

Effect of Compatibilizing Agents on the Mechanical Property of Rice Husk Flour as Nano-Potential Filler in Polypropylene Biocomposite

A. Mounir El Sayed,¹ A. B. Shehata,¹ N. A. Darwish,¹ A. A. Abd El Megeed,¹
N. A. Badawy,² A. A. El-Bayaa,² S. A. El-Mogy¹

¹Polymer Metrology Lab, Chemistry Department, National Institute for Standards, Giza, Cairo, Egypt

²Al-Azhar University for Girls, Chemistry Department, Cairo, Egypt

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ABSTRACT: In this article, rice husk flour filler/polypropylene (RH/PP) composites with different ratios of the filler were prepared without and with maleated PP, which was used as a compatibilizer. The RH filler in the RH/PP composites was treated with acid and alkali, and their mechanical properties were measured. The mechanical properties were improved with the addition of the compatibilizer. In this study, grafting of maleic anhydride (MA) onto PP with different ratios of benzoyl peroxide (BPO) and MA was prepared. Infrared analysis showed characteristic bands at 1786 and 1863 cm^{-1} for the grafted sample (maleated PP). Also, from chemical titration, the

optimum MA and BPO contents were 4 and 1 part per hundred parts (php of polymer), respectively. The results showed that the morphology of the grafted sample was a flat with coarse surface, and that of the composite clearly elucidated that the interfacial bonding between RH and PP was enhanced by the presence of the compatibilizer. Thermal stability of the grafted PP was enhanced by the grafting process. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1310–1317, 2012

Key words: rice husk filler; polypropylene; biocomposite; mechanical properties; compatibilizer

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.¹ The recent research has been devoted to prepare composites depending essentially on polypropylene (PP) and rice husk flour filler (RH); it was found that these composites are poor in the compatibility in any composition. In general, natural fillers, including rice husk,^{1–4} wood,^{5–6} luffa,⁷ jute,^{8,9} and grass¹⁰ have several advantages such as light weight, low cost,¹¹ non toxic⁴, cheaper than inorganic fillers,¹² and reduced erosion of the manufacturing machinery used.^{4,13} RH contains cellulose 35%, hemicellulose 25%, lignin 20%, ash 17% (where ash contains 94% silica), and others 3% by weight.^{1,3,14} RH is named as lignocellulosic material because the lignin and cellulose materials are the main components of it. Their composites have reasonable strength and stiffness,⁷ absence of production of residues or toxic by-products when burnt,¹⁵ they can be recycled easily,¹ and have low CO₂ emission when compared

with inorganic-filler reinforced polymer composites.^{16,17} Natural filler reinforced polymer composites are not only inexpensive but also are able to minimize the environmental pollution caused by the characteristic biodegradability.^{18,3}

PP is selected as one of the most popular candidates as a matrix material due to its versatility to accept numerous types of fillers and reinforcements. Some of the properties that can be improved by forming composite material are strength, fatigue life, stiffness, temperature-dependent behavior, corrosion resistance, thermal insulation, wear resistance, thermal conductivity, attractiveness, acoustical insulation, and weight. Many authors have studied effect of the filler volume fraction on the tensile behavior of injection molded rice husk-filled PP and ethylene composites. The main disadvantage in natural filler/plastic composites is the poor compatibility between the hydrophobic polymeric matrix and the hydrophilic fillers. This leads to the formation of a weak interface that causes poor mechanical properties. This problem can be alleviated by the use of compatibilizing agents,^{2,19–21} which have dual characteristics to adhere well with lignocellulosic filler and matrix. Other important disadvantage of this type of composites is the high sensitivity of natural fillers toward water. This disadvantage can be overcome by treating RH with hydrochloric acid and sodium hydroxide.

Correspondence to: A. M. E. Sayed (mounir_99@yahoo.com).

The aim of this work is to improve the compatibility between RH and PP via the addition of maleated PP compatibilizer during the melt mixing of the product. The improvement of the compatibility leads to the enhancement in the mechanical properties^{5,6,22} of the composites.

EXPERIMENTAL

Materials

PP was supplied by oriental petrochemicals company (Egypt; in the form of homopolymer pellets). It has a density of 0.9 g cm^{-3} , and melt flow index of 9.36 g per 10 min (230°C per 2.16 kg load cell). RH used through this study was obtained from a local rice mill (Cairo, Egypt). Irganox 1010 was supplied from Ciba in white powder form. It has a specific gravity of 1.45 and amelting point of $110\text{--}125^\circ\text{C}$. It is used to prevent thermomechanical degradation during mixing and pressing processes. Maleic anhydride (MA) was purchased from Merck in a white crystals form. It has a density of 1.48 g cm^{-3} and melting point of 52.8°C . It was used in the grafting process of PP polymer. Benzoyl peroxide (BPO) was purchased from Merck in a white powder form. Its melting point is 105°C . It was used during this study to initiate the grafting process. Hydrochloric acid was obtained from Adwic in the form of colorless liquid. Its molecular weight is 36.46 g mol^{-1} . Approximately 10% of the acid was used for the treatment of RH. Sodium hydroxide was obtained from Adwic in the form of odorless white solid. It is used together with the diluted HCl also for treatment process of RH. Potassium hydroxide was obtained from Win lab Laboratory Chemicals in white pellet form. It has melting point of 420°C and density of 2.04 g cm^{-3} .

Experimental techniques

Preparation of RH

The RH used in this study is generally 80–100 cm long, so it was cut into small pieces, and then grinded in a mixer grinding machine. RH was oven dried at 100°C for 24 h to expel moisture before blending with PP and then stored in polyethylene bags before compounding.

RH length distribution

The length distribution of RH is measured by mesh technique of different standard sieve openings, that is, 0.250, 0.200, 0.125, 0.105, and 0.090 mm. Table I shows the various standard openings of the used sieves, the remained mass on each sieve, and the calculated percentage distribution. The total mass of

TABLE I
Calculation of Distribution Percentage

Standard opening (mm)	Remained mass (g)	Distribution (%)
0.250	0.60	57.14
0.200	0.20	19.05
0.160	0.10	9.52
0.125	0.03	2.86
0.105	0.05	4.76
0.090	0.07	6.67

RH sample was 1.05 g. The percentage of distribution is calculated by the following eq. (1):

Distribution (%)

$$= \frac{\text{the remained mass on each sieve}}{\text{total mass}} \times 100 \quad (1)$$

Treatment of RH by acid and base

RH was first treated with 10% HCl. The amount of dilute acid used was 5 L kg^{-1} of rice husk powder. The mixture was maintained at $90\text{--}95^\circ\text{C}$ for 90 min. with mild stirring. After cooling the mass, the mixture was filtered. The residue was washed with water several times to free it from acid, then the resultant is dried in air circulating oven that is maintained at 100°C . This is followed by treating RH with 2% NaOH solution in a similar way as in acid treatment.²³ This would remove low molecular weight cellulose (acid treatment) and a part of silica and lignin (alkali treatment).

Grafting process

Preparation of the compatibilizer

The radical grafting of MA onto PP was performed in xylene solution under nitrogen atmosphere in the presence of BPO. Grafting process was first carried out in Pyrex three-necked, round-bottom flask equipped with a condenser, a heating unit, and a magnetic stirrer. PP was dissolved in xylene at $135\text{--}140^\circ\text{C}$. After PP being completely dissolved, certain amounts of MA and initiator dissolved in xylene were added to PP solution, and then nitrogen atmosphere was inlet for 5 min to remove air-oxygen. The solution was stirred for 5 h.

Characterization of the prepared compatibilizer

The characterization of the prepared compatibilizer is performed by the following techniques:

Fourier transforms infrared. Thin films were prepared from the resulting product by compression-molding, and then Fourier transforms infrared (FTIR) spectra

TABLE II
Mix Formulations (in php) of PP Mixes without
Compatibilizer in Case of Untreated and Treated RH

Ingredients	Sample number						
	A	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆
PP	100	90	80	70	60	50	40
Untreated/ treated RH	0	10	20	30	40	50	60
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1	0.1

were recorded on a Nicolet 380 spectrometer in the spectral range of 4000–400 cm⁻¹.

Chemical titration. One gram of the purified PP-g-MA sample was dissolved in 100 mL xylene at refluxing temperature (135–140°C) for half an hour. Then, the hot solution was titrated immediately with 0.025N KOH/C₂H₂OH after adding phenolphthalein as indicator. Titration was stopped when the coloration remained for 30 s. The sample was completely soluble at the refluxing temperature and did not precipitate during titration. Few drops of deionized water were added to hydrolyze the anhydride group before titration. The graft degree G_d can be calculated from eq. (2):

$$G_d(\%) = \frac{98.06 \times C \times (V - V^\circ)}{2 \times 1000 \times m} \times 100 \quad (2)$$

where V and V° (mL) represent volumes of KOH/C₂H₂OH solution used for titrating grafted PP and pure PP, respectively; C (mol L⁻¹) is the molar concentration of KOH/C₂H₂OH solution; 98.06 (g mol⁻¹) is the molecular weight of MA; m (g) is the mass of the grafted PP; and the number 2 represents one anhydride group that would hydrolyze into two carboxylic acid groups after opening up of the anhydride ring.²⁴

The percentage yield of the grafted sample was also calculated according to eq. (3):

$$\text{Yield}(\%) = m/m^\circ \times 100 \quad (3)$$

Where m and m° are the masses of the final grafted product and the initial reactant, respectively.

Morphological structure analysis. The morphologies of commercial PP, the compatibilizer, as well as the RH/PP composite were studied by using scanning electron microscope (SEM). This analysis shows the change in the particle morphology after the grafting process, and the effect of the compatibilizer on enhancing the compatibility between RH and PP.

Thermogravimetric analysis. Thermogravimetric analysis (TGA) was performed on an analyzer (Model TA-50, Shimadzu, Japan) on 5 mg sample, at a heating rate of 10°C min⁻¹. TGA was conducted with

the compounds placed in a high quality nitrogen atmosphere to avoid unwanted oxidation.

Compounding and mixing

The mixing of all ingredients was carried out using CWB barabender internal mixer (Type: EPL-V7752, USA) with a rotor formulations speed of 70 rpm at 190°C for 10 min. The mix without and with compatibilizer in the case of untreated and treated RH are shown in Tables II and III, respectively.

Mechanical properties

Tensile strength, elongation at break, and modulus were determined using a Zwick (Germany) tensile testing machine (Model Z010) at a temperature of 23 ± 2°C and a crosshead speed of 50 mm min⁻¹ according to ASTM D 638. Sheets of dimensions 230 × 230 × 2.8 mm³ were prepared using a hydraulic press under a pressure of 150 kg cm⁻². Dumbbell-shaped samples were cut from the moulded sheets by using ASTM Die D. Three identical samples of each composition were measured and the average values were reported. Tensile strength, elongation at break, and elastic modulus were recorded and automatically calculated by the instrument software.

Hardness test was performed according to ASTM D 2240 using hardness tester (Zwick 3150, Germany). The samples used for this test are at least 6 mm in thickness. The average of five different measurements distributed over the specimen was taken.

RESULTS AND DISCUSSION

Characterization of the grafted sample

Infrared analysis

Figure 1 illustrates the FTIR spectra of the pure PP, MA, and the grafted samples in the spectral range of 4000–400 cm⁻¹, respectively. New absorption bands were observed at 1863 cm⁻¹ (asymmetric C=O stretching) and 1786 cm⁻¹ (symmetric C=O stretching) for PP-g-MA. These bands are characteristic of MA grafted PP.

TABLE III
Mix Formulations (in php) of PP Mixes with
Compatibilizer in Case of Untreated and Treated RH

Ingredients	Sample number						
	A	A ₁	A ₂	A ₃	A ₄	A ₅	A ₆
PP	100	90	80	70	60	50	40
Untreated/ treated RH	0	10	20	30	40	50	60
Antioxidant	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Compatibilizer	3	3	3	3	3	3	3

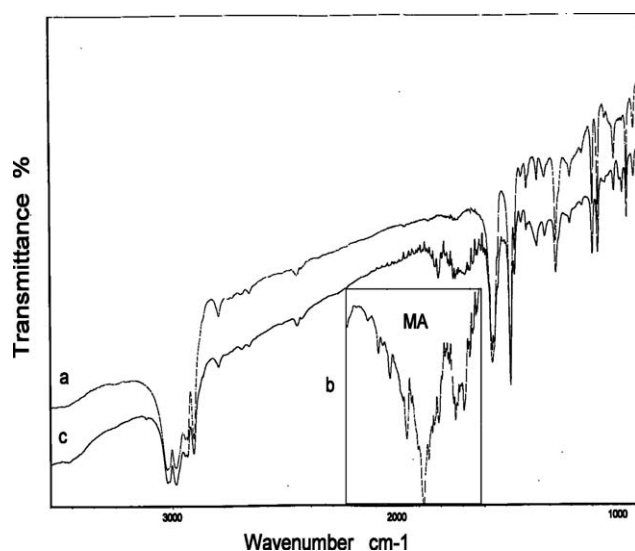


Figure 1 FTIR spectra of (a) blank PP, (b) MA, and (c) PP-g-MA.

Graft degree and graft yield

The grafting of MA onto PP was normally carried out at a high temperature to generate free radicals from the thermal decomposition of the initiator (peroxide). The graft degree (G_d) and the percentage yield were calculated and plotted versus the BPO content as seen in Figure 2(a). The MA content was chosen to be 2 php.^{25,26} The figure shows a slight increase in G_d at lower contents of BPO, whereas the percentage yield remains unchanged. On further addition of BPO, both G_d and yield increased up to 1 php of BPO and finally reached to a steady state. As the BPO content increased, more PP radicals are formed leading to a higher G_d . After the G_d reached

a maximum, a further increase in BPO did not show an improvement in the extent of grafting. In the meanwhile, the free radicals of polymer are generated at a higher BPO concentration that may enhance the crosslinking of polymer molecules, due to radical growth and recombination reactions.²⁶ To obtain the optimum amount of MA at which the optimum G_d can be obtained, a relationship between the graft degree (G_d) and the percentage yield against the MA content at 1 php of BPO initiator was shown in Figure 2(b). The figure shows that, at lower MA content, 1–2 php, about 80% yield was obtained. Then after 2 php of MA until 6, the percentage yield decreased drastically to 30% and the decrease was nearly linear. The figure also shows that G_d increases to a maximum with the increase of MA to 4 php. Then G_d decreases with further increase of MA content to 5–6 php. Similar results were also obtained elsewhere.²⁵ It can be assumed that during thermal decomposition of the peroxide (RO-OR), the radicals formed eliminate hydrogen from PP molecules (PH). Then, MA is added to PP macroradicals (P^{\cdot}) forming MA macroradicals which decay by hydrogen abstraction from PP or by reaction with another radical of the system. This means that the amount of MA from 1 to 4 php is very suitable for the grafting of MA onto PP macroradicals. However, when the amount of MA was increased up to 5–6 php, part of this amount was consumed by reaction with peroxide radicals RO^{\cdot} , thus the grafting process would be limited.²⁶ In this work, MA grafted PP product was prepared by using 4 phr of MA and 1 php of BPO, because higher G_d and reasonable graft yield were obtained at these optimum values.

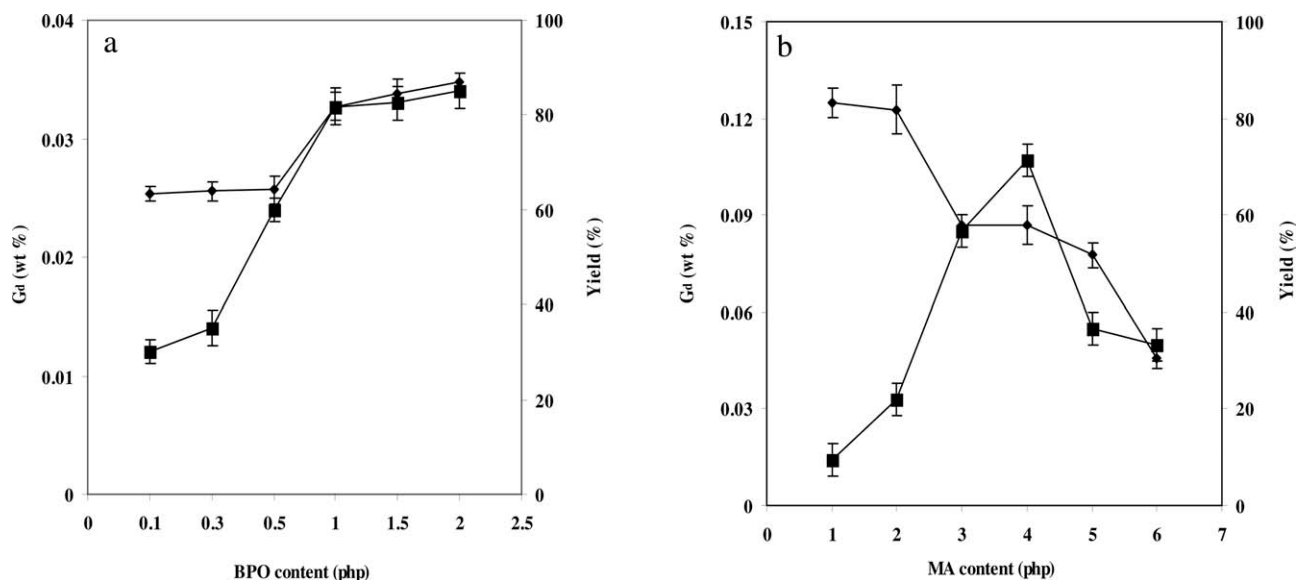


Figure 2 (a) Effect of BPO content on graft degree (■) and yield (◆) of the PP-g-MA (MA = 2 php); (b) effect of MA content on graft degree (■) and yield (◆) of the PP-g-MA (BPO = 1 php).

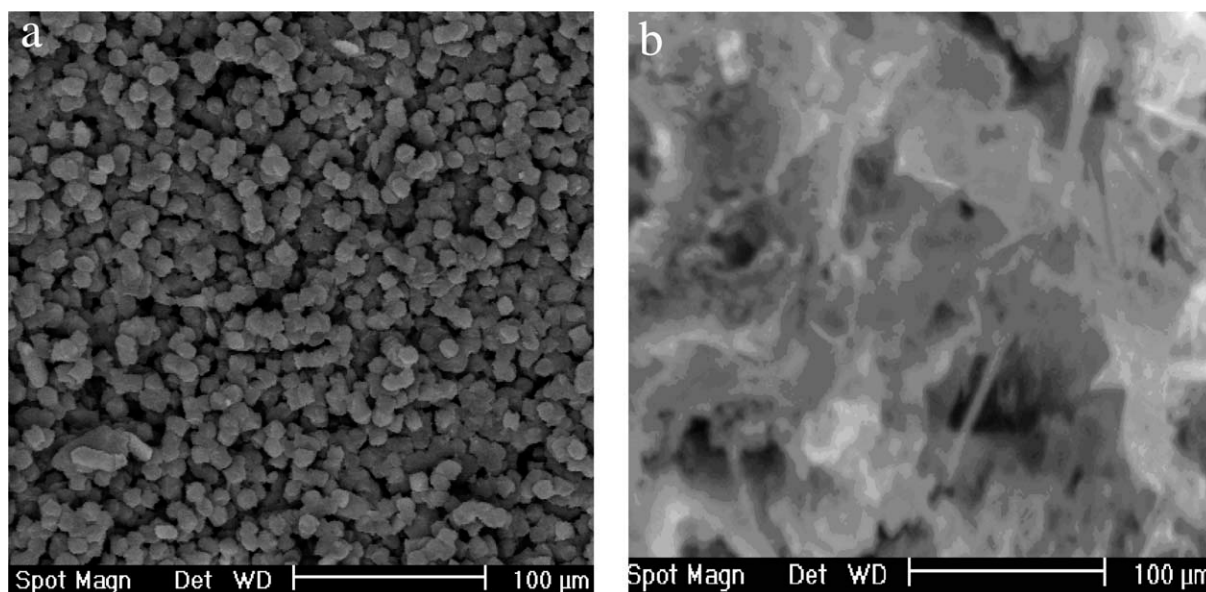


Figure 3 Surface morphologies of (a) PP and (b) PP-g-MA (PP/MA/BPO = 100/4/1).

Particle morphology of PP-g-MA powders

The morphologies of the blank PP and the PP-g-MA samples were studied by using SEM techniques to show the change in the particle morphology before and after the grafting process. Figure 3(a–b) shows the SEM micrographs for the commercial PP and the PP-g-MA samples, respectively. The commercial PP powders are composed of small globe particles with diameter of 8.5–10.5 μm as shown in Figure 3(a). After grafting process was performed, the particle morphologies of the PP-g-MA powders changed, no globe particle exists, and becomes flake morphology

with coarse surface as shown in Figure 3(b). Some particles get smaller, whereas some others get larger.

Thermogravimetric analysis

In this study, TGA technique is used to show thermal stability of the polymer before and after the grafting process. The TGA thermograms of both ungrafted and grafted PP showed that the decomposition process was performed in one step (Fig. 4). The values corresponding to thermal analysis are shown in Table IV. The initial decomposition temperature and the weight loss values of the grafted PP were increased when compared with those of ungrafted PP. This indicates that the grafting process improved the thermal stability of the grafted PP samples.

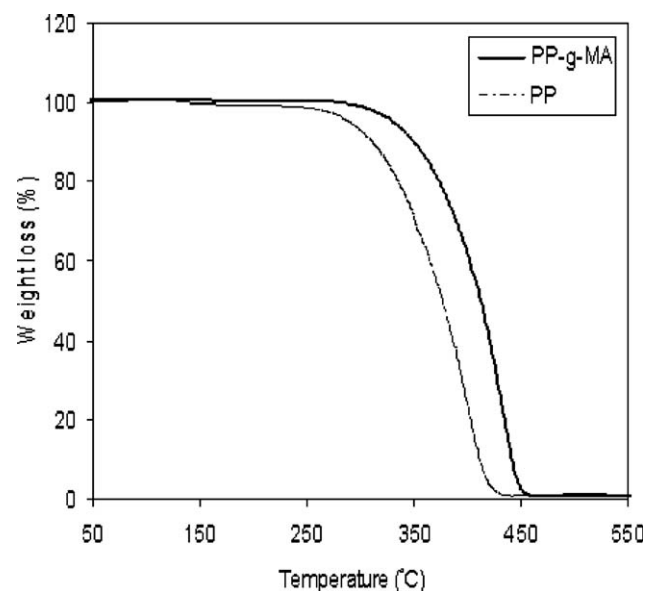


Figure 4 TGA curves of PP and PP-g-MA (PP/MA/BPO = 100/4/1).

Mechanical properties of untreated RH/PP composites in absence and presence of compatibilizing agent

Mechanical properties of rice husk filler–PP composites as a function of the filler loading in absence and presence of compatibilizing agent are shown in Figure 5(a–d). Figure 5(a) shows that the presence of the compatibilizer enhances the tensile strength of the composites by about 27% at 30 php filler content. This indicates that the maleated PP improves the

TABLE IV
Thermal Stability of Ungrafted and Grafted PP

Sample	Initial decomposition temperature (°C)	Weight loss (%)
Ungrafted PP	341.5	98.0
Grafted PP	380.0	98.9

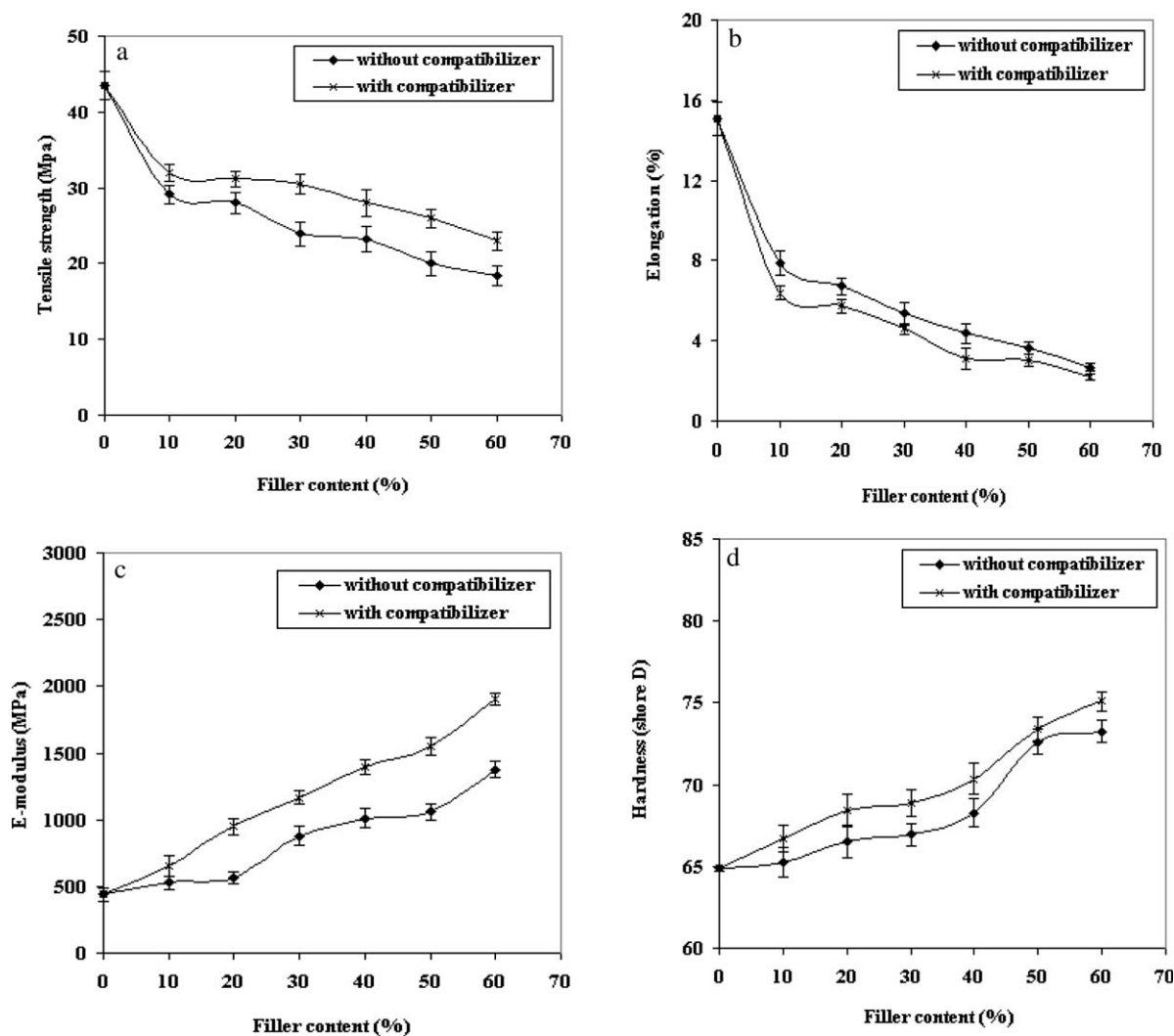


Figure 5 (a–d) Mechanical properties of RH/PP composites as a function of untreated filler content (RH): (a) tensile strength; (b) elongation percentage; (c) elastic modulus; (d) hardness without and with compatibilizing agent.

interaction between RH and PP causing the stresses transferred from PP to RH to become more effective;²⁷ whereas the elongation decreased with the filler content and in the presence of the compatibilizer Fig. 5(b). On the other hand, the modulus of the compatibilized composites was increased by about 32% at 30 php filler content when compared with those of the uncompatibilized composite as can be seen in Figure 5(c). This can be explained by the fact that the compatibilizing agent increases the stiffness of the composite which is responsible for modulus. Figure 5(d) shows that the incorporation of the RH filler into the PP matrix reduced the flexibility of the polymer matrix resulting in rigid composites. So, hardness gradually increased with an increase in the filler content. The figure also shows that the compatibilized composites seem to have higher hardness when compared with the uncompatibilized ones. This is due to the detrimental effect of RH addition

into PP in the presence of the compatibilizer becomes apparent.

Mechanical properties of treated RH/PP composites in absence and presence of compatibilizing agent

The tensile strength values of the treated composites were slightly decreased by about 7% (for 30 php filler content) than those of untreated ones as can be shown from Figure 6(a). This is attributed to the effect of chemical treatment where part of the lignin was removed by alkali treatment, which has an influence on the strength of the filler and the tensile strength of the composites.¹⁶ Figure 6(b) showed a decrease in the elongation of the treated RH/PP composites; whereas, the elastic modulus of the treated RH/PP composites have higher values by about 26%, at 30 php filler content, than those obtained in the case of the untreated RH/PP

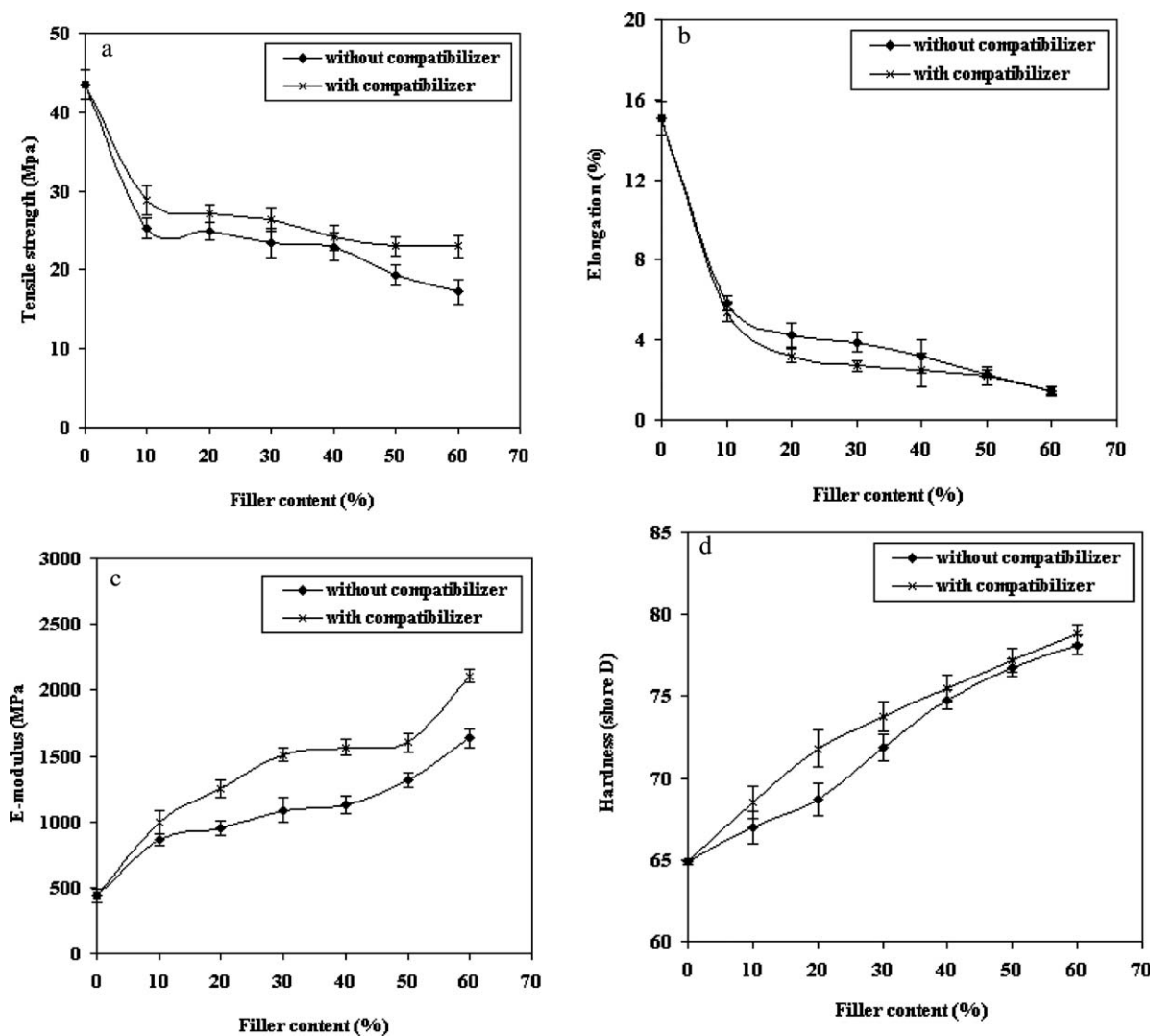


Figure 6 (a–d) Mechanical properties of RH/PP composites as a function of treated filler content (RH): (a) tensile strength; (b) elongation percentage; (c) elastic modulus; (d) hardness without and with compatibilizing agent.

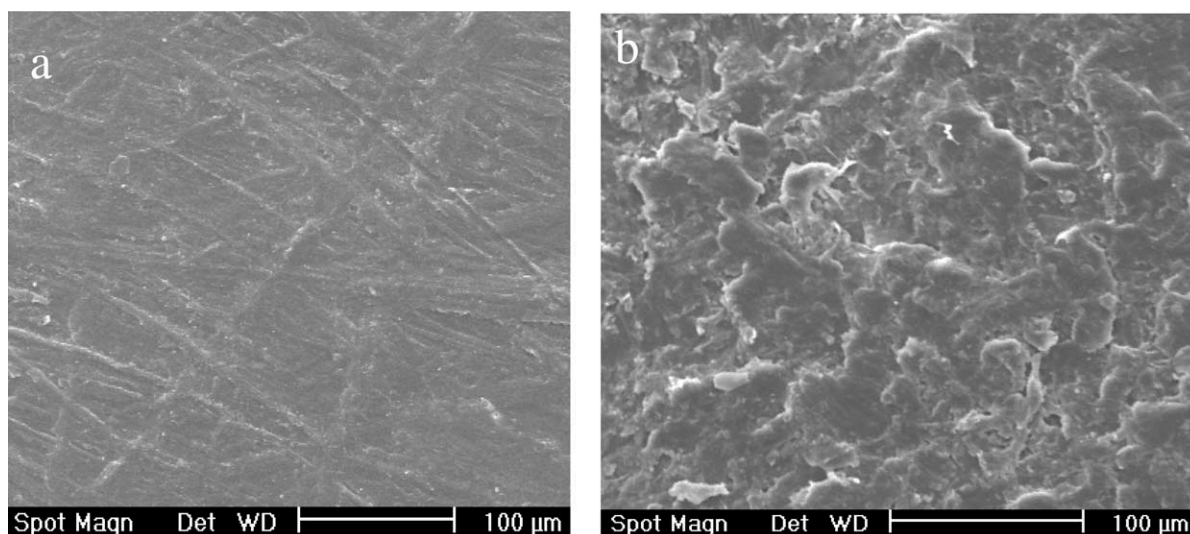


Figure 7 SEM micrographs of the surfaces of RH/PP composites at 20 php of filler: (a) without the compatibilizer and (b) with the compatibilizer.

composites Fig. 6(c). Also, the hardness values of the treated RH/PP composites were found to be higher than those of the untreated ones as can be seen in Figure 6(d).

Morphological properties of RH/PP composites

Figure 7(a–b) shows the SEM micrographs of 20 php of RH/PP composites without and with the compatibilizer, respectively. Figure 7(a) indicates that few filler particles are to be seen at the surface with the matrix polymer. Some cavities were found where the filler has been pulled out from PP. The presence of these cavities may be due to the difference in the polarity between RH and PP, which in turn reduced the interfacial bonding between the two substrates, while in the presence of the compatibilizer, the interfacial bonding is clearly improved Fig. 7(b).

CONCLUSION

The chemical titration results indicated that the optimum concentration of MA and BPO were 4 and 1 php, respectively. Morphological data showed that the compatibilizer exists as a flat morphology with coarse surface. The FTIR spectrum showed characteristic bands at 1786 and 1863 cm^{-1} for the compatibilizer. The grafting process enhances the thermal stability of the grafted PP samples. The incorporation of RH into PP matrix resulted in an enhancement in tensile strength of the composites in the presence of the compatibilizer. Acid/alkali-treated RH improved the modulus and the hardness of the composites. The presence of the compatibilizer clearly enhanced the interfacial bonding between RH and PP.

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