to adjust its moisture contents and then it was stored over a desiccant. Maleated polypropylene (MAPP) was obtained from Uniroyal Chemical, Inc., in the form of Polybond-3200TM.

Preparation of the Composites. A laboratory-size, conical corotatory twin-screw extruder Haake, Model Rheomex CTW 100p, was employed for compounding RHF and PP. The screw speed was 40 rpm and the temperature range varied from 170 to 190 °C. Four levels of filler loading (10, 20, 30 and 40 wt%) were used. The coupling agent MAPP was added with concentration of 0.5, 1.0, 1.5 and 2.0 wt% with respect to the mass of the polymer matrix. After pelletizing the composites were compression molded at 2.5 bar. The hot press procedure involved preheating at 190 °C for 10 min followed by compressing for 4 min at the same temperature.

Characterization. Scanning electron microscopy (SEM) was performed in a JEOL microscope, Model JSM 6060, using gold-coated samples. The composites were cold-fractured for SEM analysis. Melt flow indices (MFI) were determined using a Universal Ceast V2.6D melt-flow indexer according to ASTM 1238 (2.16 kg, 230 °C). Differential scanning calorimetry measurements (DSC) were carried out under nitrogen with a Thermal Analyser Instruments Universal 2010 V4.4E. The heats of fusion were normalized on the basis of the weight fraction of PP present in the sample. PP crystallinity (X_c) was calculated as the ratio of the measured ΔH to the specific heat of fusion of 100% crystalline iPP, taken as 190 J/g.[14] The DSC measurements were performed from 25 to 200 °C, at 10 °C/min. Thermogravimetric analysis were carried out using a thermoanalyzer TA Instruments, Model 2050 V.5 4. Samples of about 11 mg were scanned at a heating rate of 20 °C/min, under a N_2 flow. The dynamic-mechanical properties were studied using a Perkin–Elmer DMA, Model 2980 V1.5B, in N_2 atmosphere, heating rate of 5 °C/min, 1 Hz. The tests were performed using a three point bending-rectangular measuring system.

Results and Discussion

Characterization of the Filler. The morphology of the RH and of RHF obtained after milling and screening was observed by means of SEM images (Figure 1). It was verified that the external surface of the pristine rice husk was



(a)

(b)

Figure 1. SEM images of: (a) rice husk (RH); (b) rice husk flour (RHF).

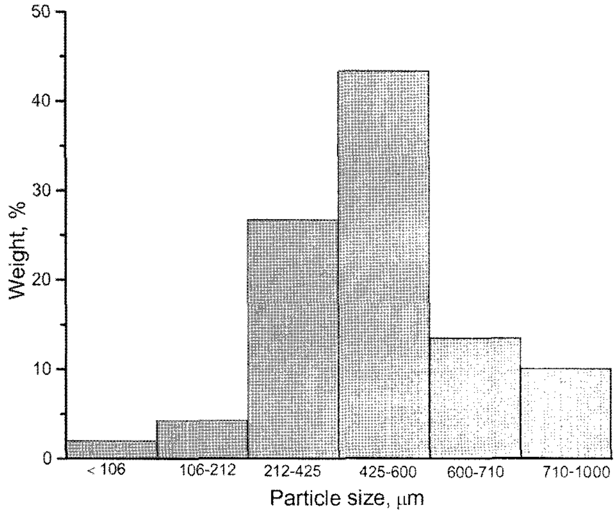


Figure 2. RHF particle-size distribution.

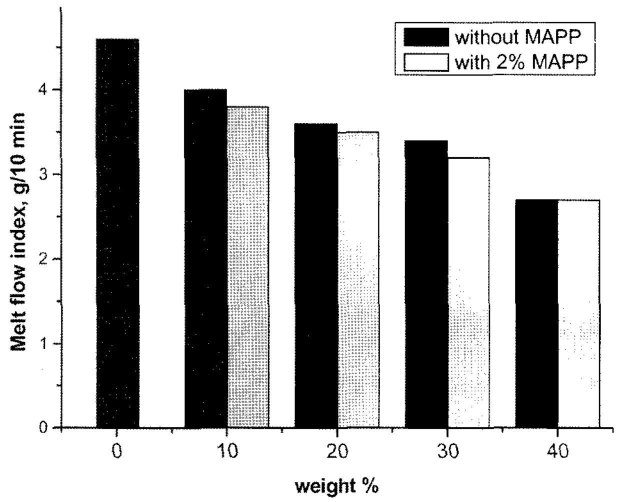


Figure 3. Melt flow index of the composites.

very rough, showing many aligned lumps (Figure 1(a)). After milling the size of the particles was strongly reduced but a large distribution of shapes and sizes was observed (Figure 1(b)). Some particles with smooth surfaces were present, probably showing the internal surfaces of the parent rice husk.

The size distribution of the RHF particles was determined by means of mass weight of screened samples (mesh sizes from 16 to 150). The results are shown in Figure 2. It can be observed that most of the particles (~70%) showed sizes from 212 to 600 micrometers.

Characterization of the Composites.

Melt Flow Index (MFI): The effect of RHF concentration on the melt-flow behavior of the composites is shown in Figure 3. It was observed that MFI decreased with RHF concentration. According to Joseph *et al.*[15] the presence of fibers restricts the flow of the polymer matrix and this restriction increases with fiber loading. This can be explained by

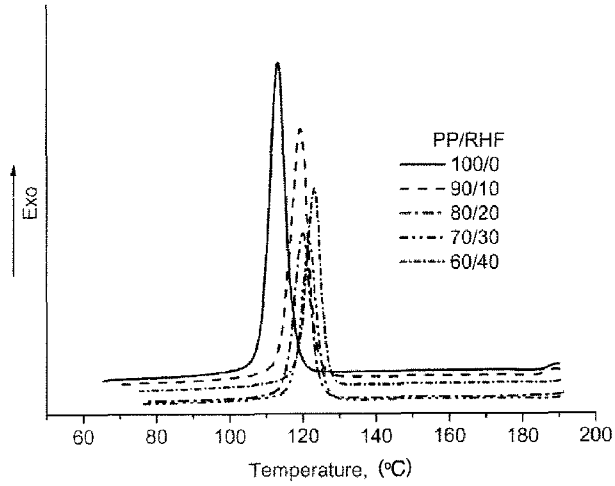


Figure 4. Cooling thermograms of the composites.

Table I. Thermal Properties Determined by DSC

PP (%)	RHF (%)	T_m (°C)	ΔH (J/g PP)	X_c (%)	T_c (°C)
100	0	163	93	44	113
90	10	164	91	48	119
80	20	164	111	59	120
70	30	164	111	58	122
60	40	164	99	52	123

the reduction of the macromolecular flow in the vicinity of the dispersed particles. Addition of MAPP was observed to show a tendency to lower even more these values. Such behavior suggests the establishment of new interactions between the filler and the polymer matrix thus diminishing the PP chains and RHF particles slippage.

Crystallization and Melting Behavior (DSC): The presence of RHF showed significant effects on the cooling behavior of the composites. The DSC thermograms obtained during cooling are shown in Figure 4. Only one exothermic peak was registered for all the samples. For PP processed without RHF the crystallization peak was observed at T_c=113 °C while for the composites these exothermic peaks shifted to higher temperatures in all cases. The determined T_c values are shown in Table I. The higher T_c values of the composites indicate that the crystallization is favored in the presence of the rice husk particles. The T_c increase can be considered to be due to the nucleation effect of the rice husk: fibers act as sites for heterogeneous nucleation thus inducing the crystallization of the matrix.[1,16]

Figure 5 shows the heating thermograms of selected samples obtained from the second heating range. For both neat PP and PP/RHF composites only one single endothermic peak was observed at similar temperatures (near 164 °C), corresponding to the melting of the α-crystalline phase of the PP sequences. These results indicate that the presence of

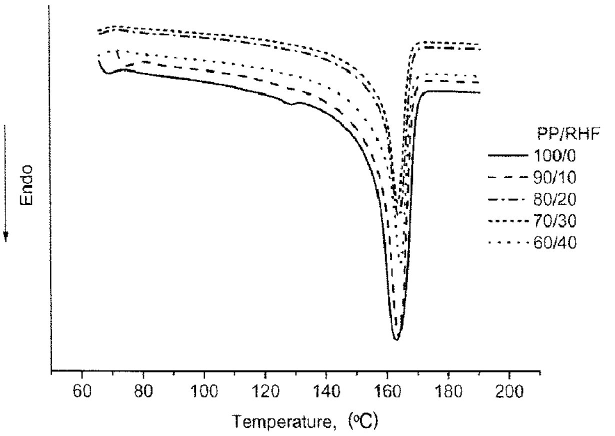


Figure 5. Heating thermograms of the composites.

RHF did not significantly affect the crystalline structure of the polymer. The area of the melting peak diminished with increasing RHF level since PP concentration in the composites lowered. However after normalizing the melting enthalpy with respect to the fraction of PP in the composites (Table I) it was possible to verify that the melting peak showed a significant increase. Calculations based on the extrapolated melting enthalpy for a 100% crystalline sample lead to the degree of crystallinity, X_c, reported in Table I. These results confirmed the behavior observed during heating that the filler favors the crystallization of the polymer matrix probably due to the creation of nuclei on the filler surface that induce the formation of a transcrystalline layer.[17]

Addition of MAPP did not significantly affect the thermal behavior of the composites studied by DSC. This result has been already observed by other researchers.[18]

Thermogravimetric Analysis (TGA): Thermogravimetric analyses have been extensively used to study the thermal stability of polymer composites. This is a very important issue for natural fiber-based composites since these materials commonly degrades early thus limiting its maximum temperature of processing and using. Figure 6 shows the thermal degradation pattern of RHF, PP and its composites, determined under nitrogen. Out of the plotted curve, RHF showed a low thermal event below 100 °C corresponding to dehydration of the sample. The mass loss in this step was around 3.5 wt%. The effective thermal degradation of the rice husk constituents begins above 200 °C and refers to bonds cleavage of hemicellulose, cellulose and lignin, in this order.[18] It can be observed that rice husk presented a high residual mass at the end of the experiment, around 29%. Even considering that the analysis was performed in nitrogen atmosphere, this was an especially high value and it was related to the high silica content of rice husk.[18]

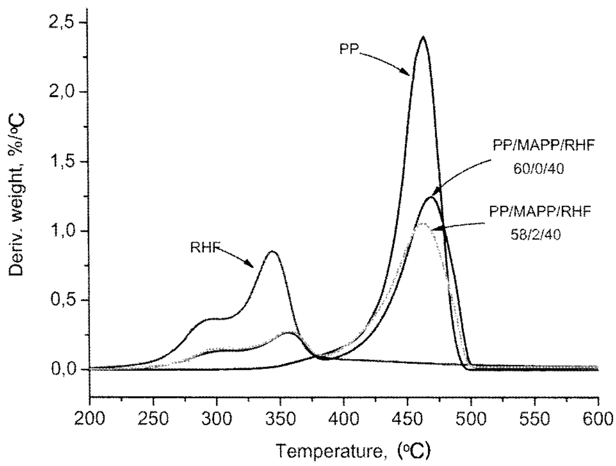


Figure 6. DTG curves of the composites.

It is possible to verify that the thermal decomposition of PP homopolymer occurs in a single step, beginning around 320 °C, with maximum at about 462 °C, leaving a very low residual mass (0.7%). This low residual mass indicates that most of the hydrogen and carbon atoms present in PP chains forms volatile compounds during the analysis. For rice husk-filled polypropylene composites, it can be seen that the degradation begins below 300 °C, accompanying the profile of the rice husk alone. The temperature of the maximum degradation rate of PP in the composites seems to occur at a slightly higher temperature than that of the pristine polymer in most compositions, suggesting that the filler is inducing some kind of thermal stabilization on PP molecules. No definitive tendency of the effect of MAPP was observed on the temperature of maximum degradation rate of PP.

Dynamic Mechanical Analysis (DMA): Increased adhesion among natural fiber/polymer composites is shown to significantly affect its dynamic mechanical properties.[19,20]

Figure 7(a) shows the temperature dependence of the storage modulus (E') for unfilled PP and for the non-coupled composites. In all the systems it can be verified that the storage modulus drops upon increasing temperature due to the increased segmental mobility of the polymer chains with heating. Increasing the RHF content a significant improvement of stiffness was verified. This is the expected effect caused by the addition of more rigid fillers into semi-rigid polymer matrices.

The effect of MAPP on the storage modulus curves is illustrated in Figure 7(b). These patterns reveal the differences between the pure polymer matrix and both composites, coupled and uncoupled. According to Figure 7(b) it can be observed that the storage modulus of the MAPP-treated composite is the highest one. This result demonstrates the effectiveness of MAPP in improving the adhesion among the polymer matrix and the filler.

Representative tanδ curves are represented in Figure 8. All curves exhibit two relaxation peaks in the range of temperature analyzed. Such peaks are located respectively in the vicinity of 20 °C and 80 °C. It is important to point out that the temperatures of both peaks are strongly dependent on the applied heating rates.

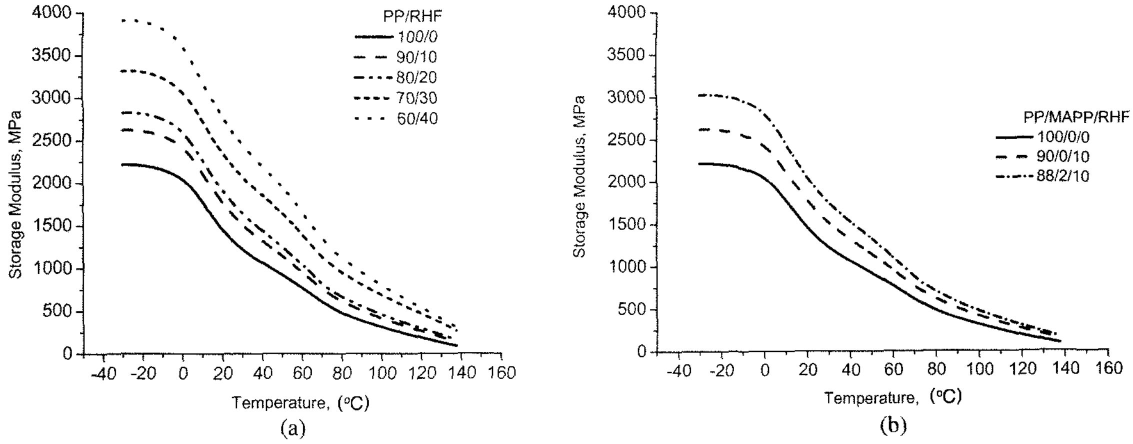


Figure 7. Storage modulus behavior of the composites.

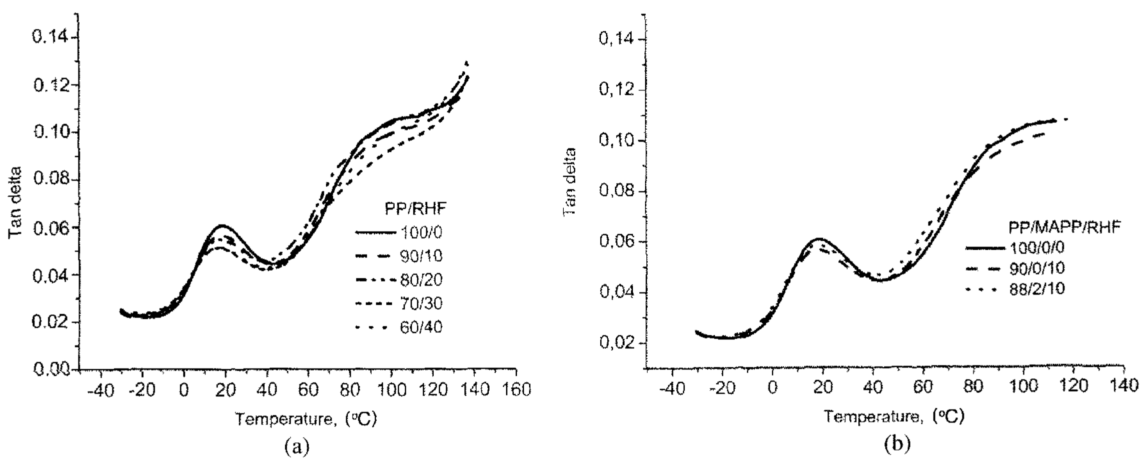


Figure 8. Tan δ behavior of the composites.

The low-temperature peak is related to the glass-rubber transition of the amorphous polymer fractions and is taken as the glass transition temperature (T_g).[21,22] It can be seen that the area under these peaks decreases with RH content and this is easily related to the decreasing PP concentration in the composites. On the other hand, the tan δ curves can be a measure of the damping properties of the materials. Although the composition of the systems is the key parameter in determining the damping properties other factors such as the interaction among the dispersed phase and the polymer matrix will also affect damping. A slight increase in tan δ values has been found in the coupled composites in the region of the T_g transition. Although this is only a marginal effect it can be related to the interfacial action of MAPP that improves the damping properties of the materials.

The high-temperature peak corresponds to the α transition related to the PP crystalline fractions.[21] Two different mechanisms are proposed to explain this relaxation: a) mobility of rigid amorphous molecules entrapped as defects in the crystals[23] and/or b) lamellar slip and rotation of the crystals.[21] In our systems it was verified that the α transition peaks of the coupled composites were higher than the non-coupled ones. Some authors have proposed the existence of enhanced transcrystallinity around the fibers in the coupled composites that could be responsible for this effect.[21,24]

The PP glass transition temperature determined from the tan δ curves showed a marginal decreasing in the presence of RHF, from 19 to 17 °C. The amorphous phase of the polymer is responsible for the glass-rubber transition and it is the place where the reinforcement particles must be located.[22] Therefore, the amorphous polymer chains are supposed to show high segmental mobility when they contain the dispersed particles.

Conclusions

PP composites were prepared with up to 40 wt% RHF. Lower MFIs were found in the composites as compared to the polymer matrix. The degree of crystallinity and the crystallization temperature of the matrix were shown to increase in the composites, as well as the temperature of the maximum degradation rate of PP and the storage modulus of the materials.

The results presented in this work indicate that it is possible to enhance the properties of rice husk-filled PP through addition of MAPP. The interfacial effect of the maleated PP was seen on the melt flow index of the composites as a result of PP-chains slippage restriction. The presence of the coupling agent did not affect the thermal properties of the composites. However, the dynamic-mechanical properties of the materials, naming storage modulus and loss modulus, were improved after the addition of MAPP showing that better interactions among the matrix and the dispersed phase were accomplished.

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