

UTILIZATION OF MICROCRYSTALLINE CELLULOSE AND RICE-HUSK CELLULOSE AS REINFORCEMENT IN POLYPROPYLENE COMPOSITES

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Abstract - Rice husk is an important residue from the agro-industry. In this study, pure cellulose was extracted from rice husk and added to polypropylene in a melt mixer. The properties of these PP/RHC composites were compared to the properties of PP/commercial microcrystalline cellulose composites (PP/MMC). The cellulosic fillers were treated with vinyltriethoxysilane (VTES) with the objective of improving adhesion. PP modified with maleic anhydride (PPMA) was also added. In our work, the cellulose was isolated from rice husks using environmental friendly techniques. In composites containing silane, MCC and RHC were first treated with VTES with the objective of promoting filler dispersion and compatibility. Concentrated PP/cellulose masterbatches were prepared using xylene. In the next step, the masterbatches were diluted with PP using a mixer Haake. Dynamic-mechanical analyses showed that the use of 5% cellulose did not show improvements in the storage modulus (E'), even after silanization or PPMA addition. However, increasing the cellulose content to 10% increased E' was around 250% percent at ambient temperature.

Keywords: *Microcrystalline cellulose, rice husk cellulose, composites, coupling agents, polypropylene.*

Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the current research on new materials, products, and processes. Biodegradable plastics and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets today dominated by products based exclusively on petroleum feedstock [1]. Cellulosic fibers have been used as cost-cutting fillers in plastic industry. Among the various factors, the final performance of the composite materials depends to a large extent on the adhesion between the polymer matrix and the reinforcement and therefore on the quality of the interface [2].

Microcrystalline cellulose (MCC) from various origins has been widely used in medical, food and cosmetic industrial applications. It has been utilized for example as a binder and filler in medical tablets, supporter for various biologically active substances, stabilizer in various suspensions, controller of flow and fat replacer in food [3].

Rice husk (RH) is one of the major agricultural residues generated as a byproduct during the rice milling process. The Food and Agriculture Organization of the United Nations (FAO) forecasts that the global rice production stood at around 466 million tones in 2010/2011. About 23% of this amount consists of RH. The Brazilian rice production has been in the order of 12 million tone/year and Rio Grande do Sul (the southernmost state of Brazil) is responsible for 60% of this production. Most of the RH produced is either used as a bedding material for animals and discarded in land fillings or simply burned in the fields leading to air and soil pollution. The expressive content of near 20% silica in RH and, after burning, more than 90% silica in RH ash have stimulated extensive research which suggested the potential use of RH and its ash as sources of inorganic chemicals [4].

Polypropylene (PP) is one of the most important and widely used polyolefins. Its low density, low production costs, design flexibility and recyclability make it a popular choice as matrix material. PP is hydrophobic, leading to compatibility issues when fillers with polar surfaces, such as cellulose, are used. This can be resolved by incorporating functionalized PP, such as PP grafted with maleic anhydride, or through the addition of other coupling agents. The similarity of PP and PP-g-MA structures permits the occurrence of segmental co-crystallization that is desirable for cohesive coupling, while the carboxylic anhydride groups can provide covalent bonding to the surface of a dispersed phase of cellulosic fibres [5]. Other well-studied coupling agents are based on alcoxysilanes, which are mainly used for hydroxyl-containing fillers, such as glass fibers. As cellulose molecules show many free hydroxyl groups on its surface, the interaction among these groups and the reactive alcoxyl groups of the VTES coupling agent is expected to decrease the hydrophilic character of MCC and RHC.

In the present work we propose the use of rice husk as a new source of cellulose to prepare PP composites. The RHC is obtained using a totally chlorine-free technique (TCF) [4]. For comparison, PP/MCC composites were also prepared. PP-g-MA and VTES were used as coupling agents. The composites were characterized with respect to its thermal stability, morphology and thermomechanical behavior to evaluate the impact of the compatibilisation processes on the composites performance.

Experimental

Materials

MCC (Quimsul), VTES (Wacker Chemie), PP (0.91 g/cm³, MFI = 3.5 g/10 min, Braskem), PPgMA (Polybond 3002, Chemtura), hexane (Fmaia, Brazil), ethanol (Fmaia, Brazil), sodium hydroxide (Labsynth, Brazil), hydrogen peroxide (CAQ Quimica, Brazil), nitric acid (Fmaia, Brazil), acetic acid (CAQ Quimica, Brazil), tetra-acetylenediamine (TAED) (Acros Organics, New Jersey, USA), xylene (Dinâmica Química), and toluene (Quimsul) were used as received. Rice husks (Engenho Meirebe, RS) were treated according to the procedures described in Methodology.

Methodology

Isolation of cellulose from rice husk: The procedure has been already described [4].

Silane treatment of fibres: MCC and RHC (25 g) were dispersed in toluene (250 mL) and stirred for 1.5 h at ambient temperature. Appropriate amounts of VTES were added to achieve a concentration of 1% v/v. The dispersions were subjected to ultrasound treatment to ensure fibres were completely coated with the coupling agent. Fibres were treated for 10 min at 25°C, with a frequency of 20 kHz. After this, the toluene was left evaporate under ambient conditions. The treated celluloses were dried in a vacuum oven for 1 h at 100°C to remove any residual solvent. Dried samples (MCC-Si and RHC-Si) were stored in desiccators (0% relative humidity).

Preparation of masterbatches: Masterbatch composites of PP + MCC-Si or RHC-Si were prepared with a mass fraction of 50:50. PP (15 g) was added to xylene (300 mL) and stirred for 3 h at 130°C, until the polymer was completely dissolved. MCC-Si and RHC-Si were added and the solution stirred for a further hour. To ensure the adequate mixing, the dispersion was submitted to ultrasonic disruption (10 min, 25°C, 20 kHz). Films were cast onto glass plates and kept at ambient conditions to allow the xylene to evaporate. Masterbatch films for subsequent use were prepared using a heated press. Films were pressed between platens, heated to 185°C, held for 3 min and then cooled slowly to ambient temperature. The films were stored in sealed plastic bags at ambient conditions.

Preparation of composite films: PP composites containing 5% w/w MCC-Si or RHC-Si and some containing 2.5% w/w PPgMA were prepared by diluting the concentrated masterbatch with appropriate amounts of PP. A Haake Rheometer 600p mixer was used to compound the materials. Roller-blade type rotors at 50 rpm were used for 5 min. The mixing temperature was 185°C to ensure complete polymer melting and to prevent degradation of MCC and RHC. Torque versus time data were recorded for all compositions. Composite films were moulded with a heated press, using the same conditions as those used for masterbatch films (185°C, 3min, at 2500 lbf).

Characterisation

Characterisation of the celluloses: MCC, RHC, MCC-Si and RHC-Si were characterized by Fourier transform infrared spectroscopy (ATR-FTIR) in the range 450–4000 cm⁻¹ with 64 scans and a resolution of 2 cm⁻¹, in a Nicolet 6700 spectrophotometer. Scanning electron micrographs were obtained to observe the morphology of the celluloses using a JEOL® microscope JSM 6060 operating at 20 kV. The test specimens were attached to an aluminum stub and sputtered with gold to eliminate the electron charging effects.

Thermomechanical analysis (DMA): The dynamic-mechanical properties of the composites were studied using a Perkin–Elmer DMA, Model 2980 V1.5B, in N₂ atmosphere, heating rate of 3° C/min, 1 Hz. The tests were performed using a three point bending-rectangular measuring system.

Scanning electron microscopy (SEM): Scanning electron microscopy was used to observe the morphology of the composite films using a JEOL® microscope JSM 6060 operating at 20 kV. The test specimens were attached to an aluminum stub and sputtered with gold to eliminate the electron charging effects.

Results and Discussion

Cellulose surface modification

FTIR spectroscopy was used to observe the silane-treated celluloses, to verify the presence of the coupling agent at the surface of the fibres. The MCC and RHC spectra show several bands characteristic of the cellulose. Apart from these bands, the MCC-Si and RHC-Si spectra show a band at 1134 cm⁻¹, assigned to the stretching of Si-O-Si bonds, as shown in Fig 1. This band is superimposed to the stretching of the Si-O-C in the region of 1095-1015 cm⁻¹. Such FTIR spectra confirm the presence of the VTES in the surface of MCC-Si and RHC-Si.

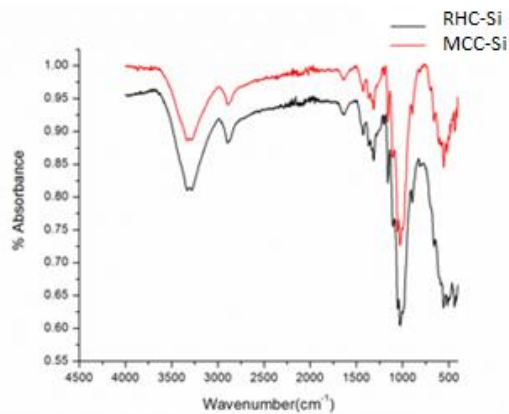


Figure 1. FTIR spectra of MCC-Si and RHC-Si

Fig 2 shows the morphology of the celluloses before and after the silane treatment. In both cases (MMC and RHC), smoother surfaces seems to be present after the surface treatment. This morphology reflects an effect of particles aggregation due to the presence of the VTES. Such aggregates have to be disrupted under mechanical shearing during composites processing.

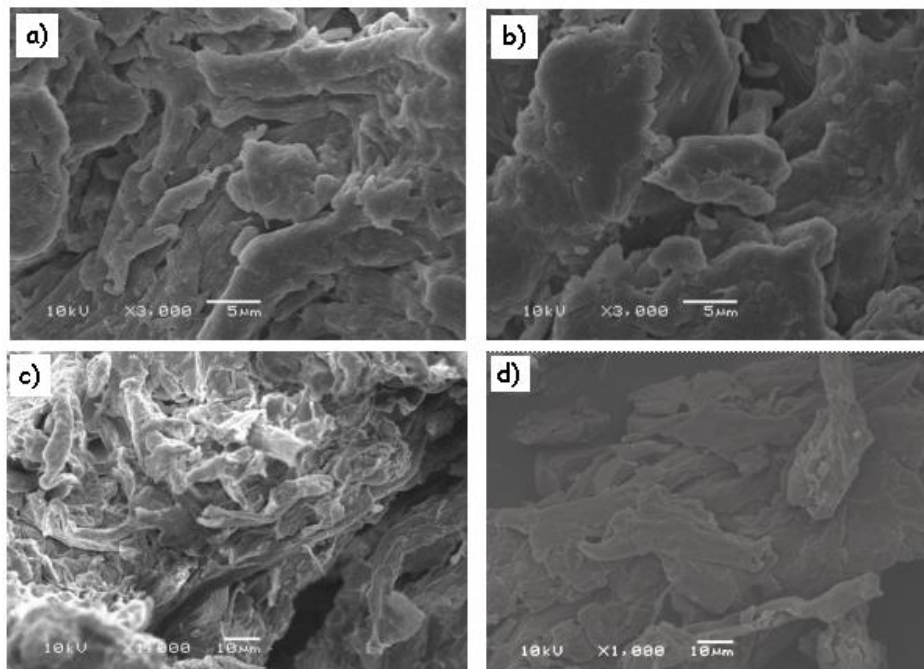


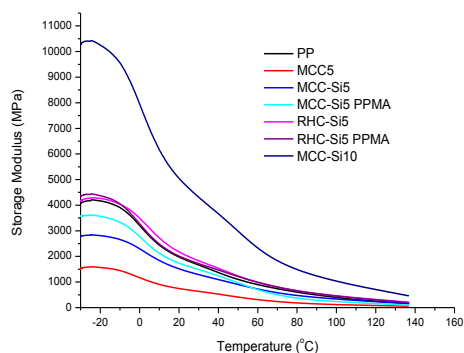
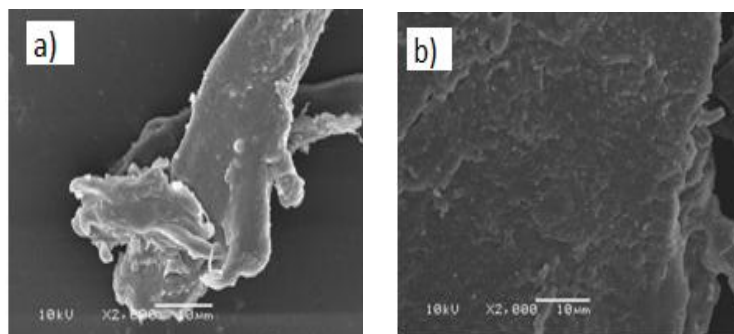
Figure 2. SEM images of: a) MCC; b) MCC-Si; c) RHC; d) RHC-Si

Preparation and characterization of the composites

The composite films obtained by press were visually homogeneous. Table 1 shows the formulation of the prepared composites. The variation of the storage modulus with the temperature for PP and its composites, as determined by DMA, are presented in Fig 3. It was observed that any composition containing 5 wt% cellulose did not improve significantly the property in comparison to the PP matrix. On the contrary, some compositions decreased the storage modulus within the whole range of temperature. This occurred mainly with the composites prepared with MCC, both with pure as well as with silane-treated MCC, in spite of the slight positive effect of the treatment with silane. The addition of PPgMA also produced a small increase in the property but not enough to go beyond pure PP. Both compositions containing 5 wt% RHC-Si (with and without PPgMA) showed behavior very close to the polymer matrix. However, it was observed that increasing the MCC-Si content to 10% increased significantly the storage modulus in the whole range of temperature. Near the ambient temperature (25°C) this increase was around 250% percent. Such result matches recent findings of the literature in which high amounts of nano- or micro- cellulosic fillers are necessary to achieve good mechanical properties – 16.5 wt% for Shanmuganathan et al. [6] and 30 – 40 wt% for Larsson et al. [7].

Table 1 - Formulation of the composites

Sample	RHC	RHC-Si	MCC	MCC-Si	PPgMA
PP	0	0	0	0	0
RHC-Si5	0	5	0	0	0
RHC-Si5 PPMA	0	5	0	0	2.5
MCC5	0	0	5	0	0
MCC-Si5	0	0	0	5	0
MCC-Si5 PPMA	0	0	0	5	2.5
MCC-Si10	0	0	0	10	0

**Figure 3.** Storage modulus of PP and composites**Figure 4.** a) MCC5; b) MCC-Si5 PPMA

As shown in Fig 4, the composites containing silane and PPMA exhibit better compatibility, judged by the more homogeneous fractured surface found in these compositions.

Conclusion

Rice husk is an abundant residue from agro-industry, which does not find economic applications. Pure cellulose was extracted from rice husk using environmental friendly procedures. This cellulose can be an alternative to MCC in the preparation of polymer composites giving materials with better mechanical properties. The silanization of the filler and the addition of PPgMA helped to improve even more the properties.

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