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Utilization of Recycled Polymer Matrices For Production of Eco-Composites

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Abstract: One of the big new areas of development of the advanced composite materials is in combining natural fibers with thermoplastics for producing lightweight, environmentally friendly, cost-effective composite material.

The aim of this work is to show the possibilities of recycling and reuse of thermoplastic polymer matrices with rice hulls (RH) and kenaf fibres (KF) using the conventional techniques, extrusion and compression moulding. The matrices (polypropylene (PP) and poly(lactic) acid (PLA)) were recycled one and two times and the fibers/filler were compounded with recycled matrix. The processing and material properties have been studied on the composites with recycled matrix and compared to the composites with virgin matrix.

Characterization of all composites includes mechanical, morphological and thermo-gravimetrical analysis. The flexural properties for PP recycled based composites were held close to the flexural properties for composite based on neat PP, but for PLA recycled based composite the flexural properties are decreased for about 50%. The thermal stability of recycled matrices based composites is very similar to the thermal stability of the composites with virgin matrix. SEM analysis has shown that the fillers/fibers are covered by the recycled polymer matrix, indicated on the satisfied durability of the recycled polymer matrices. The obtained results have shown that both polymer matrices (biodegradable and no degradable) could be recycled with acceptable mechanical properties and they can be successfully used for production of eco-composites.

Keywords: eco-composites, polypropylene, poly(lactic acid), rice hulls, kenaf fibers, extrusion compression moulding.

Introduction

The growing environmental awareness and new rules and regulations are forcing the industries to seek more ecologically friendly materials for their products. In recent years, the development of biocomposites from biodegradable polymers and natural fibers have attracted great interests in the composite science, because they could allow complete degradation in soil or by composting process and do not emit any toxic or noxious components. For example automotive applications based on natural fibers with polypropylene as matrix material are very common today. Biodegradable polymers from renewable resources are becoming more and more interesting in a society where a large part of the garbage and waste consist of polyolefins [1-4]. There are many different polymers of renewable materials: for example polylactic acid, cellulose esters, poly hydroxyl butyrates, starch and lignin based plastics. Among these, PLA has the potential for use in electronic and construction applications because it can be fabricated with desired physical properties, such as heat resistance, mechanical properties, moldability, and recyclability. Its heat resistance and impact strength are inferior to those of conventional plastics such as acrylonitrile-butadien-styrene (ABS) and polycarbonate. As an oil-based product, PP could not be classified as a biodegradable polymer, but by introducing thermo-sensitive catalysts to increase the degradability, PP takes an important place in eco-composite materials. For example, Mohanty et al. have demonstrated that the NF reinforced PP composites have potential to replace glass-PP composites [5]. It has also been reported that PP can be modified by maleic anhydride, as an effective adhesion promoter [6].

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Natural fibers have many advantages compared to synthetic fibers, for example low weight, and they are recyclable and biogradable. They are also renewable and have relatively high strength and stiffness and cause no skin irritations. Many investigations have been made on the potential of natural fibers as reinforcements for composites and in several cases the results have shown that the natural fiber composites own good stiffness [1-6]. However the main drawback of natural fiber may be their hydrophilic nature, which decreases the compatibility with hydrophobic polymeric matrix. In these (natural fiber-reinforced) composite fields, therefore, most of the research has used different kinds of coupling agents for improving interfacial properties between the polymer matrices and natural fibers in order to enhance the physical and mechanical properties of the final products.

The purpose of this study was to investigate the recycling ability of the matrices: PP and PLA and their applications for production of the kenaf fiber reinforced composites and rice straw reinforced composites. The matrices were recycled one and two times with a twin-screw extruder. The fibers/fillers were compounded with matrix and coupling agent by melt mixing and the compounds were compression molded. A maleic anhydride (MA) grafted PP (MAPP) and maleic anhydride grafted PLA (MAPLA) were used as a coupling agent to improve the compatibility and adhesion between the fibers and matrix. The mechanical properties of the composites were studied according to the flexural testing and the thermal properties were studied with thermo gravimetric analysis (TGA). Further, the morphology was studied with scanning electron microscopy (SEM).

Experimental

Materials and methods

Matrices: Polypropylene PP and Polylactic acid PLA. They are suitable matrices for extrusion of composite materials. In order to promote the matrix/fiber compatibilisation, different amount of MA grafted PP and MA grafted PLA have been added during the blending (reactive blending).

Reinforcements: Kenaf fibers and Rice Straw. They were dried at 80^{O}C for 7-9h before they were mixed to produce composites.

First, the matrices were recycled one and two times (PPx1, PPx2 and PLAx1) by extrusion procedure with a twin-screw extruder. The obtained recycled matrices were cut in pellets form to perform the sheets.

The preparation of the composites have been preformed by melt mixing, in a Brabender-like apparatus with progressively increasing RPM (speed screw). During the blending the coupling agent (MAPP and MAPLA) has been added.

The polymer and coupling agent were first mixed then have been added the fibers. The fiber content in all composites was 30 wt. %. The kneading temperatures were 185^{O}C and 175^{O}C for PP and PLA, respectively. They have been mixed for 10 minutes with progressively increasing RPM. The obtained composites were cut in pellets form to perform the sheets.

The main goal is represented by the use of recycled polymeric matrices that can obtain the composites with good practical characteristics for using as building materials. For this purposes different composites have been prepared, as reported in table 1.

Table1. Prepared composites

Composites	Matrix	Fiber
PP/RH/CA*	PP	Rice Hulls
PPx1/RH/CA	PP recycled one time	Rice Hulls
PPx2/RH/CA	PP recycled two times	Rice Hulls
PP/K/CA	PP	Kenaf fibers
PPx1/K/CA	PP recycled one time	Kenaf fibers
PLA/RH/CA	PLA	Rice Hulls
PLAx1/RH/CA	PLA recycled one time	Rice Hulls

* CA = coupling agent

Test samples for mechanical testing were fabricated by hot-press forming with a compression moulding press. The pellets from the composites were put in moulding frame with desired dimensions and they have been molded by thermo compression at T= 185^{O}C and 175^{O}C (in the cases of PP and PLA, respectively) for 10 minutes with increasing pressure up to 10 000 pounds. After expire of the heating time, the press was cooled by circulating cold water.

From the recycled matrices and from all composites the plates with thickness 3mm were produced.

The flexural testing was performed according to ASTM standard for flexural testing on a Universal Instron Machine (Model 4301) using unnotched samples. The tests were performed at crosshead speed of 2mm/min, span 48 mm, at room temperature. Each result obtained represents the average of six samples. Thermal degradation temperature was measured by a thermo gravimetric analyzer (TGA) Perkin Elmer in a nitrogen atmosphere. The samples of about 10 mg were heated from 50 to 600^{O}C at a heating rate of 20^{O}C/min under nitrogen flow (rate of 25ml/min). Morphology of the cryogenically fractured surfaces of composites was analyzed using a JEOL SEM (vacuum Au/Pd alloy deposition of the samples in a Polaron Sputtering apparatus was performed previously).

Results and Discussion

The mechanical properties of the recycled matrix were compared to neat matrix and the mechanical properties of the composites with recycled matrix were compared to the composites with neat matrix. Table 2 shows the summary of the results for the matrices. There aren't drastically differences between mechanical properties of the neat matrix and recycled matrices. The flexural strength for PP neat and recycled: PPx1 and PPx2 are very similar but flexural strength for PLA neat and recycled PLA x1 are the same. The modulus for PPx1, and PPx2 are higher than PP neat but for PLA and PLAx1 there aren't any differences. The flexural strengths for PP are decreased for a little (about 5 %) with increasing of the number of recycles of the PP but the flexural modulus are increased for about 25%.

Table 2. The flexural tests of neat and recycled matrices

Samples	Stress at peak [MPa]	Standard Deviation	Modulus [MPa]	Standard Deviation
PP neat	51,5	5,5	1081	120
PP x1	52,8	2,1	1305	64
PP x2	49,5	2,9	1341	101
PLA neat	32,0	3,8	2416	204
PLA x1	32,0	6,1	2431	193

Table 3 shows the summary of the flexural results for kenaf - composites with neat and recycled matrices and rice straw - composites with neat and recycled matrices. The obtained values for PP recycled based composites for flexural strength and modulus are very similar with value for composite with neat PP. There are differences between flexural strength of the composites reinforced with RH and composites with Kenaf. Generally, the kenaf - composites have better mechanical properties than rice straw composites. But for PLA recycled based composite the obtained results from flexural tests are lower than composite based on neat PLA.

Fig. 1 a) and b) shows the influence of the recycled matrices on the properties of the composites. As shown in Fig. 1, which presents the property retention of the composites based on neat PP, PPx1 and PPx2 (in dependence of the number of recycles of the matrices), the flexural properties for PP recycled based composites were held close to the flexural properties for composite based on neat PP. But for PLA recycled based composite the flexural properties are decreased for about 50%. It was noticed that the obtained PLA recycled based composite was with darker colour than composite with neat PLA and very stiff. The reason for the decrease in the flexural properties for this composite is probably decline in the molecular weight of PLA or something with the RH caused by repeated kneading.

Table 3. The flexural tests of composites with neat and recycled matrices

Samples	Stress at peak [MPa]	Standard Deviation	Modulus [GPa]	Standard Deviation
PP / RH / CA 65/30/5 wt/wt	42,6	3,4	1,9	0,082
PPx1 / RH / CA 65/30/5 wt/wt	42,2	1,2	1,8	0,041
PPx2 / RH / CA 65/30/5 wt/wt	39,6	4,6	1,8	0,063
PP / Kenaf / CA 65/30/5 wt/wt	51,3	4,8	2,1	0,068
PPx1 / Kenaf / CA 65/30/5 wt/wt	51,1	3,0	2,3	0,204
PLA/RH/CA 65/30/5 wt/wt	28,8	6,6	3031	182
PLAx1RH/CA 65/30/5 wt/wt	14,8	1,3	2275	457

A research group Oksman et al. [7] have studied the recycling properties of the PLA/kenaf composite. The physical properties and molecular weight were held close to 90% of that of the initial PLA/kenaf composites. The reason for the decrease in the physical properties decline was mainly the decline in the molecular weight of PLA and the kenaf fiber's length caused by repeated kneading. However, the physical properties of the PLA/kenaf composite probably can be kept constant by the adjustment of the ratio of the initial PLA/kenaf composite and the recycled PLA/kenaf composite.

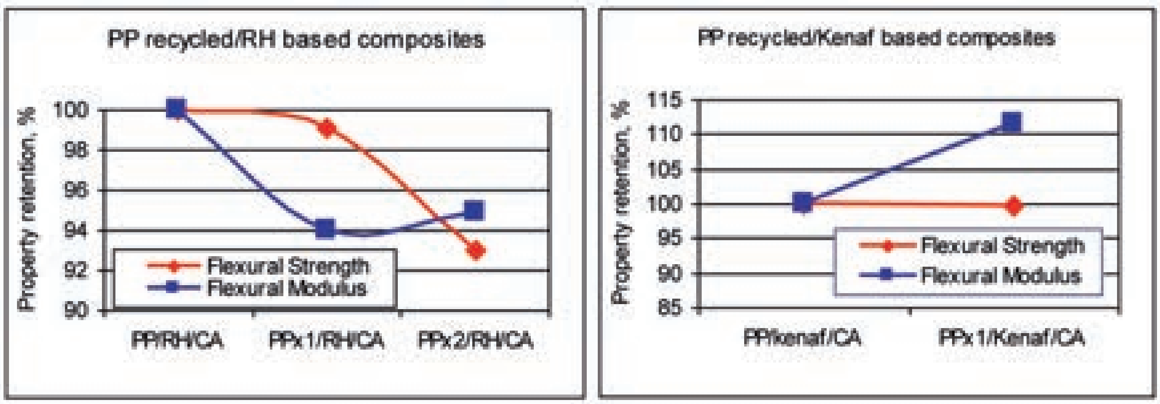

Fig. 1.a) Influence of the recycled PP on the properties of the PP/RH and PP/kenaf composites

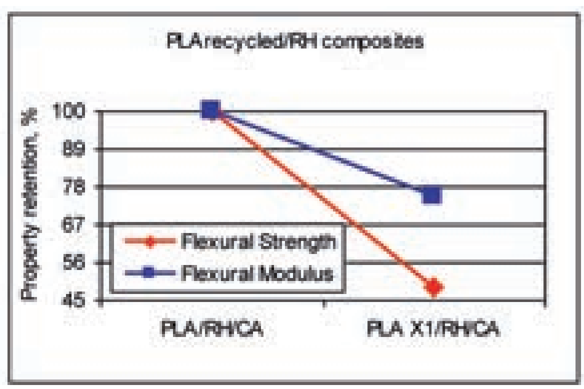

Fig. 1. b) Influence of the recycled PLA on the properties of the PLA/RH composites

Thermal degradation of PP and PPx1, PPx2 occurred at 443,9 ^{O}C, 432,9 ^{O}C and 422^{O}C respectively and in case of PLA and PLA x1 the thermal degradation occurred at 372,4 ^{O}C and 374,5 ^{O}C respectively. The thermal stability of the recycled PPx1 and PPx2 are almost without differences but a little smaller than thermal stability of the PP neat, but the thermal stability of the PLAx1 is the same as thermal stability of the PLA neat (see Table 4). In the case of PP recycled based composites and PLA , the incorporation of the recycled matrix one and two times has a very small affected thermal degradation temperature, (see Table 5). The composites with recycled matrices showed a lower degradation temperature (less than 40^{O}C) than a composite with neat matrix, and a two-stage loss of mass was mainly observed for all composites, see fig.2. These lower degradation temperatures may be attributed to the decrease of molecular weight of PLA and PP by more times kneading. It can be generally said that the increase of molecular weight by cross-linking reaction between matrix and fibers, or molecular chain – extension of the matrix itself, could increase the thermal degradation temperature [7-10].

Table 4. Weight residual for neat and recycled matrices

	Td [°C] (weight residual) ~ 90 %	*Td* [°C] (weight residual) ~ 50 %	*Td* [°C] (weight residual) ~ 10 %
PP neat	377,60 (90,38 %)	429,32 (50,38 %)	449,79 (10,38 %)
PP x1	357,49 (90,89 %)	414,67 (50,87 %)	438,64 (10,89 %)
PP x2	354,87 (86,37 %)	403,64 (46,37 %)	427,15 (11,37 %)
PLA neat	332,22 (90,53 %)	362,52 (50,53 %)	380,07 (10,53 %)
PLAx1	329,68 (90,54%)	364, 21 (50,54 %)	382,98 (10,54 %)

Table 5. Weight residual for composites with recycled matrices

	Td [°C] (weight residual) ~ 90 %	*Td* [°C] (weight residual) ~ 50 %	*Td* [°C] (weight residual) ~ 10 %
PP/RH/CA	344,43 (89,74 %)	411,21 (49,74 %)	452,17 (9,74 %)
PPx1/RH/CA	309,09 (87,51 %)	385,22 (47,51 %)	458,82 (12,51 %)
PPx2/RH/CA	343,53 (86,82 %)	405,97 (46,82 %)	475,27 (11,82 %)
PLAx1/RH/CA	299,42 (88,41 %)	341,70 (48,41 %)	529,70 (13,41 %)
PP/K/CA	356,81 (85,94 %)	408,94 (50,94 %)	441,96 (10,94 %)
PPx1/K/CA	356,92 (86,98 %)	412,35 (51,98 %)	443,77 (11,98 %)

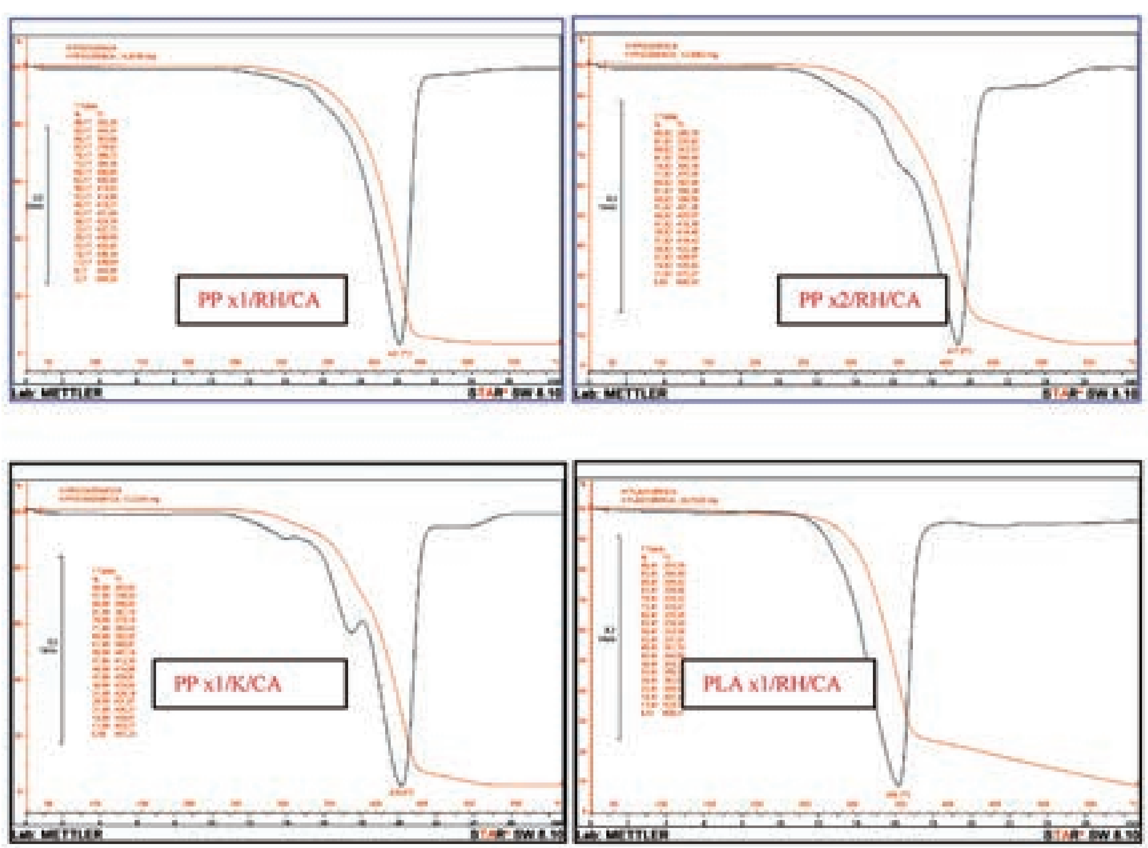

Fig.2. TGA and DTG of recycled matrices based composites

Many of properties in composite materials would be affected by their morphology. Fig. 3 shows SEM micrographs of the fractured samples of the composites with neat and recycled matrices. In the present study, although some voids can be observed between the RH and PLA or PP phase in the composites, but in all features, can be clearly seen that the RH and Kenaf fibers are coated with matrix polymer. Incorporation of CA into PP/RH, PP/Kenaf and PLA/RH enhanced the interfacial bonding between matrix and fibers. These findings suggest that the interaction between matrix and RH or kenaf are very good, resulting in high interfacial adhesion. These features are typical of compatible polymer composites.

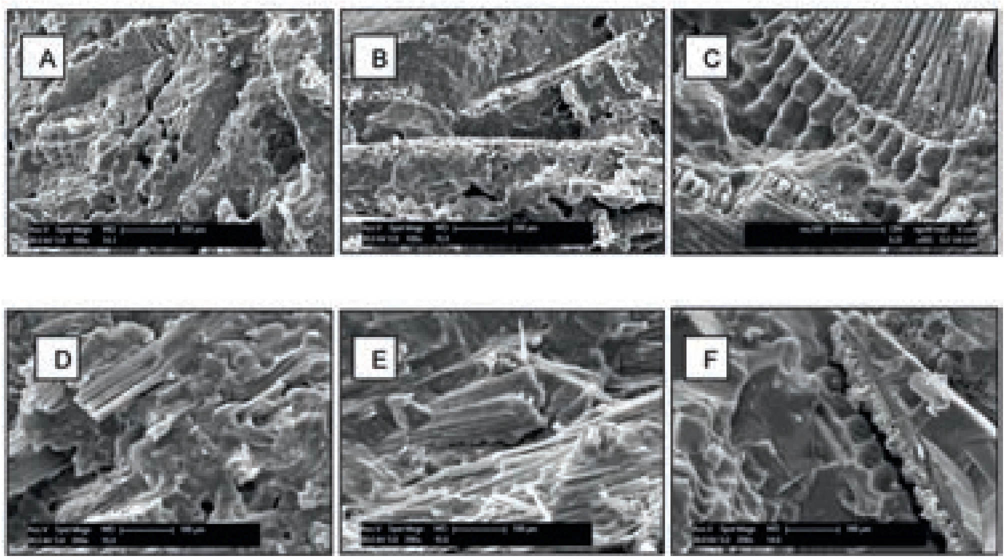

Fig.3. SEM micrographs of interface between matrix and fibers in: PP/RH/CA composite (A), PPx1/RH/CA composite (B), PPx2/RH/CA composite (C), PP/K/CA composite (D), PPx1/K/CA composite (E), PLAx1/RH/CA composite (F)

Conclusion

Based on this work devoted to study the effect of recycled matrices PP and PLA in composites reinforced with rice straw and kenaf fibers, on the mechanical properties, thermal stability and morphology of the composites, the following conclusions can be drawn:

The flexural properties of the PP recycled based composites are very close to flexural properties of the composite with neat PP. In particular, PP-based composites with kenaf fibers have sown high mechanical properties.

The flexural properties of the PLA recycled based composite are lower (about 50%) compared to composite with neat PLA,

The thermal stability of the PP recycled and PLA recycled composites is slightly lower compared to composite with neat matrix,

SEM analyses show that in all composites the interaction between matrix and RH or kenaf are very good, resulting in high interfacial adhesion.

In particular recycled matrices especially recycled PP are effective materials for production of the natural fiber composites with high mechanical and thermal stability properties, for building applications.

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