Effect of Chemical Treatment of Wood Flour on the Properties of Styrene Butadiene Rubber/Polystyrene Composites

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ABSTRACT: Composites from SBR/PS blend and the chemically treated wood flour have been prepared. The materials used for such treatment are NaOH, MAN, MAN-glycidyl methacrylate, and silane coupling agent, used to improve the dispersion of wood flour in the SBR/PS blend. The effects of chemical treatment on curing characteristics, and physicomechanical and electrical properties of SBR/PS composites were studied. The rheological as well as the mechanical parameters were improved by using the modified wood flour with MAN-glycidyl methacrylate (SMG), followed by SM obtained at 15 phr, while the other treatments slightly affect these parameters. The permittivity ε' and dielectric loss ε'' were measured in the frequency range from 100 Hz up to 100 kHz and at temperatures ranging from 30 up to 90°C. The dielectric investigations indicate that the samples containing wood flour treated with both SMG and SM increase the values of ε' and decrease those of ε'', which allow such samples to be used in insulation purposes. The increase in the relaxation time and the crosslinking density ν for such composites indicate the increase in filler–polymer interaction rather than filler–filler interaction. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5861–5870, 2006

Key words: composites; wood flour; SBR/PS

INTRODUCTION

The idea of using wood flour as reinforcement in composite materials is not a new or recent one. In the past, composites, such as coconut fiber/natural rubber latex, were extensively used by the automotive industry. However, during the 1970s and 1980s, cellulose fillers were gradually substituted by newly developed synthetic fillers because of better performance. Since then, the use of cellulose filler has been limited to the production of rope, string, clothing, carpets, and other decorative products. Over the past few years, there has been a renewed interest in using these fillers as reinforcement materials in the plastic industry. Recently, interest has arisen because of the increasing cost of plastics, and also because of the environmental aspects of using renewable and biodegradable materials.[1]

Unfortunately, the high hydroxyl group content of cellulose is the main cause of poor compatibility between hydrophilic natural fillers and hydrophobic polymers used as matrix. This is a difficulty encountered during the incorporation of these natural fillers into the polymeric matrix. The polarity of wood-based fillers adversely affects the dispersion of such polar materials in the nonpolar matrix.[2] A number of attempts had been made to improve the adhesion of cellulosic fillers to the polymer matrix. These attempts include both physical and chemical modification of the wood flour.[3,4] The change in the properties of the filler caused by chemical treatments showed characteristic behaviors depending on structural changes.

Chemical modification of the surface of organic fibers by alkalization[5] or with different silane coupling agents had been reported.[6]

A series of studies on wood modified with various cyclic anhydrides (maleic, phthalic, succinic) which were then further reacted with glycidyl methacrylate, phenyl, or allyl glycidyl ether had also been reported.[7–10]

The present study deals essentially with the influence of wood flour treatment and loading on the physicomechanical and electrical properties of SBR/PS blend. Swelling studies to determine the rubber–filler interaction were also carried out.

EXPERIMENTAL

Materials used

Polystyrene (PS, grade 160) was supplied by Sabic SA (Saudi Arabia), with a melt flow index of 3 g/min and density of 1.05 g cm^{-3}. Styrene-butadiene rubber (SBR, 1502) was a product from Bayer AG (Germany). Filler

used was wood flour (supplied by Sweden) of particle size 1 mm that passes through a sieve of mesh size 16. Other chemicals such as sulfur, zinc oxide, stearic acid, mercapto benzo-thiazole (MBT), and phenyl-β-naphthyl amine (PBN) are of commercial grades used in industry. Sodium hydroxide, maleic anhydride (MAN), glycidyl methacrylate, and triethoxyvinylsilane as coupling agent were obtained from Merck (Darmstadt, Germany). All solvents used were obtained from BDH Chemicals Ltd. (Poole, England).

Treatment of wood flour

Wood flour was dried at 70°C for 24 h in a vacuum oven and part of it was treated with aqueous solution of NaOH (10 wt %). The filler was immersed in the solution for 1.5 h at room temperature (mercerized) and then washed several times with distilled water, then with a mixture of water–ethanol (50 : 50) and finally with ethanol.

Part of NaOH treated wood flour was immersed in a 0.6N solution of MAN in xylene and then heated at reflux temperature (140°C) for 24 h. Then, the esterified wood particles were separated from the xylene solution and intensively washed with distilled water to eliminate the unreacted anhydride. Finally, the wood flour was dried at 70°C in a vacuum oven until constant weight was achieved.

Part of the esterified wood flour with MAN was refluxed with a mixture of glycidyl methacrylate and MAN in DMF as a solvent in the ratios of 24.5, 12, 63.5% respectively, at 120°C for 1.5 h. After the completion of the reaction, samples were washed with acetone to remove unreacted chemicals and then dried at 103°C ± 1°C to constant weight.

Coupling agent (2 wt % of triethoxyvinylsilane) solution in water was added in high-speed mixer to a part of the dried untreated wood flour. After mixing for about 5 min, the wood flour was removed and dried at 80°C in an oven for 1 h. When most of the water was evaporated, the temperature was raised to 120°C, for 30 min, to achieve the reaction of wood flour with the coupling agent.

Five different types of wood flour were used:

1. Untreated wood flour (B)
2. Mercerized wood flour (NaOH) (S)
3. MAN-treated wood flour [esterified] (SM)
4. MAN-glycidyl methacrylate [oligoestrified] treated wood flour (SMG)
5. Coupling agent treated wood flour (CA)

Mixing procedure

Mixing of composites was carried out in a Brabender (C. W. Brabender instruments, Hackensack, NJ; 230 V, 40 A) at 170°C, 50 rpm for 10 min. The PS was preheated for 2 min before the rotor was started and was

melted in the mixer for 2 min. Then different concentrations of wood flour were added to the molten PS and the mixing was continued for another 2 min. SBR was added as a last component and was mixed for an additional 4 min. Then the ingredients were added to the mix on a laboratory two-roll mill having an outside diameter of 470 mm and a working distance of 300 mm; speed of the slow roll was 24 rpm and the friction ratio was 1.4 : 1. Table I shows the composition of the composites. The rheometric characteristics of the composites were studied[12] using a Monsanto oscillating disc rheometer R-100. The composites were then press heated to produce molded sheets (1 and 3 mm thick) for physicomechanical and electrical measurements.

Techniques of characterization and measurements

Acid value determination: About 0.1 g of sample treated with MAN was weighed accurately into a flask and about 10 mL of acetone was added. Then, 10 mL of 0.1N HCl was added by pipette and further 100 mL of distilled water was added. It was titrated with 0.1N KOH using phenolphthalein (PhPh) as indicator. Acid value was calculated using the equation described elsewhere.[11]

Infrared spectra were recorded on a JASCO FT/IR 300 E Fourier transform infrared (FTIR) spectrometer. Nuclear magnetic resonance (^{1}H NMR) spectrum was run at 260 MCPS on a Jeol-Ex-270 NMR spectrometer.

Monsanto oscillating disc rheometer 100 was used for determination of rheometric characteristics of the rubber blends according to ISO 289-1994. The vulcanization process was performed under pressure of about 4 MPa and a temperature of 162°C.

The stress at yield and rupture, strain at yield and rupture, and Young's modulus were determined on dumbbell-shaped specimens using a Zwick tensile machine (model 1425). This is carried out in accordance with ISO 37. The mean of four readings were taking into consideration.

The test of hardness was carried out using the Shore A device according to ISO 868. All tests were conducting at room temperature (25°C ± 1°C).

TABLE I
Composition of the Composites

Ingredients	phr
SBR	50
PS	50
Stearic acid	2
Zinc oxide	3
MBT	0.8
PBN	1
Sulphur	2
Wood flour	0, 5, 10, 15, 20

phr indicates part per hundred parts of rubber.

Water absorption

Dried samples were immersed in distilled water at 25°C. Weights of the samples were recorded at different times. Samples were wiped with tissue paper to remove surface water before weighing. Finally the percentage of weight gain was calculated as follows:

$$W_g = \frac{W_e - W_o}{W_e} \times 100\%$$

where W_g is the percent of weight gain, W_e is the equilibrium weight after water treatment, W_o is the oven dry weight before water treatment (the mean of five readings were considered).

Swelling test

Test samples were swollen in toluene at room temperature 25°C for 24 h. Equation of Lorenz and Parks[12] was applied to study rubber–fiber interaction, which is expressed as follows:
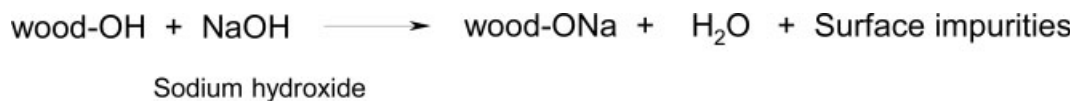
$$\frac{Q_f}{Q_g} = a\,e^{-z} + b \tag{1}$$

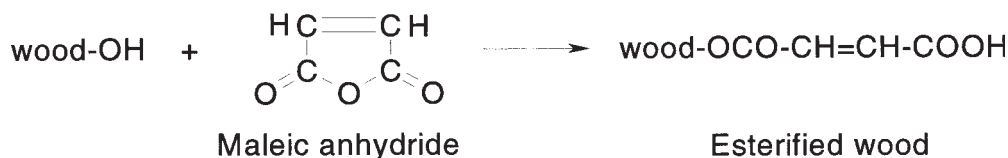where Q is defined as grams of solvent per gram of hydrocarbon and is calculated by

$$Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100/\text{Formula weight}} \tag{2}$$

The subscripts f and g in eq. (1) refer to filled and unfilled SBR/PS vulcanizates respectively. z is the ratio by weight of filler to polymer hydrocarbons in the vulcanizate, while a and b are constants. The higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix.

The formation of such crosslinking is achieved by determining its density from equilibrium swelling measurements through the molar mass between crosslinks is M_c according to Flory–Rehner relation.[13]

$$M_c = \frac{-\rho_p\,V_s\,V_r^{1/3}}{\left[\ln(1 - V_r) + V_r + \chi V_r^2\right]}$$

where ρ is the density of SBR/PS blend, V_s is the molar volume of the solvent (toluene), χ is the interaction parameter between SBR/PS and toluene, V_r is the volume fraction of swollen rubber and can be obtained from the masses and densities of rubber sample and the solvent. The degree of crosslinking is given by

$$\nu = 1/(2M_c)$$

The mean of samples was taken into consideration.

Dielectric measurements were carried out in the frequency range of 100 Hz up to 100 kHz using an LCR meter type AG-411 B (Ando electric Ltd., Japan). The capacitance C, loss tangent $\tan \delta$ and AC resistance measured directly from the bridge from which the permittivity ε', dielectric loss ε'', and R_{DC} were calculated. A guard ring capacitor (type NFM/5T, Wiss Tech. Werkstatten GMBH, Germany) was used as a measuring cell. The cell was calibrated using standard materials.[14] The mean of three measured samples were taken into consideration. The experimental error in ε' and ε'' was found to be ±3% and ±5% respectively.

RESULTS AND DISCUSSION

### Characterization of modified wood flour

The following main reactions of the functional groups in this work are considered as follows:

- Alkylation with sodium hydroxide

wood-OH + NaOH $\longrightarrow$ wood-ONa + H_2O + Surface impurities

Sodium hydroxide

- Esterification with MAN

wood-OH + Maleic anhydride $\dashrightarrow$ wood-OCO-CH=CH-COOH

Maleic anhydride   Esterified wood

The ester content of the MAN modified wood flour was calculated from acid value. This value (210 mg KOH/g) indicated the degree of chemical reaction between the —OH groups of wood flour and the MAN.

- Oligoesterification with MAN and glycidyl methacrylate

Maleic anhydride   Glycidyl methacrylate

Oligoesterified wood
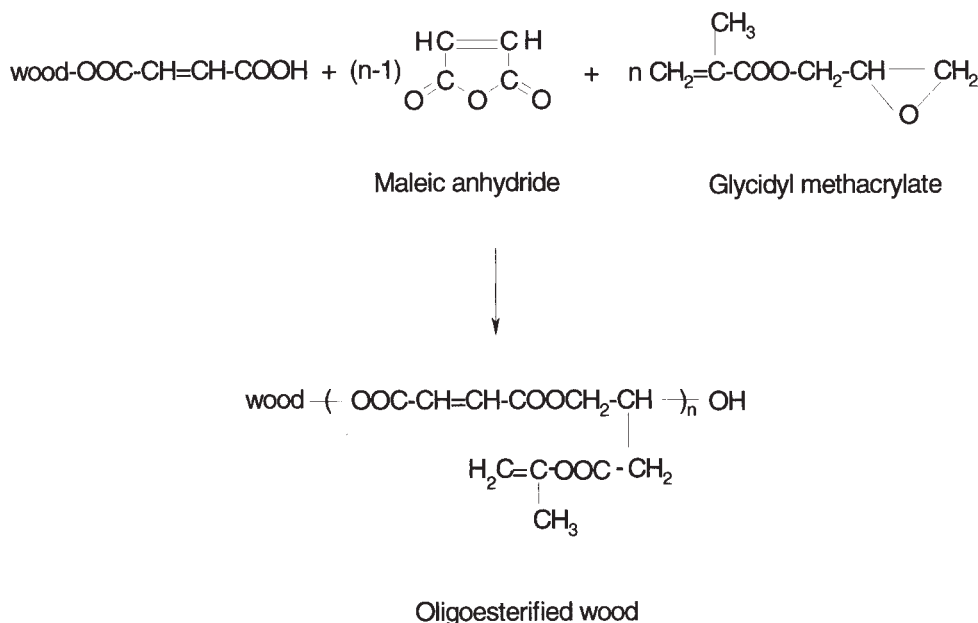
- Coupling agent
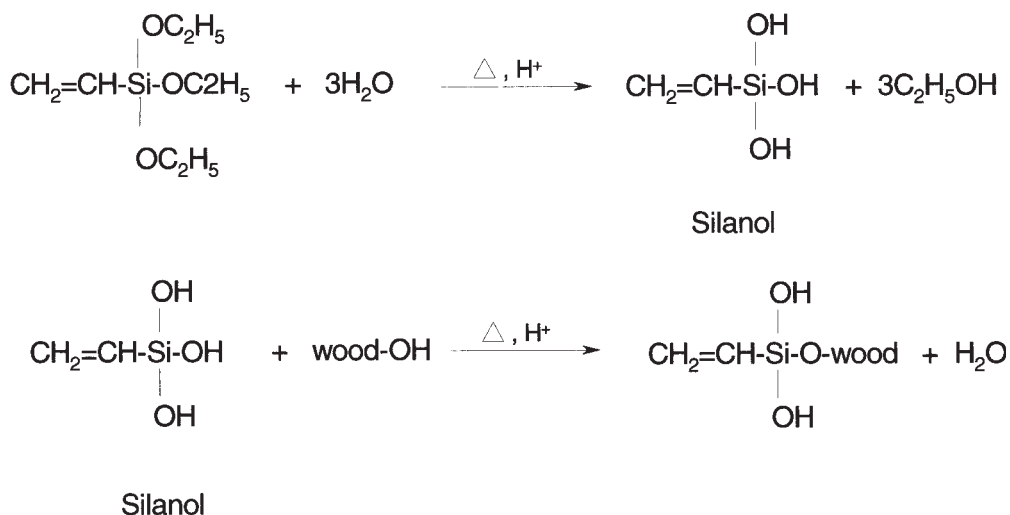
Silanol

Silanol

It is known that the ethoxy groups (OC_2H_5) in the silane can be hydrolyzed to produce silanol [$-Si(OH)_3$ structure] (1). During the wood flour pretreatment process, these silnol groups can either develop covalent siloxane bonds (2) or form hydrogen bonds with OH groups of wood.

The IR spectrum for the untreated and treated wood flour with NaOH, MAN, MAN+ glycidyl methacrylate and silane coupling agent are shown in Figure 1.

The absorbance peaks in this study have been identified and shown in Figure 1. Chemical treatments reduce the hydrogen bonding due to removal of the hydroxyl groups by the reaction with the chemical modifiers. The peak between 1736 and 1740 cm^{-1} seen in untreated wood flour (B) disappears upon alkali treatment. This is due to the removal of the carboxylic group by alkali treatment (S); this process is called deesterification.[15] The carboxylic group may also be present in the fiber as traces of fatty acids present in oils.

Figure 1 is representative for the system of esterification and oligoesterfication reaction (SM and SMG). The most important features of the spectra are the carbonyl absorption occurring at 1735 cm^{-1} (which is due to the ester bond between the wood and the anhydride moiety), and the absorption band at 1657 cm^{-1} (due to the C=C bond).
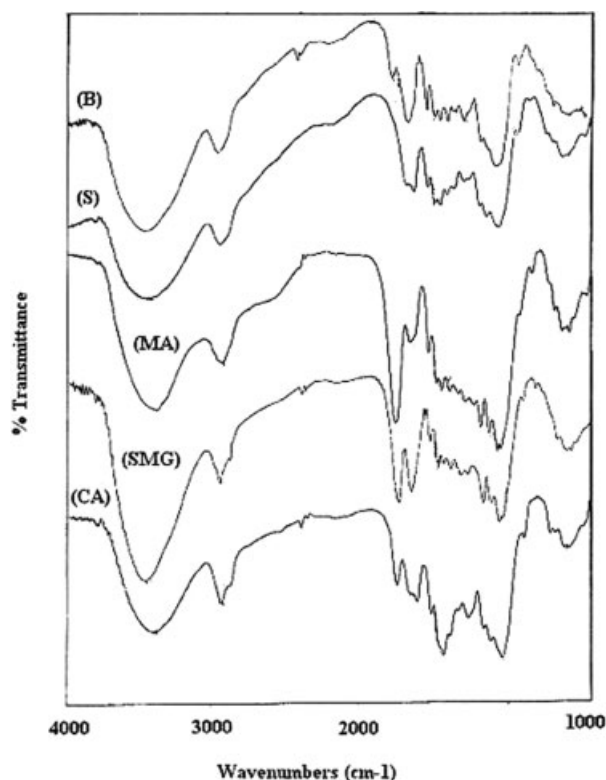
Figure 1 The IR spectrum of the treated wood flour.

The rheological characteristics

Table II represents the effect of filler loading on the curing characteristics before and after different treatments.

From this table, it is seen that the maximum torque increases with loading for all compositions. Maximum torque (M_H) gives an idea about the shear modulus of fully vulcanized compound at the vulcanization temperature.[16] The increase in the maximum torque with increasing filler loading is attributed to the presence of filler in the matrix that reduced the mobility of the macromolecular and consequently increased the torque of the vulcanizate. Comparing the values of M_H for the different treatments, one can see that it increases in the order B < CA < S < SM < SMG. This indicates that the SMG and SM in the SBR/PS wood flour composites improve the interaction between the filler and the matrix, than the other treatments which may cause more effective transfer of the stresses from matrix to filler.

Minimum torque (M_L) is an indirect measure of the viscosity of the compound,[17] or it can be generally treated as the measure of the stiffness of the vulcanized test specimen taken at the lowest point of the curve. Minimum torque also increased with increased loading and it follows the same trend as that of M_H.

The scorch time (t_{s2}) values in Table II indicate that samples loaded with the filler exhibit longer scorch time than do the unloaded ones and it increases by treating the wood flour in the order B < CA < S < SM

< SMG. It is also observed that the scorch time increases until 15 phr, then decreases.

Studies on the effect of filler loading for all composites show that the cure time reaches a maximum value at a loading of 15 phr of filler for both treated and untreated wood flour and follow the increase in the order B < CA < S < SM < SMG. When the filler concentration increases above 15 phr, the optimum cure time T_{c90} slightly decreased. The same trend was observed with the cure rate index (CRI).

Mechanical properties

Stress at yield and rupture

Figure 2 shows the stress at yield and rupture of composites as a function of filler loading before and after different treatments of the filler. The addition of wood flour gradually increases the stress at yield and rupture until reaching the loading of 15 phr. Further loading leads to gradual decrease in the stress at yield and rupture.

This gradual increase of the stress until the concentration of 15 phr could be attributed to the improvement in the interfacial bonding between wood flour and the matrix (SBR/PS).[18] Wood flour has a high modulus and therefore acts as reinforcing filler. On

TABLE II
Rheometric Characteristics of SBR/PS Composites

Filler content (phr)	M_L (dN m)	M_H (dN m)	Tc_{90} (min)	t_{s2} (min)	CRI (min^{-1})
Untreated (B)					
0	15	29	14	2	6
5	18	32	14	2	8
10	20	34	14	3	9
15	23	38	16	6	10
20	25	42	14	2	8
NaOH (S)					
5	22	40	16	5	9
10	24	43	17	7	10
15	27	46	19	11	12.5
20	28	50	16	7	11
MAN (SM)					
5	24	44	17	10	11
10	26	45	18	10	12.5
15	28	48	20	13	14
20	29	52	17	9.5	13
MAN-glycidyl methacrylate (SMG)					
5	28	50	19	11	12.5
10	28	52	21	14	14
15	30	54	24	18	17
20	31	54	20	13.5	15.5
Coupling agent					
5	20	35	14	2	8
10	23	39	16	5	9
15	25	41	18	9	11
20	27	48	15	4	9

M_L indicates the minimum torque, M_H the maximum torque, T_{c90} the optimum cure time, t_{s2} the scorch time, and CRI the cure rate index.
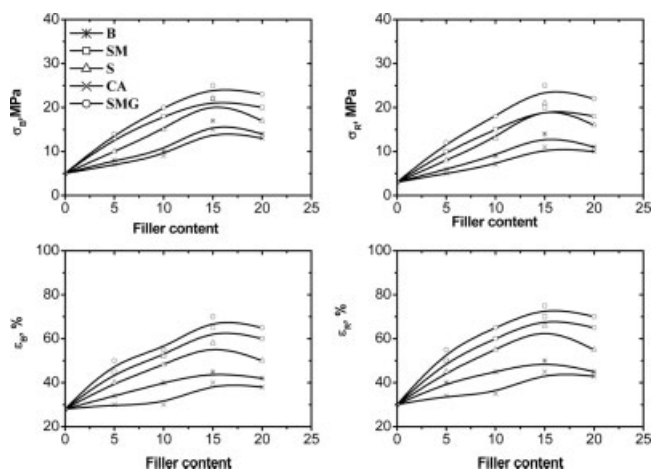
Figure 2 Mechanical properties versus filler content at room temperature: stress at yield σ_B, stress at rupture σ_R, strain at yield ε_B, strain at rupture ε_R.

the other hand, for low concentrations of filler, good embedding may be obtained and an increase in stress occurs.[19] As the filler loading increases, it can be anticipated that filler particles will not be dispersed and wetted efficiently by the matrix.[20] These inherent defects can act as concentration points and, consequently, decreases the stress at yield and rupture of the composites. Also it is interesting to note that the values of stress at yield and rupture can be arranged in the order of B < CA < S < SM < SMG respectively, for the sample loaded with 15 phr.

Strain at yield and rupture

The incorporation of wood flour into SBR/PS blends increases the strain at yield and rupture until 15 phr, as shown in Figure 2. Then the strain decreased with the addition of more filler. With increasing wood flour loading, the stiffness and brittleness of the composites increases. This means that incorporation of more filler seems to cause interruption in the alignment process of the chains. Also, as filler loading increases, a higher restriction to molecular motion of the macromolecules is expected.

It is notable that the higher values were obtained for the SMG followed by that of SM for the sample loaded with 15 phr.

Elastic modulus and hardness

Figure 3 shows the dependence of both Young's modulus and hardness on the wood flour loading before and after the different treatments of SBR/PS composites, respectively. It can be seen that the values of both increase with increasing of wood flour loading. The addition of rigid and stiff particles filler would increase the modulus of the composites because of the introduction of restrictions on the mobility of the
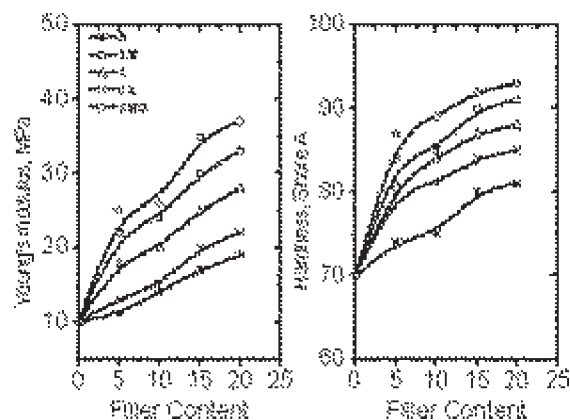

Figure 3 The variation of Young's modulus and hardness, Shore A versus filler content at room temperature.

polymer molecules. Also it is clear that this increase follows the same trend that was obtained before, i.e., B < CA < S < SM < SMG. This result is expected because, as more wood flour is incorporated into the matrix, more rigid composites are obtained.[21]

Water absorption

Figure 4 shows that the filler treatments (15 phr) influence the water absorption of composites in different ways. The highest water absorption (at 25 days of immersion) is obtained in composites containing the filler treated with NaOH, S, (its water absorption is higher than the composite with untreated filler, B). Water absorption is mainly due to the hydroxyl groups on the cell walls of the wood. The alkylation increases the accessibility of water molecules to particle surface, because the surface area is increased, thus enhancing the OH group's availability. The lower values of the water absorption are obtained in those composites containing the esterified and oligoesterified filler (SM and SMG). This could be attributed to the lower amount of free OH in wood flour, because some of them could be interacting with MAN or MAN with glycidyl methacrylate.
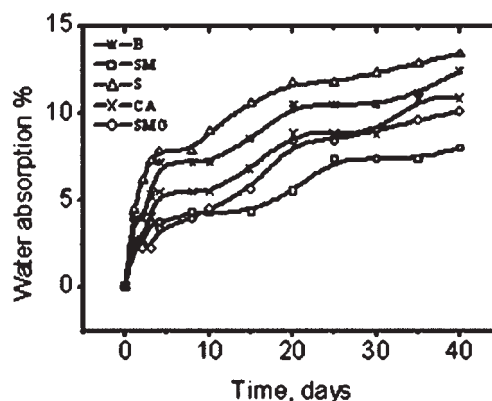

Figure 4 Variation of percentage water absorption versus time for wood flour–SBR/PS composites (15 phr).
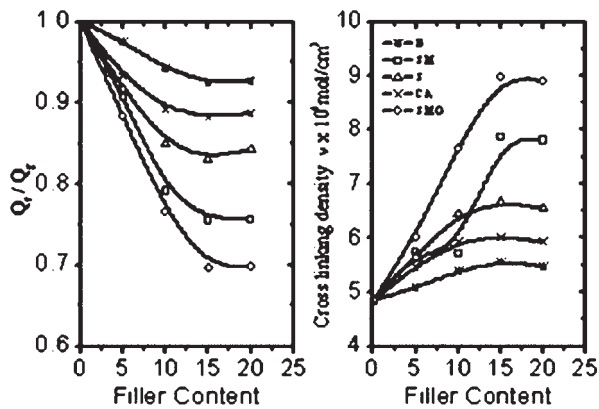
Figure 5 The variation of swelling parameters versus filler content at room temperature.

Equilibrium swelling

The values of Q_f/Q_g and the crosslinking density ν which was determined from the equilibrium swelling measurements are illustrated graphically in Figure 5. It can be seen that Q_f/Q_g decreases with increasing filler content up to 15 phr after which there is no significant change. From this graph it can be noted that the lowest value of Q_f/Q_g is obtained at 15 phr SMG samples, which confirms that 15 phr SMG brings about sufficient adhesion between the filler and SBR/PS blend. The lower the Q_f/Q_g values, the higher will be the extent of interaction between the filler and the matrix. This result clearly indicates that increasing filler loading up to 15 phr weakens the polymer–filler interaction.[22]

To study the effect of the above-mentioned treatments on the formation of such crosslinking, the crosslinking density was determined using Flory–Rehner equation given earlier and the data obtained are illustrated graphically in Figure 5. This figure shows that the crosslinking density increases by increasing the filler content. This increase is much more pronounced up to 15 phr after which there is a plateau, i.e., formation of stable matrix.

In general, it was found that alkaline treatment improves only the dispersion of the particles but not their adhesion to the polymer matrix, because of higher availability of OH groups in the particles surface, which in turn favors the water absorption and hence the composites swelling.

Comparing untreated wood flour (B) with wood flour treated with coupling agent, for the composites made from coupling agent treated wood flour (CA), a slight improvement in rheological characteristics and physicomechanical properties was observed. When wood flour was treated with a coupling agent, hydroxyl groups can be produced by the hydrolysis of silanes with absorbed water. They were supposed to link to the wood flour through the formation of hydrogen bonds with hydroxyl groups at the surface of the wood flour.[4] The remaining chain of silanes

could adhere to SBR/PS with the help of a van der Waals type of weak interaction. In this way silane made a link between wood flour and SBR/PS. As a result, the mechanical properties were slightly improved, compared with those of untreated filler. This is because the hydrogen bonding and van der Waals are weak forces and insufficient to make a strong bridge between the filler and polymer.[23]

Dielectric measurements

Permittivity ε' and dielectric loss ε''

The permittivity ε' and the dielectric loss values ε'' for SBR/PS blend 50/50 loaded with different concentrations of untreated wood flour and those treated with different materials as mentioned in the experimental part were measured in the frequency range of 100 Hz up to 100 kHz and at temperatures 30, 60, and 90°C. The measured values of ε' and ε'' at 30°C versus the applied frequency for the untreated wood flour and for SMG treated wood flour which was taken as an example are illustrated graphically in Figure 6.

This figure shows that in both cases the values of ε' and ε'' increase pronouncedly by increasing the filler content up to 10 phr after which the increase in both values is very slight.

Also it was noticed that the values of ε' slightly increase after treating the wood flour with SMG when
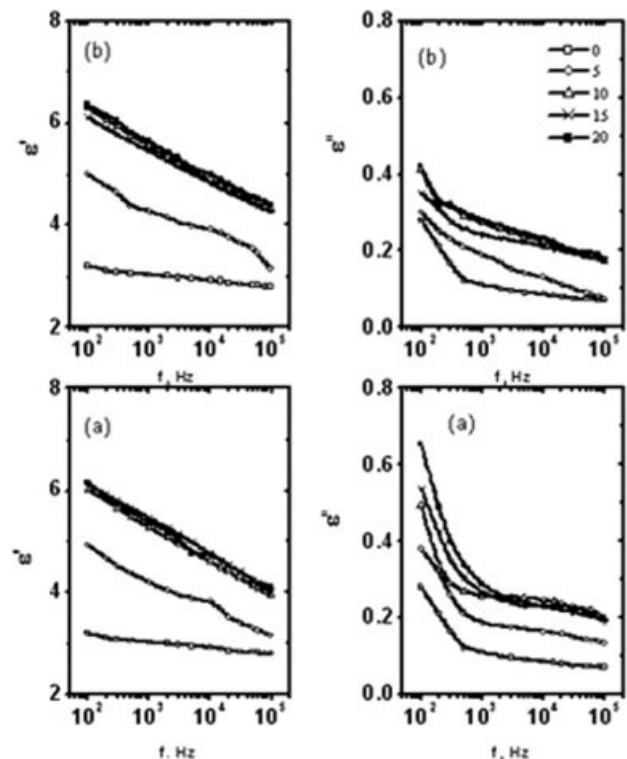

Figure 6 The variation of ε' and ε'' versus applied frequency for SBR/PS at 30°C filled with (a) B and (b) SMG.

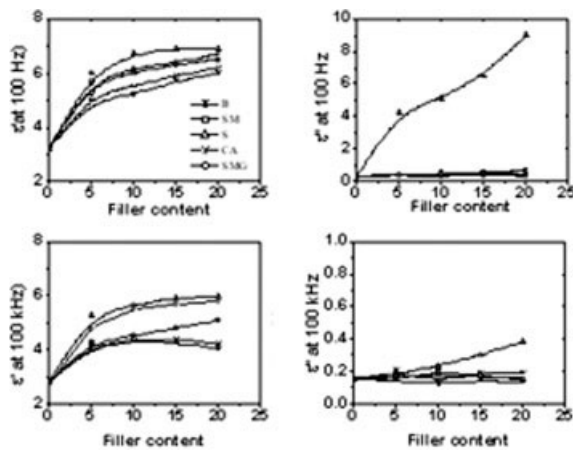**Figure 7** The variation of ε' and ε'' versus filler content at two fixed frequencies (100 Hz and 100 KHz).

compared with those containing untreated one. The slight increase in ε' is accompanied by a pronounced decrease in ε'', especially in the lower frequency range. The decrease in ε'' may be due to the reduction of the OH group content as a result of the oligoesterified wood formation which is clear from the IR spectra. Anyhow, the slight increase in ε', which is accompanied by a decrease in ε'' values, can be taken as an evidence for the improvement in the dielectric properties of the investigated samples loaded with the treated wood flour.

To understand the effect of different treatments upon the dielectric properties of the wood flour/SBR/PS composites, the values of ε' and ε'' are illustrated graphically in figure 7 versus filler content at two fixed frequencies at 30°C. From this graph it is notable that the values of ε' follow the order of B < CA < SM < SMG < S respectively, at both frequencies. It is clear that the values of ε' increase by increasing the filler content up to 15 phr after which a slight increase is noticed. This behavior is much more recognized at lower frequency rather than at a higher one. It is also found that samples containing wood flour treated with sodium hydroxide (S) possess the highest loss values. On the other hand, the samples of SGM and SM loaded with 15 phr increase the values of ε' and decrease those of ε'', which allow such samples to be used in insulation purposes. The above-mentioned results find further justification through all the mechanical parameters discussed earlier.

The effect of temperature on both permittivity ε' and dielectric loss ε'' at fixed frequency (100 Hz) for SBR/PS loaded with 10 phr of wood flour are illustrated graphically in Figure 8. From this figure it is notable that both values increase by increasing the temperature, and this increase is more pronounced after 60°C. It is worth mentioning that both the composites containing the untreated wood flour and those treated with NaOH (S) possess the highest loss values, espe-

cially after 60°C, which decrease to some extent their insulating properties. For other samples with SM, CA, and SMG it is preferable to use them at temperatures not more than 60°C, e.g., the values of the dielectric loss rise for samples of SMG from 0.6 at 60°C to 4.66 at 90°C.

Dielectric relaxation

Dielectric relaxation occurs when a dielectric material is polarized by the application of an external field, and then polarization relaxes on the removal of the field. After a certain relaxation time τ, the molecules of the material relax to the equilibrium configuration, where $\tau = 1/(2\pi f_m)$ and f_m is the critical frequency at which the dielectric loss ε'' has its maximum value. The relaxation time depends upon the nature of the material, that is, its state, size, and shape. So it is reasonable to study the different relaxation mechanisms to follow up the changes that occur due to the different treatments upon the filler–polymer matrix interaction.

From Figure 6 it is clear that ε' increases by increasing the percentage of wood flour while it decreases by increasing the applied frequency which shows an anomalous dispersion.

Regarding the relaxation mechanisms associated with such dispersion, as it is clear from Figure 6, the dielectric loss values ε'' are found to be broader than Debye function, which indicates more than one relaxation mechanism. Also it is clear from this figure that the values of ε'' in the lower frequency are high. These higher values may be due to DC conductivity[24,25] resulting from the increase of ion mobility or Maxwell Wagner effect or both. To confirm this, the DC conductivity σ was calculated from the measured resistance at 30°C and is illustrated graphically in Figure 8. From this figure it is notable that σ values slightly increase by increasing the filler content for the samples of SMG, SM, and CA. On the other hand, these
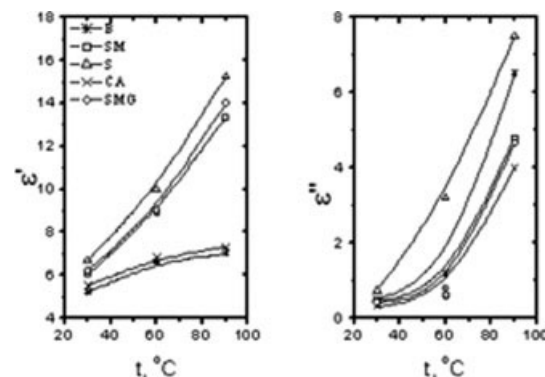

Figure 8 The variation of ε' and ε'' versus temperature at fixed frequency (100 Hz) for SBR/PS loaded with 10 phr of wood with different treatments.
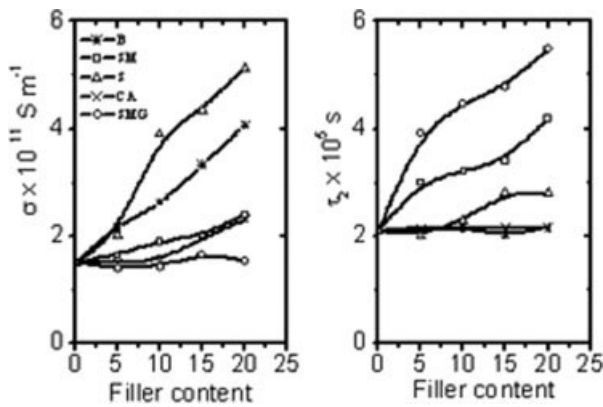
Figure 9 The variation of DC conductivity σ_{DC} and relaxation time τ_2 versus filler content.

values are found to increase pronouncedly for composites containing untreated wood flour and those treated with NaOH (S). In case of untreated wood flour samples (B), this increase is due to the hydrophilicity of wood flour.

Analysis of the absorption curves relating ε'' and the applied frequency at 30°C after subtracting the conductivity part was done in terms of superposition of Fröhlich and Havriliak-Negami functions according to the following equations.[26]

Conductivity term: The dielectric loss due to DC conductivity, ε''_σ, at the different frequencies ω were calculated using the equation[9]

$$\varepsilon''_\sigma = \frac{9 \times 10^{11} \times 4\pi\sigma}{\omega}$$

Fröhlich equation:

$$\varepsilon''(\omega) = \sum_{i=1}^{n} \frac{\varepsilon_s - \varepsilon_\infty}{P_i} \arctan\left[\frac{\sinh P_i/2}{\cosh \ln (\omega \, \bar{\tau}_i)}\right]$$

where P_i is a parameter describing the width of distribution of relaxation times and equals $\ln(\tau_1/\tau_2)$. $\bar{\tau}$ is the mean relaxation time and equals $(\tau_1\tau_2)^{1/2}$. ε'' is the dielectric loss, while ε_s and ε_∞ are the static permittivity and the permittivity at infinite frequency, respectively.

Havriliak-Nagami function:

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty) \, \cos (\beta \, \theta)}{\{(1 + 2(\omega\tau)^{1-\alpha} \, \sin (\pi\alpha/2) + (\omega\tau)^{2 \, (1-\alpha)})\}^{\beta/2}}$$

$$\theta = \arctan \frac{(\omega\tau)^{1-\alpha} \, \cos \pi\alpha/2}{1(\omega\tau)^{1-\alpha} \, \sin \pi\alpha/2}$$

where α and β are constants called the Cole-Cole and Cole–Davidson distribution parameters (which are found to be constants for these samples and equal to 0.5 and 0.5 respectively). ε_s and ε_∞ are the static per-

mittivity and the permittivity at infinite frequency, ω is the applied frequency $= 2 \pi f$, while τ is the relaxation time. Example of the analyses is given in Figure 10. The first relaxation time lies in the lower frequency range of about $(2.8–3.2)10^{-4}$ s, which may be attributed to Maxwell Wagner effect that always appear in such range of frequency because of the multiconstituents of the sample as a result of the ingredients added to the blends during vulcanization. This region is found to be unaffected by either the filler content or the type of treatment. The second absorption region with relaxation time in the order of 10^{-5} s that is fitted by Havriliak-Nagami function could be attributed to the orientation of the large aggregates caused by the movement of the main chain, which are expected to
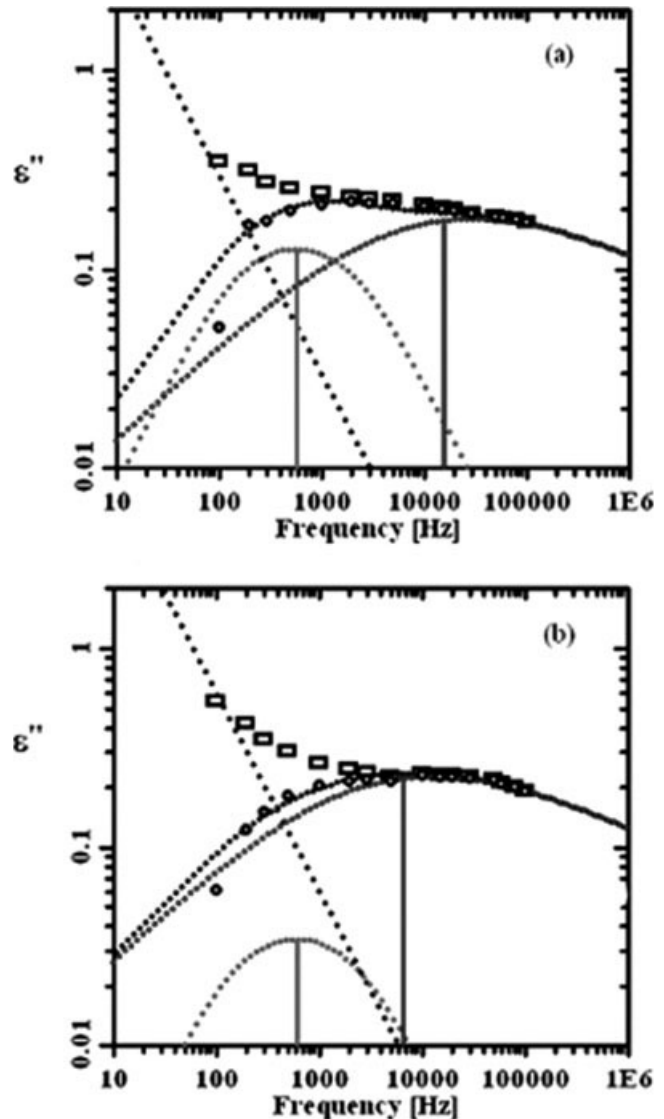

Figure 10 Example of the analyses for SBR/PS filled with 15 phr wood flour. (a) B and (b) SMG. Fitting the experimental data after subtraction of the losses due to DC conductivity with Froehlich term and a Havriliak Nagami function.

be formed by the addition of different ingredients to the blend during preparation.

Figure 9 represents the variation of the relaxation time associated with the second region (τ_2) versus filler content for the whole treatments under investigation. From this figure one can see that τ_2 is unaffected by filler content for composites containing untreated wood flour and those containing wood flour treated with the coupling agent (CA) while it slightly increases when wood flour is treated with NaOH (S). Also it is notable that τ_2 increases pronouncedly by increasing the filler content for the composites containing wood flour treated with SMG and SM. The increase in the relaxation time may be due to the increase in filler–polymer interaction rather than filler–filler interaction due to such treatment. This conclusion is justified by the crosslinking density values obtained from the swelling measurements given earlier.

From Figure 10 it is clear that the contribution of the first relaxation process for the SMG sample becomes less than that for that untreated one. This decrease may confirm the presumption that the contribution of the interfacial polarization is reduced by such treatments because of the restriction of OH group in the wood flour and consequently the values of conductivity decreased.

CONCLUSIONS

- All the rheological as well as the mechanical parameters under investigation are improved by loading the SBR/PS with different wood flour concentrations. The optimum improvement was obtained at 15 phr.
- An important increment in particle dispersion was obtained by modifying the wood flour with MAN and glycidyl methacrylate (SMG).
- The best treatments that give the optimum rheological as well as mechanical properties are SMG, followed by SM. The other treatments are found to slightly affect these parameters.
- The samples containing wood flour treated with both SMG and SM increase the values of ε' and decrease those of ε'', which allow such samples to be used in insulation purposes, specially those containing 15 phr filler.

- It is preferable to use these composites at temperatures not exceeding 60°C, otherwise these composite will lose their insulation properties.
- The increase in the relaxation time τ_2 and the crosslinking density, ν, for composites containing wood flour treated with both SMG and SM indicates the increase in filler–polymer interaction rather than filler–filler interaction.

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