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Mechanical Properties and Water Absorption Behaviour of Chopped Rice Husk Filled Polypropylene Composites

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ABSTRACT

The reinforcing effect of chopped rice husk (CRH) into polypropylene has been studied. Composites containing different amounts of CRH with 0 to 40 parts per hundred part of polymer (php) were prepared using a co-rotating twin screw extruder and characterized by mechanical properties and also water absorption. In order to increase the interphase adhesion, polypropylene grafted with maleic anhydride was added as a coupling agent to all the composites studied. It was found that the tensile and flexural modulus of the composites containing 40 php of CRH increased approximately by 33% and 100%, respectively. The results also showed that while flexural strength was moderately improved by increasing of CRH into the matrix, elongation-at-break and energy-at-break decreased dramatically. A reasonable adhesion between the main components was also observed by examining the scanning electron micrographs. Water absorption experiments showed that although the diffusion coefficient increased with CRH loading, all the composites followed case I diffusion.

Key Words:

lignocellulosic composite;
mechanical properties;
morphology;
polypropylene;
chopped rice husk.

INTRODUCTION

Lignocellulosic-plastic composites are a new group of composites in which natural fibres are introduced in a plastic material by using different plastic processing technologies. These composites are cheaper and have higher strength and modulus in comparison with the composite produced with synthetic fibres specially, when differences between fibres densities are considered [1].

The main groups of plastics that are used in lignocellulosic-plastic composites are semicrystalline plastics such as polyethylene (PE) and polypropylene (PP). Only thermoplastics that melt at temperatures below 200ºC are commonly used in making the composites because of the limited thermal stability of natural fibres. Currently, PE is the most attractive thermoplastic in making the natural fibre-plastic composites which are main-

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ly used as the exterior building components. Composites made from PP are used in automotive applications and have recently been investigated for using as building profiles [2].

It is expected that lignocellulosic composites have several advantages over the composites produced from synthetic fibres. The advantages of natural fibre-made composite are its low density, low production cost of moulded products and biodegradability. They can also easily be recycled [3]. Only a minor quantity of natural fibres is usually stored for feeding animals or producing energy. The major quantity is burnt without any use.

Rice husk (RH) is among natural fibres. It is the outer covering of paddy and accounts for 20% of its weight [4]. RH is removed by rice milling and it contains cellulose 35%, hemicellulose 25%, lignin 20% and ash 17% (94% silica) by weight [5]. It is necessary to investigate the possibility of using RH as unwanted materials after rice milling, into plastic materials and making useful composites.

Several main factors should be taken into account when designing the composites made of RH and PP. Poor compatibility between the hydrophilic fibres and the hydrophobic thermoplastic matrix leads to the poor dispersion of the fibres into the matrix. This is because, the strong hydrogen bonds exist between the fibres, hold them together. The result is a weak interface that cannot efficiently transfer stress to the fibre. Therefore, coupling agents are required to enhance the interaction between natural fibres and hydrophobic thermoplastic matrices [5-12]. On the other hand, the hydrophilic nature of the fibres makes them very sensitive towards water absorption which decreases the mechanical properties to a great extent. Therefore, the fibres must be dried before being processed.

Panthapulakkal et al. [5], have studied the effect of various coupling agents based on ethylene-(acrylic ester)-(maleic anhydride) terpolymers and ethylene-(acrylic ester)-(glycidyl methacrylate) terpolymers on the mechanical properties of composites containing rice husk flour (RHF) and high density polyethylene (HDPE). They found that the best property was achieved by introducing of 8% glycidyle methacrylate into the composite.

Lee et al. [6], have reported that the addition of polypropylene grafted with maleic anhydride (MAPP) was able to improve the mechanical properties of wood-plastic composites (WPC). This improvement was attributed to the increase of compatibility between the wood flour and PP. Hristov and Vasileva [7], and Stark and Rowlands [8], have also found that MAPP has a positive effect on the mechanical properties of WPC and can improve the tensile modulus, yield strength and impact strength of the composite. Toro et al. [9] have found that PP grafted with monomethyl itaconate (PP-*g*-MMI) improves the interfacial adhesion in polypropylene-*co*-ethylene/RH composites.

The RH ash which is produced by burning of RH has a high content of silica. Depending on the procedure employed during burning, two types of ashes are produced, i.e. white (WRHA) and black rice husk ash (BRHA). Although a large amount of published papers exists on using WRHA and BRHA in plastics [13-28], there are a few reports on PP/RH composites [4,9,29-34].

The objective of this work is to explore the effect of CRH loading on tensile, bending and impact properties as well as water absorption of the PP/CRH composites. The fracture surface of the composite is also examined in order to study fibre-matrix interaction and distribution of fibre into the matrix.

EXPERIMENTAL

Materials

Chopped Rice Husk

RH was obtained from a local rice milling plant. It was air-dried and then the dry grinding of RH was carried out in a Wieser grinding machine (WG-LS 200/200). CRH was dried at 120ºC for 24 h before extrusion, and used without any treatment.

Polypropylene and Other Additives

The PP homopolymer was supplied by Bandar Imam Petrochemical Co., Iran, as the grade PI0800 and with the melt flow index of 8 g/10min. MAPP with melt flow index of 450 g/10min (190ºC and 2.16 kg) was obtained from DuPont as the grade Fusabond MD353D and used as a coupling agent. Irganox 1010 supplied from Ciba, was also added into the composites as a heat stabilizer.

Table 1. The formulations used in making the PP/CRH composites.

Ingredients	Content
PP	97
MAPP	3
Heat stabilizer	0.1
Chopped rice husk	0/10/20/30/40

Compounding

Composites including different amounts of CRH with 0 to 40 parts per hundred part of polymer (php) were prepared by using a Brabender Plasticorder model DSE 20 twin-screw compounder, equipped with the co-rotating screws of 20 mm in diameter and L/D of 40. The temperatures of five different barrel zones and the die were set to 165, 165, 215, 210, 195 and 185ºC, respectively. PP with heat stabilizer and also CRH were added into the extruder by using separate feeders and the twin-screw speed was set to 130 rpm. The pellets were dried at 120ºC for 24 h prior to injection into the mould. The injection machine used was manufactured by Imen machine Co., Iran. Samples for different experiments were prepared by injection of the material into the appropriate mould. The recipes for preparation of PP/CRH composites are presented in Table 1.

Tensile Testing

The tensile properties of dumbbell-shaped specimens were performed on an Instron testing machine (model 6025) at a cross-head speed of 5 mm/min. The thickness and width of the samples were 4 and 10 mm, respectively and the average of five determinations were taken.

Flexural Testing

Flexural properties were examined in a three point bending mode on the same Instron testing machine and at the constant deflection rate of 2 mm/min. The samples were in the shape of rectangular bars of 10 mm×10 mm×110 mm and the span length was taken to be 50 mm.

Impact Testing

The impact strength of the PP/CRH composites was studied by using a Zwick impact pendulum machine (model 5102) in the Izod impact mode according to ASTM D256. The experiment was carried out on the notched samples and at least ten specimens of each composite were tested to obtain a reliable average and standard deviation.

Scanning Electron Microscopy

The surface of the virgin rice husk and also the morphology of the fracture surface of each composite were studied by using a Cambridge scanning electron microscope (model S360). The lengths of 50 RH particles were also measured in order to obtain the CRH length distribution. The fracture surfaces were prepared by snapping the composites to half at liquid nitrogen temperature. The samples were mounted on the sample stub and the surface was sputtered with gold.

Water Absorption

The flexural samples were dried in 120ºC for 24 h before being immersed in water at room temperature. The samples were removed from the water at different time intervals, dried by a piece of cloth and weighed. Each value obtained is the average of three determinations.

RESULTS AND DISCUSSION

CRH Length Distribution and Surface Morphology

The length distribution of CRH is shown in Figure 1. More than 70% of the fibres were found to be in the

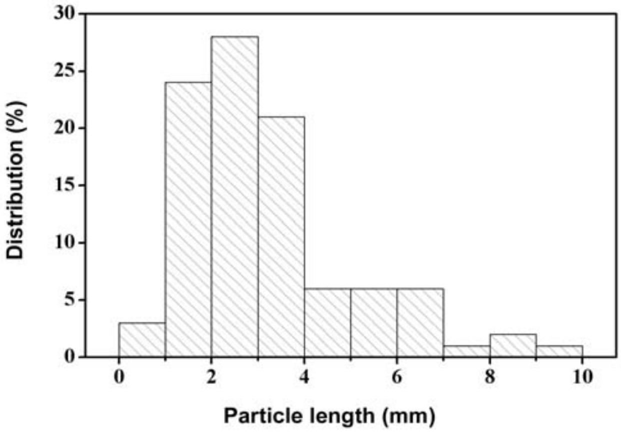
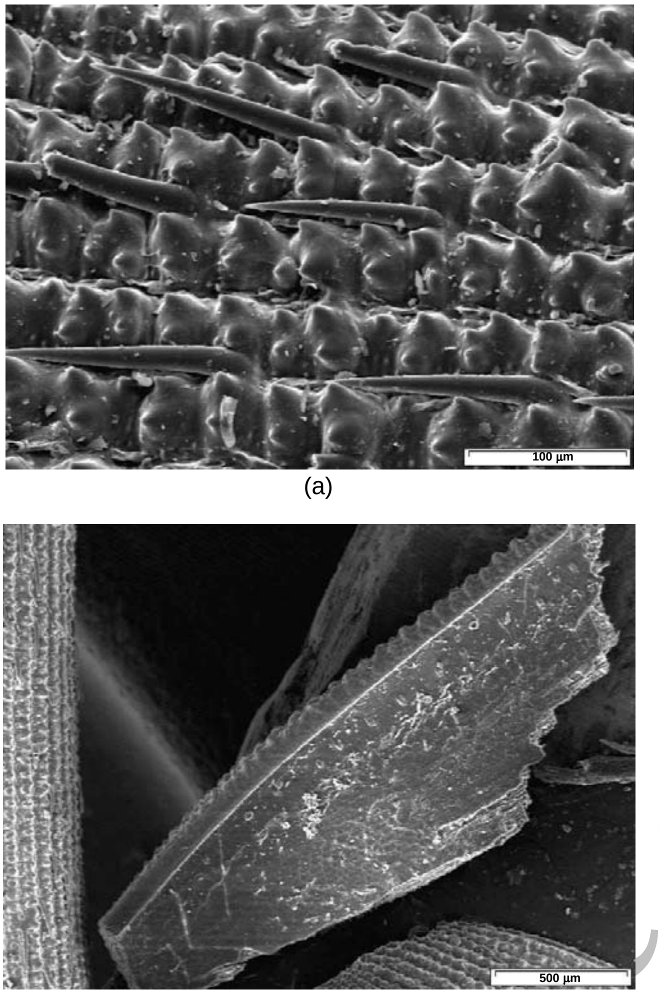


Figure 1. Particle size distribution of CRH.



(a)

(b)

Figure 2. SEM Micrographs taken from (a) outer, and (b) inner surface of CRH.

range of 1 to 4 mm. Figures 2a and 2b show the SEM micrographs taken from the outer and inner surfaces of CRH, respectively. It can be seen that a large number of knobs exist on the outer surface of the virgin CRH. Hair-like structures were also observed in the gaps between the ridges in some regions. It can be assumed that this cogged structure has a contribution in adhesion between CRH and the polymer matrix. However, in contrast to the outer surface, the inner part was found to be rather smooth with no knob on the surface.

Mechanical Properties of PP/CRH Composites

The tensile stress-strain curves of composites with different CRH loadings are shown in Figure 3. The detrimental effect of CRH addition into PP containing MAPP (the matrix) became apparent such that CRH reduced the ductile behaviour of the matrix by making the composites more brittle. While the matrix showed ductile behaviour via a neck formation, the composites consisting CRH revealed brittle behaviour with no necking. Although the tensile strength of a composite is more sensitive to the matrix properties, its modulus is dependent on the fibre properties. To improve the tensile strength, a strong interface, low stress concentration and fibre orientations are required, whereas high fibre aspect ratio and fibre wetting determine tensile modulus [1].

The variation of tensile yield stress, tensile modulus, tensile yield strain and energy-at-break of PP/CRH composites are shown in Figures 4-7, respectively. The yield stress remained relatively constant within the experimental error, although it could have a slight drop for the composite containing 20 php of

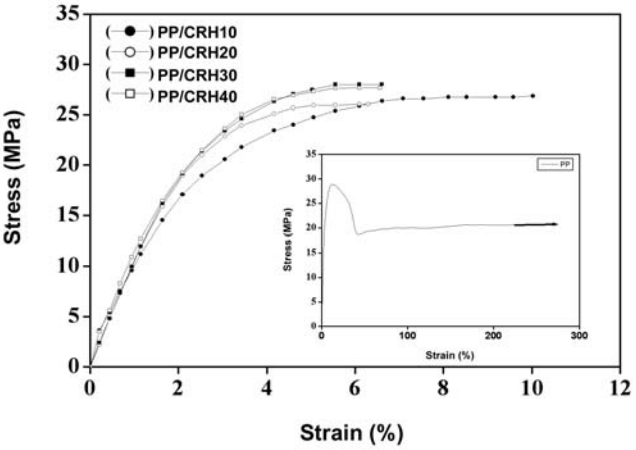


Figure 3. Stress-strain curves of PP/CRH composites.

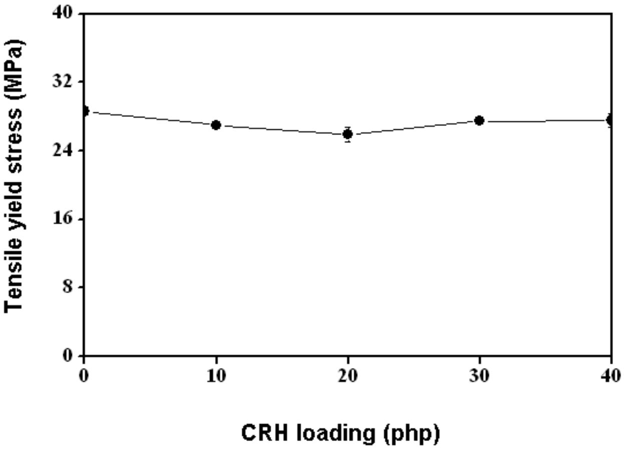


Figure 4. Variation of tensile yield stress with CRH content of the composite.

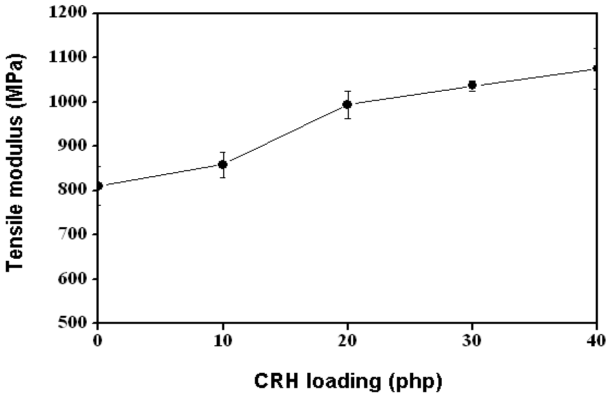


Figure 5. Variation of tensile modulus against CRH content of the composite.

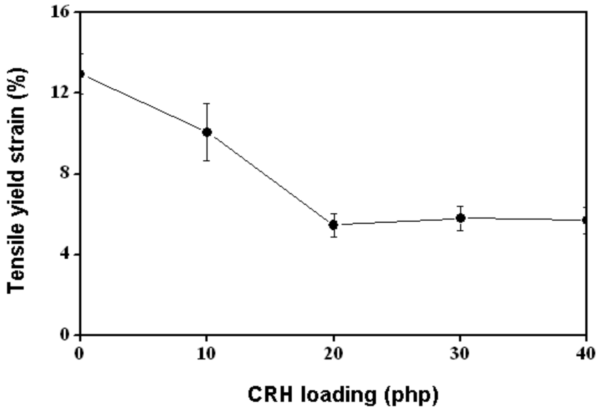


Figure 6. Variation of tensile yield strain with CRH content of the composite.

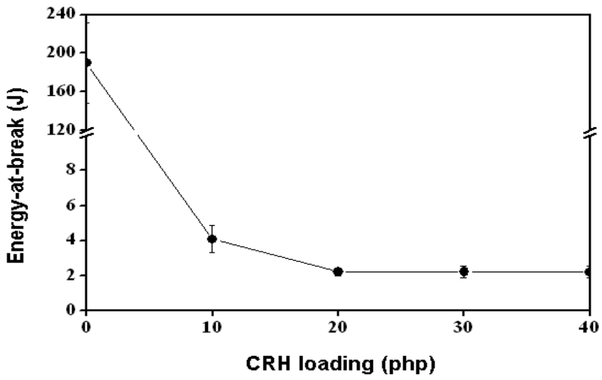


Figure 7. Variation of energy-at-break with CRH content of the composite.

CRH. The tensile modulus increased by about 33% for the composite containing 40 php of CRH. The results obtained by other researchers showed that the tensile strength and modulus decreased and increased with RH content, respectively [29-30].

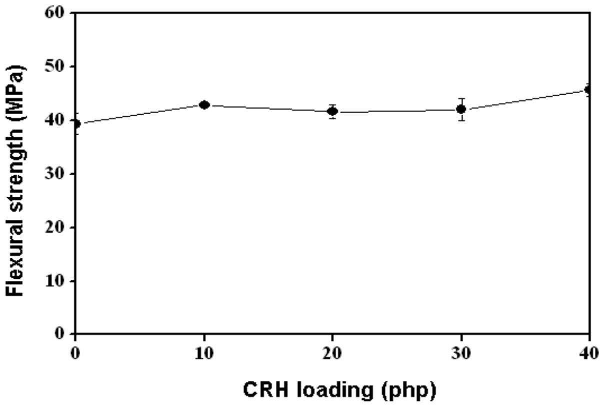


Figure 8. Variation of flexural strength with CRH content of the composite

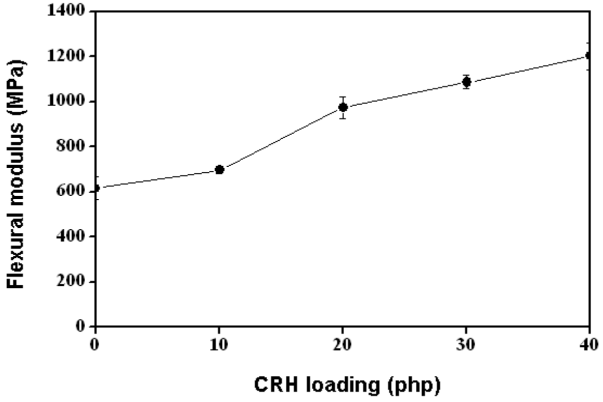


Figure 9. Variation of flexural modulus against CRH content of the composite.

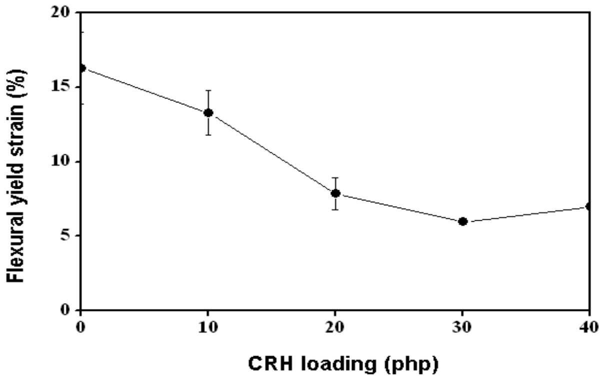


Figure 10. Variation of flexural yield strain with CRH content of the composite.

The yield strain and energy-at-break were significantly affected by the addition of CRH into the composite and they both decreased sharply up to 20 php and then remained relatively constant.

Figures 8-10 show the variations of flexural

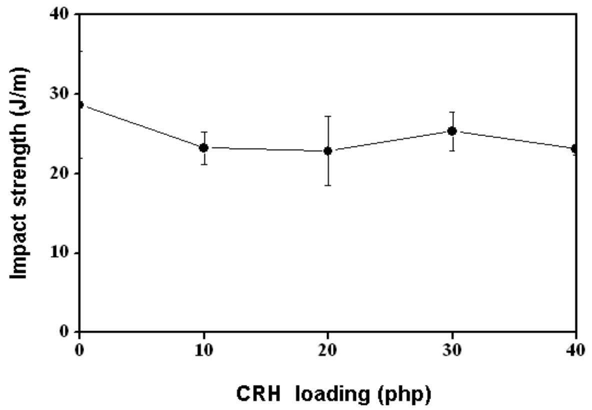


Figure 11. Impact strength with CRH content of the composite.

strength, flexural modulus and flexural yield strain with CRH content, respectively. It was found that although the flexural strength increased slightly for the composite containing 40 php of CRH, the flexural modulus was approximately doubled comparing to the matrix alone. This is in agreement with relatively good interaction between the two components. It was also found that the flexural yield strain reduced at low CRH concentration but it remained constant for the composites containing 20 php or higher amount of CRH.

The impact properties of the composites are shown in Figure 11. The impact strength showed a slight decrease in value after addition of 10 php of CRH into the matrix. However, it leveled off when higher amount of CRH was added into the composite. The ductile deformation of the matrix is inhibited because of the presence of CRH. However, this negative effect of the filler addition can be compensated by the energy which is required for pulling out of CRH from the matrix. This is why the impact strength remained relatively constant and did not decrease continuously with increasing CRH into the composite.

Morphology

Figures 12a-12d show the SEM micrographs of frac-

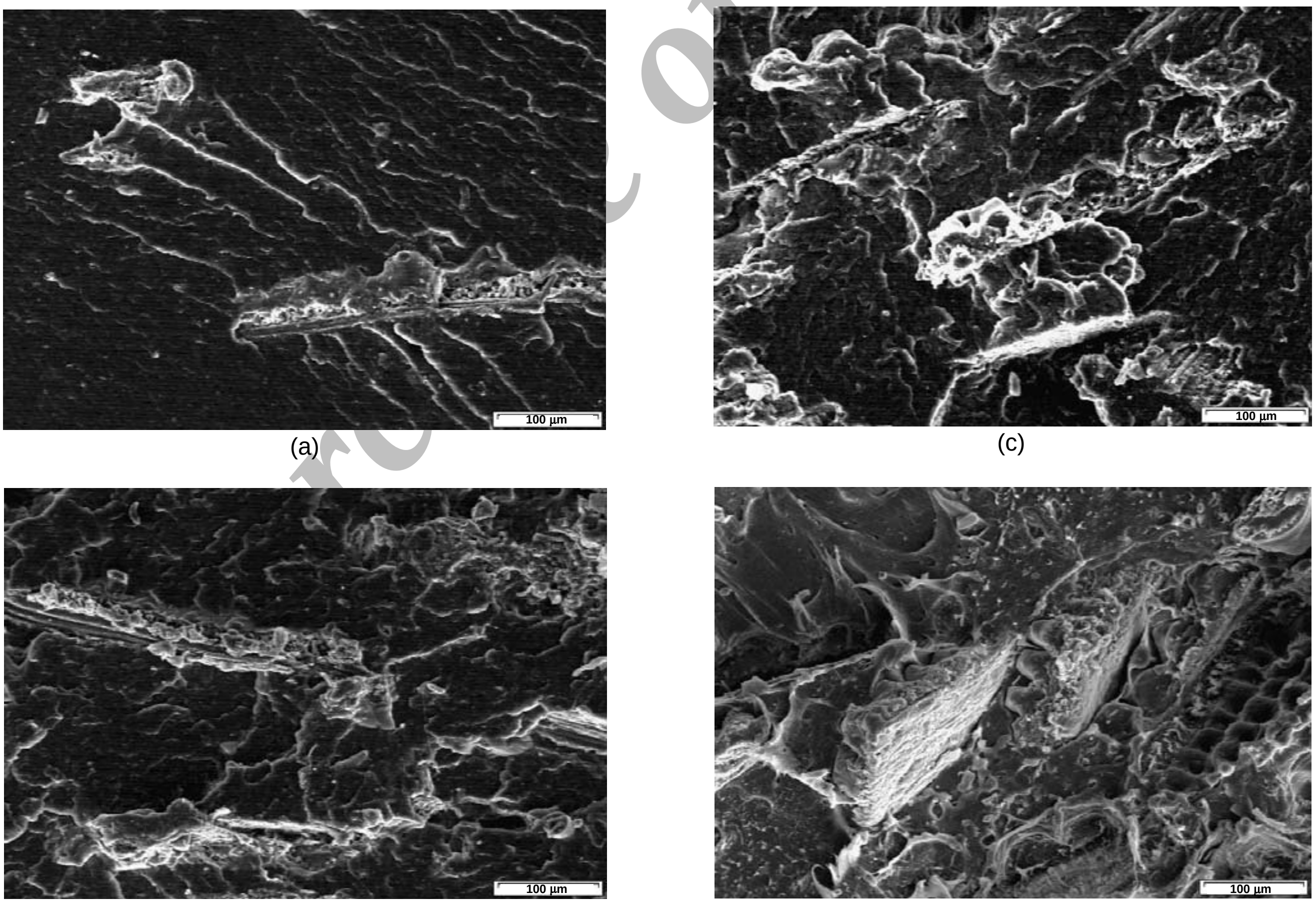


Figure 12. SEM Micrographs of the composites with different CRH loadings: (a) 10 php, (b) 20 php, (c) 30 php, and (d) 40 php of CRH in the composites (×200).

ture surfaces of 10 to 40 php of CRH filled composites, respectively. As it can be seen from the figures, CRH distribution into the matrix is reasonably well and in contrast with the results reported by Yang et al. [32], no voids are found in the composites. It seems that although the cogged structure of CRH in combination with using MAPP in the composite has a profound effect in creating a reasonably good interaction between the components, which have been confirmed with the mechanical studies, the bonding is not very strong and perfect because some debonding can also be seen on the interface of CRH and the matrix.

Water Absorption

The amounts of water absorption of all the composites at room temperature were calculated according to the following equation [29]:

$$M_t(\%) = \frac{w_t - w_0}{w_0} \times 100 \qquad (1)$$

where M_t is the amount of water absorbed at time t and w_t and w_0 are the weight of the sample at time t and the initial weight of the sample, respectively.

Three different mechanisms have been proposed for moisture penetration into the composite. The main process is the diffusion of water molecules inside the microgaps between the polymer chains. The other two mechanisms are capillary transport of water into the gaps and flaws created at the interface of fibre and polymer matrix because of incomplete wettability and impregnation and also diffusion of water molecules into the microcracks formed in the matrix during the compounding process [35].

There are three categories for diffusion behaviour. In case I, the rate of diffusion is much less than that of the polymer segment mobility (relaxation).

Penetrant mobility is much greater than the polymer relaxation in case II and the diffusion is characterized by the development of the boundary between swollen outer part and the inner core of the polymer.

Non-Fickian or anomalous diffusion occurs when the penetrant and polymer segment mobilities are comparable. This is an intermediate behaviour between cases I and II.

These cases can theoretically be distinguished by [36]:

$$\frac{M_t}{M_m} = kt^n \qquad (2)$$

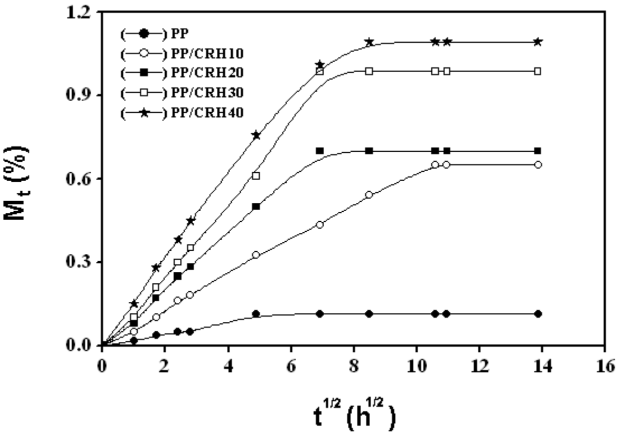


Figure 13. Water absorption of the composites against $t^{1/2}$ at different CRH loadings.

where M_m is the maximum moisture content and k and n are constants. The values of n are 0.5 and 1 for cases I and II, respectively. However, it is between 0.5 and 1 for non-Fickian diffusion.

The data obtained from water absorption experiment were analyzed by using eqn (2). The n value was found to be constant at 0.50 ± 0.05 for all the composites studied. This is in agreement with case I Fickian diffusion.

Figure 13 shows the variation of water absorption against $t^{1/2}$ for all the composites. The amount of water absorption of the composites increased with increasing CRH loading. However, the equilibrium inside the composites is rapidly reached and it is remained constant independent of time for all the composites studied as it is expected to occur for case I diffusion. It is also anticipated that the amount of water absorption in these composites should be much

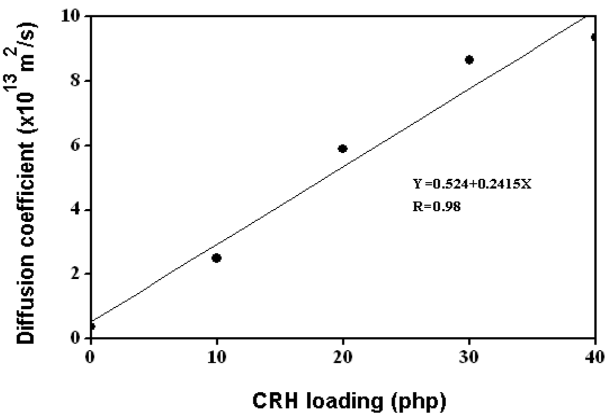


Figure 14. Variation of diffusion coefficient of the composites with CRH loading.

lower than that of the solid or wood particle board because the polymer used as the matrix is a hydrophobic material.

The diffusion coefficient (D) was calculated using the following equation [29,37]:

$$D=\frac{\pi\times h^2(M_2-M_1)^2}{16M_m{}^2(t_2{}^{1/2}-t_1{}^{1/2})^2} \tag{3}$$

where h is the sample thickness and M_1 and M_2 are the moisture content at times t_1 and t_2, respectively. The variation of diffusion coefficient with CRH loading is shown in Figure 14. It can be seen that the diffusion coefficient increased linearly with CRH content of the composites.

CONCLUSION

The possibility of using CRH in PP was studied by examination of the mechanical properties of the composites produced. The results showed that the tensile modulus increased about 33% and the flexural modulus nearly doubled in a composite consisting 40 php of CRH. The results also revealed that although tensile yield stress remained relatively constant, flexural strength increased by 16%. It was also found that the tensile and flexural yield strains as well as energy-at-break for the composites were lower than that of the matrix. Impact strength decreased for the composites but the reduction was not significant and did not change sharply with CRH content. These studies showed that the mechanical properties of the composites remained in an acceptable level even if 40 php of CRH was added into the matrix. The existence of relatively good dispersion and adhesion between the components were also found from the examination of SEM micrographs. The results obtained from water absorption experiments revealed that the diffusion coefficient increased with CRH loading and all the composites followed case I diffusion.

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