Mechanical Properties and Water Absorption of Low-Density Polyethylene/Sawdust Composites

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ABSTRACT: The mechanical properties and water absorption of low-density polyethylene/sawdust composites were investigated. The relationship between the filler content and the composite properties was also studied. Different degrees of esterification of the sawdust with maleic anhydride were obtained with different reaction times. The experimental results demonstrated that the treatment of sawdust by maleic anhydride enhanced the tensile and flexural strengths. The water absorption for maleic anhydride treated sawdust indicated that it was more hydrophobic than untreated sawdust. The effects of the addition of benzoyl peroxide during the preparation of composite samples on the water absorption and mechanical properties were also evaluated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1337–1342, 2008

Key words: composites; infrared spectroscopy; mechanical properties; polyethylene (PE); renewable resources

INTRODUCTION

Wood–plastic composites are known as a new generation of materials for house wares, automobiles, construction, and so forth.[1] They combine the favorable performance and low-cost attributes of both wood and plastics. In recent years, they have been developed rapidly.

Currently, various inorganic fillers such as rake, mica, clay, glass fibers, and calcium carbonate are being incorporated into thermoplastics. Nevertheless, organic fillers have drawn attention because of their abundant availability, low cost, and renewable nature. In recent years, the production of composites using natural substances as reinforcing fillers for thermoplastics, which melt at relatively low temperatures, such as polyethylene (PE) and polystyrene, has attracted considerable interest.[2] These fillers offer a number of benefits as reinforcements for synthetic polymers[1] because they have high specific strength and stiffness,[3] low hardness, which minimizes the abrasion of equipment during processing, relatively low density, biodegradability, and low cost on a unit volume basis.[4]

Unlike thermoplastic polymers, cellulosic fillers are predominantly polar because of the presence of polar groups on their different components, and thus they easily absorb moisture. The development of methods for controlling the interfacial adhesion between chemically and physically incompatible phases has been the object of considerable effort.[5] Several techniques for modifications, ranging from the esterification of fibers[6,7] to the grafting of short-chain molecules onto fiber surfaces, have been reported.[8]

This study was designed to prepare a composite from a low-density polyethylene (LDPE) matrix with alkali-treated sawdust as a filler. The effects of sawdust modifications with maleic anhydride (MAN) and the addition of 1% benzoyl peroxide for improved composite mechanical properties and water absorption were investigated.

EXPERIMENTAL

Materials

Sawdust from a commercial spruce species was used as a reinforcing filler. Only particles that passed through a 100-μm-mesh sieve were used in this study to ensure a high specific area.

LDPE (Indothene 16 MA 400), used as a polymeric matrix, was procured from M/s Indian Petrochemical Corp., Ltd. (Baroda, India), and it had a melt index of 2 g/10 min and a density of 0.92 g/cm^3.

Methods

Fiber treatment

Alkali treatment. Sawdust was immersed in a solution of NaOH (5% with respect to the raw material) for 24 h at a liquor ratio of 8:1. It was then washed several times with water, acidified water (0.1N HCl),

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and finally water again. The dust was then oven-dried at 60°C for 24 h. This treatment was expected to improve the fiber surface adhesive properties, removing impurities and leading to an increase in the effective surface area.

MAN treatment. Some of the NaOH-treated sawdust was immersed in a solution of MAN in xylene (100 g of sawdust and 30 g of MAN in 500 mL of xylene) and then heated under reflux for 2, 4, 8, or 24 h (depending on the desired reaction level). Then, the esterified sawdust was separated from the xylene solution and intensively washed with distilled water to eliminate the unreacted anhydride. Finally, the sawdust was dried at 70°C in a vacuum oven until a constant weight was achieved.

Peroxide treatment

Benzoyl peroxide (1 wt % to the polymer) was added to a melt of PE before being mixed with fibers.

Preparation of the composite samples

Composites were prepared through the mixing of LDPE and NaOH-treated sawdust or maleated saw-dust on a two-roll mill in a temperature range of 145–155°C for 15 min and then placed in a disc form 15 cm in diameter for heating and pressing in a hy-draulic press. The pressing conditions were a heat-ing temperature of 170°C and a pressure of 5 MPa for 5 min.

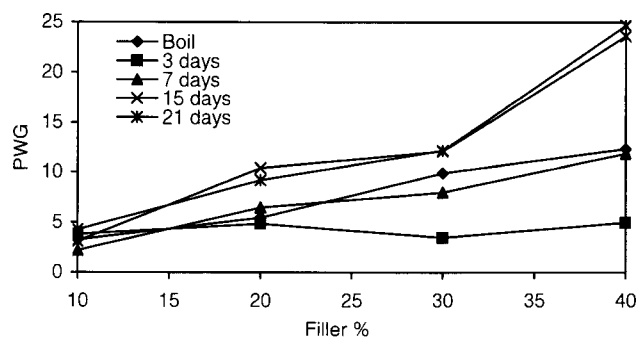### Investigations of the composite samples

Mechanical tests

Flexural and tensile tests were performed with a Lloyd LR 10k universal testing machine (Hants, UK) according to the ASTM D 790-90 and ASTM D 638-89 standard methods, respectively.

Water sorption

Small pieces of the composites were immersed in water to determine their susceptibility to moisture. The samples were placed in water and soaked for 3, 7, 15, and 21 days at room temperature or in boiling water for 2 h. The samples were weighed before and after each treatment, and the percent weight gain (PWG) was calculated as follows:

$$PWG = [(w_f - w_0)/w_0] \times 100 \tag{1}$$

where w_0 is the initial weight of the sample and w_f is the final weight of the sample.

Figure 1 Effect of the filler percentage on PWG of the composites at room temperature and at the boiling temperature.

Infrared (IR) spectroscopy

The samples were investigated with a 3000 E Fourier transform infrared spectrometer (Pittsfield, MA) between 200 and 4000 cm^{-1} with KBr techniques.

Scanning electron microscopy (SEM)

Different samples was investigated via SEM with a JEOL JXA-840A electron probe microanalyzer (To-kyo, Japan). The samples were coated with a thin layer of gold before SEM with an S1SoA Edward, sputter coater (Crawley, UK).

RESULTS AND DISCUSSION

Effect of the filler

Figure 1 shows the absorption of water by the NaOH-treated sawdust composites as a function of the filler percentage for different times. The best fil-ler percentage was 10% because it produced lower water absorption not exceeding 5% after 3–21 days of soaking. When the filler percentage increased to 20%, the water absorption increased gradually from 4.85 (3 days) to 9.19 (21 days). Also, when the filler percentage increased to 30 and 40%, the water absorption increased gradually with soaking to a maximum (ca. 25%) after 15 and 21 days with a 40% filler concentration. Also, Figure 1 shows that the fil-ler percentage had a great effect on the composite water absorption through boiling in water for 2 h. The maximum absorption of water, obtained with a 40% filler concentration, was 12%, and the minimum absorption with a 10% filler concentration was 3%. Because LDPE was hydrophobic and the sawdust was hydrophilic, the absorption of water was by the fiber alone. As the fiber loading increased, the cellu-lose content increased, and this resulted in the absorption of more water. Therefore, the water absorption was greatly improved (reduced) with a 10% filler concentration. This improvement may be related to the formation of a hydrophobic layer on
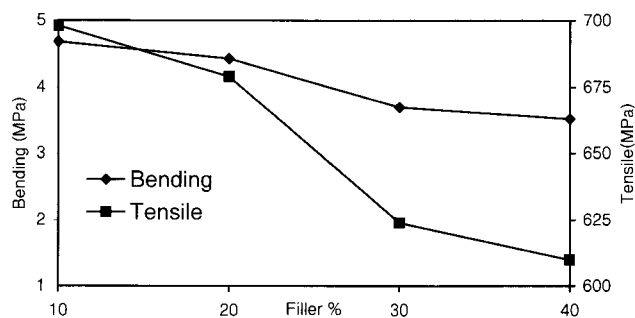
Figure 2 Effect of the filler percentage on the flexural and tensile strengths of the composites.

Figure 3 Effect of the MAN treatment on PWG at room temperature and at the boiling temperature.

the fibers that enhanced the water repellency because of the effect of coupling protection on the fiber by encapsulation in the hydrophobic polymer matrix.[9]

Figure 2 shows the mechanical properties of composites of LDPE and NaOH-treated sawdust with different weight ratios of sawdust. The flexural strength showed a gradual 24.8% decrease with an increase in the filler content. It decreased from 4.68 at a 10% filler concentration to 3.52 at a 40% filler concentration. Similar behavior was noticed for the tensile strength. Its value decreased by 12.6% from 698 at a 10% filler addition to 610 at a 40% filler addition. This was attributed to the flow and film formation of LDPE in the composite structure, which increased the internal bond strength and increased the composite strength.

Effect of the MAN treatment

The efficiency of the MAN chemical modification of sawdust after an alkaline pretreatment has been verified in different ways; one is a function of time at a given temperature, which has been pointed out previously by other authors.[10] This modification involves a chemical reaction between the —OH groups of sawdust and MAN.

Figure 3 shows that, in the case of a 70% LDPE composite with 30% sawdust filler, as the time of treatment with MAN increased, PWG decreased. In the case of boiling water, PWG decreased by 66.3%, but in the case of soaking for 3 days, it decreased by 47.7%. Also, it decreased by 58.6, 56.74, and 58.47% in the case of soaking for 7, 14, and 21 days, respectively. Therefore, the water absorption decreased with an increasing MAN treatment time. The substitution of OH groups by maleate groups due to the esterification of sawdust reduced the OH groups on the fiber, so it became more hydrophobic and reduced the water absorption of the composite. These results are in agreement with those found by other authors. Gauthier et al.[11] affirmed that if cellulose fibers are treated (by an esterification reaction)
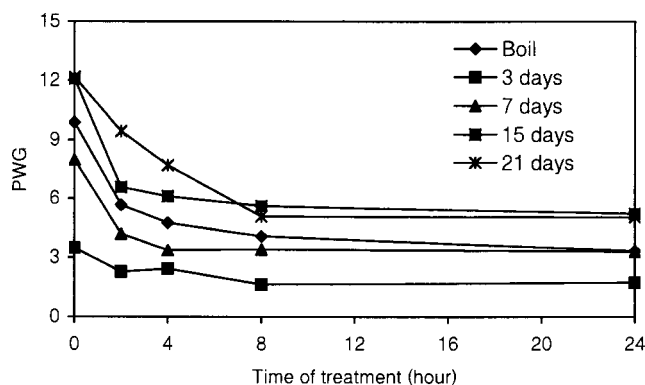
with small molecules, which penetrate the bulk of the fibers, better control of the water sorption and, therefore, the dimensional stability of the fibers is achieved.

The effect of the MAN treatment of sawdust on the tensile and flexural strengths of the composites with a filler weight ratio of 30% was also studied. Figure 4 shows the changes in the flexural and tensile strengths of composites of MAN-treated sawdust and LDPE with different MAN treatment times. The flexural and tensile strengths improved directly with the treatment of sawdust by MAN. No more improvement was noticed when the fibers were esterified for times longer than 8 h. This behavior could be attributed to the deterioration of the fibers due to the severe reaction conditions. Moreover, the important weight gain could also greatly change the chemical structure of the wood particles. Thus, the hydrogen bonding present in the wood, which provided a significant portion of the strength of the fibers, was reduced by the esterification with MAN, and this adversely affected the sawdust mechanical properties.[6]

From these results, it can be concluded that the short time of the esterification reaction (up to 8 h) improves the mechanical properties of sawdust–LDPE composites, and no further benefits can be
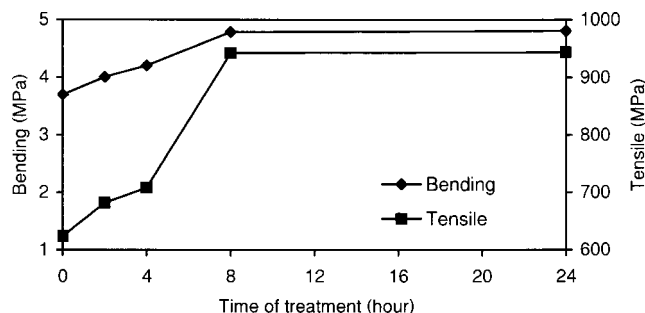
Figure 4 Effect of the MAN treatment on the flexural and tensile strengths of the composites.
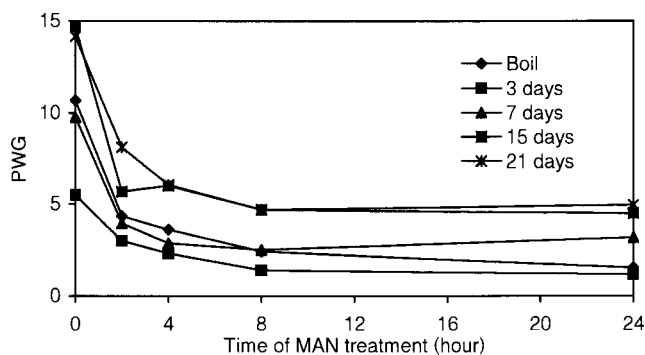
Figure 5 Effect of the addition of benzoyl peroxide on PWG.

obtained from longer reaction times during fiber modification.

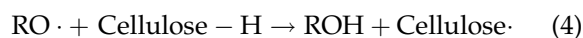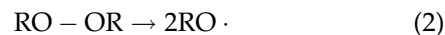### Effect of the benzoyl peroxide addition

The composite samples based on 30% filler (MAN-treated and untreated sawdust) along with the addition of benzoyl peroxide (1 wt % with respect to the polymer) to a melt of LDPE, before being mixed with fibers, were tested for water absorption from 3 to 21 days at room temperature and for 2 h in boiling water. Also, the flexural and tensile strengths were tested.

Figure 5 (cf. Fig. 3) shows that benzoyl peroxide had a great effect on reducing the water absorption of the composites made from LDPE and MAN sawdust treated for different times. The rate of water absorption was higher in the absence of benzoyl peroxide compared with that of MAN-treated sawdust in the presence of benzoyl peroxide. As the time of the MAN treatment increased, the water absorption decreased and reached the lowest value after 24 h. Also, the presence of benzoyl peroxide reduced the water absorption to a noticeable extent for different samples. Thus, for MAN-treated composites, an organic chemical (benzoyl peroxide) could be added to the hydroxyl groups on the fiber cell walls with the help of a permanently bonded chemical. Thus, the benzoyl peroxide treatment was responsible for reacting with some free —OH groups in the cellulosic structure; it behaved as a compatibilizer and reduced the water absorption.

Figure 6 (cf. Figure 4) shows that the flexural and tensile strengths were improved with the addition of benzoyl peroxide. The enhanced strength of the composites treated with benzoyl peroxide may have risen from a crosslinking or grafting reaction. Benzoyl peroxide initiated radicals, which attacked the cellulose backbone to generate cellulose radicals and subsequently promote the grafting of cellulose onto the polymeric matrix. Alternatively, the grafting of peroxide onto PE could take place through an attack

on tertiary carbons and on the few double bonds usually present in the backbone chain.[12] It is also possible that the presence of polar groups on the cellulose fibers modified the generated reactive species, thus facilitating crosslinking of the polymeric matrix.

The peroxide-initiated free-radical reaction can be represented as follows:

$$RO - OR \rightarrow 2RO \cdot \qquad (2)$$

$$RO \cdot + PE - H \rightarrow ROH + PE \cdot \qquad (3)$$

$$RO \cdot + Cellulose - H \rightarrow ROH + Cellulose \cdot \qquad (4)$$

$$PE \cdot + Cellulose \cdot \rightarrow PE - Cellulose \qquad (5)$$

IR spectra

Table I shows the most significant bands for the lignocellulosic fiber studied and the assignment for each one.[13]

A comparison of the IR spectra of untreated sawdust, sawdust treated with NaOH, and sawdust treated with MAN for 24 or 4 h are shown in Figure 7. The alkali treatment of sawdust with NaOH led to an increased degree of crystallinity as the lignin and hemicellulose polymer were removed.[14]

Figure 7(a) shows in the spectrum of untreated sawdust an absorption band at 1728 cm^{-1} corresponding to a C=O stretching vibration from hemicellulose and lignin. This absorption does not appear in the spectrum of the sawdust treated with NaOH [Fig. 7(b)]. Other typical absorption bands of lignin in the untreated sawdust spectrum are at 1510 (aromatic skeleton vibration) and 1263 cm^{-1}, and they are weaker in the spectrum of sawdust treated with NaOH. This is indicative of hemicellulose and lignin being partially eliminated after the treatment and is in agreement with reports in the literature[15] stating that the treatment of natural fibers with a diluted alkaline solution removes mainly hemicellulose and lignin present on the surface of natural fibers.
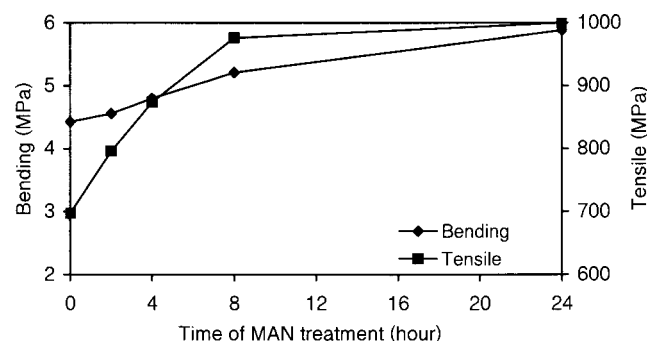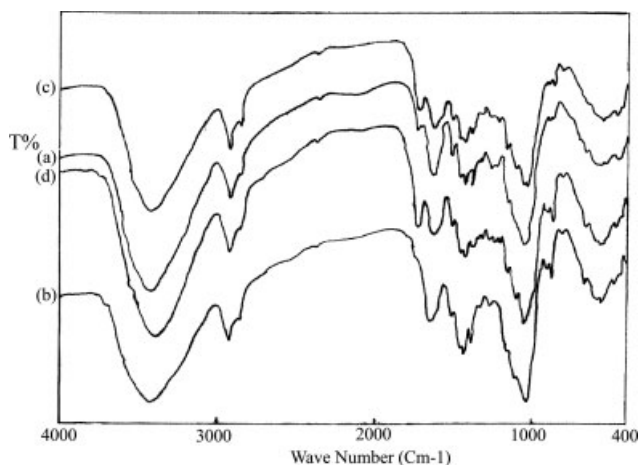

Figure 6 Effect of the addition of benzoyl peroxide on the composite properties.

TABLE I
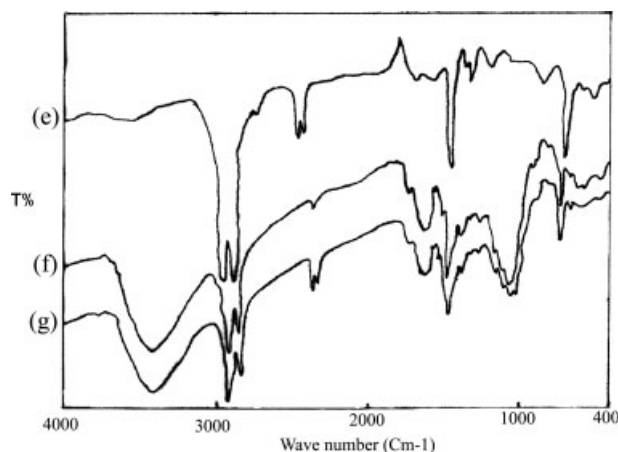**Characteristic Bands of the IR Spectra of Sawdust**

Wave number (cm^{-1})	Assignment
3450	OH stretching (hydrogen-bonded)
2885	Unmodified measurements of the crystallinity in a mixture of cellulose I and cellulose II
1740	C=O stretching of acetyl or carboxylic acid
1653/1635	Absorbed H$_2$O
1630	H—OH bond or C=C
1507	Aromatic bending C—H (ring)
1465	Lignin and CH$_2$ symmetric, bending pyran ring
1426	CH$_2$ bending (cell)
1331	OH in-plane bending (cell)
1162	Antisymmetric, bridge C—OR—C stretching (cell)
1110	C—O stretching (C—OH)
1055	Stretching C—OR (cell)
898	Antisymmetric, out-of-phase ring stretching

Figure 8 IR spectra of (e) LDPE, (f) the composite made from LDPE and sawdust treated with MAN for 4 h, and (g) the composite made from LDPE and sawdust treated with MAN for 24 h.

The major difference between the spectra obtained for treated and untreated samples was the presence of a C=O peak at 1752 cm^{-1}. Carbonyl stretching vibrations occurred in the region, and the increase in the absorption observed after the reaction with MAN was due to the formation of a bonded ester group.[16] Figure 7(c,d) shows that the longer the treatment was, the greater the intensity was of this peak.

Figure 8 shows IR spectra of LDPE, a composite made from LDPE and sawdust treated with MAN for 4 h, and a composite made from LDPE and sawdust treated with MAN for 24 h. In the LDPE spectrum, it is necessary to highlight the doublet of 1484–1464 (—CH$_2$) and 730–720 cm^{-1} (rocking —CH$_2$), the characteristic band at 1368 cm^{-1} (wagging —CH$_2$), and the bands obtained for LDPE at 990 cm^{-1} (—CH=CH$_2$).[17]

The bands of —CH at 2360–2341 cm^{-1} of LDPE clearly increased in the case of sawdust treated with MAN for 24 h versus that treated with MAN for 4 h. This means that sawdust treated with MAN for 24 h reacted more with LDPE. Also, a very sharp peak appeared at 720 cm^{-1} for the composite made from LDPE and sawdust treated with MAN because of the rocking of CH$_2$ of LDPE.[18]

SEM

Figure 9 presents SEM images of sawdust treated with NaOH and composites made from LDPE and sawdust treated with NaOH, LDPE and sawdust treated with MAN for 4 h, and LDPE and sawdust treated with MAN for 24 h (sawdust/LDPE = 45 : 105 w/w). The wood fibers possessed a cellular arrangement that could change the crack path. Therefore, in the case of sawdust treated with NaOH [Fig. 9(a)], a very irregular surface, common in this type of sample, was observed. There were some holes and some depressions where fibrous particles were missing, probably because desponding occurred. The crack did not have a straight path because it changed around the fiber cells and finally stopped.[18] On the other hand, for sawdust treated with NaOH and pressed with LDPE to form a composite [Fig. 9(b)], it was possible to observe many fibers fractured along with the matrix.

Figure 9 shows that the fracture propagated through and on the matrix, reaching the surface and revealing adhesion. However, the interaction at the interface for the sawdust treated with MAN for 24 h [Fig. 9(d)] was stronger compared than that for the

Figure 7 IR spectra of (a) untreated sawdust, (b) sawdust treated with NaOH, (c) sawdust treated with MAN for 24 h, and (d) sawdust treated with MAN for 4 h.
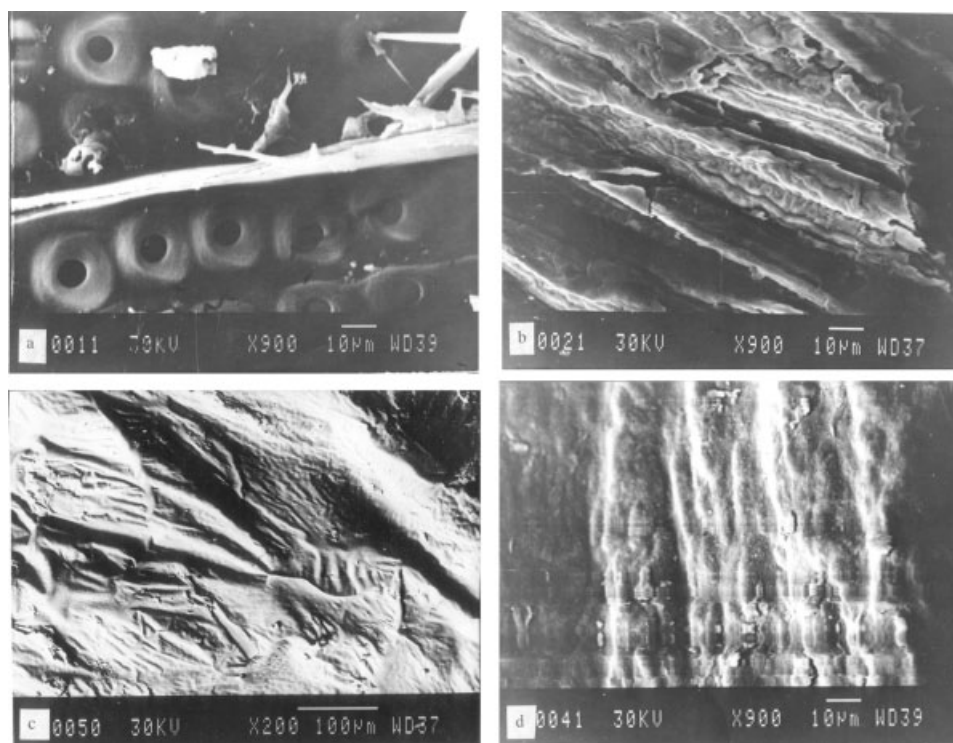
Figure 9 SEM photographs of (a) sawdust treated with NaOH, (b) the composite of sawdust treated with NaOH and PE, (c) the composite of sawdust treated with NaOH, MAN (for 4 h), and PE, and (d) the composite of sawdust treated with NaOH, MAN (for 24 h), and PE.

sawdust treated for 4 h [Fig. 9(c)]. This may have occurred because the wood fibers were saturated and penetrated with LDPE; this could explain why there was no water absorption. The wood and polymer were unified and strongly bound; this produced the strength and hardness.

CONCLUSIONS

The esterification of sawdust reduced the water absorption with respect to that of NaOH-treated dust. On the other hand, the short time of the esterification reaction improved the mechanical properties of the sawdust–LDPE composites, and no extra benefits could be deduced from the use of extended reaction times for the modification of the fibers.

A benzoyl peroxide treatment reduced the water absorption and enhanced the mechanical properties of the LDPE–sawdust composites, such as the tensile and flexural strengths.

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