

Chemically Modified Sugarcane Bagasse as an Improving Agent for the Properties of Styrene–Butadiene Rubber

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ABSTRACT: The agrowaste of sugarcane bagasse was used as a filler to improve the properties of rubber. Sugarcane bagasse waste was ground and sieved to a particle size less than 75 nm and then purified and chemically modified by an acetylation method and stearic acid adsorption. The modified bagasse was incorporated into styrene–butadiene rubber formulations with different concentrations (20, 30, 50, and 70 phr) in comparison with carbon black and hisil, commercial fillers used in industry. The physicochemical properties of the rubber vulcanizates were determined before and after thermal aging at 90°C. The retained values of the tensile strength, elongation at break, and equilibrium

swelling increased as the concentration of the modified bagasse increased in styrene–butadiene rubber vulcanizates until 50 phr; after this concentration, the retained values of each property decreased. Rubber vulcanizates containing modified bagasse with a concentration of 50 phr may be better for retained values of the physicochemical properties and equilibrium swelling in comparison with those containing carbon black, hisil, and untreated bagasse. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3470–3476, 2009

Key words: compounding; fibers; fillers; mechanical properties; rubber

INTRODUCTION

Agricultural residues are mixtures of complex polysaccharides and lignin. The most abundant and reactive groups attached to these components are hydroxyl groups; a large number of modification reactions for hydroxyl groups have been reported.^{1,2} The weak interfacial adhesion between the fiber and matrix usually results in poor mechanical properties of the composites. An improvement in the compatibility between the two components is a key to success in this area, so to introduce natural fibers profitably into a hydrophobic polymer matrix, a pretreatment of the polymer fiber surface or the incorporation of interface modifiers is generally required. To improve the compatibility of wood fiber/polymer composites, a lot of chemicals and methods have been developed, such as different treatments³ of polymer matrices (e.g., graft copolymerization or grafting fibers), coupling agents (e.g., silanes and isocyanates), and interface compatibilizers⁴ (e.g., maleic anhydride grafted polyolefins or elastomers).

In previous studies, the use of organic carboxylic acids⁵ (e.g., stearic acid, acetic anhydride, maleic an-

hydride, and phthalic anhydride) has also drawn considerable attention because of their effectiveness in improving adhesion between a natural fiber and a thermoplastic matrix. According to the principles of interface coupling, the hydrophilic carboxyl group of the organic acid as a modifier is expected to react with the hydroxyl group of the natural fiber in the surface, and the hydrophobic group should react or have relatively high compatibility with the polymer matrix. The combined effects of these interactions will effectively improve the fiber dispersion and resultant adhesive coupling.

To increase the industrial use and fulfill the various demands for functionality of different cellulosic products, cellulose is often modified by chemical means. Chemical modification implies the substitution of free hydroxyl groups in the polymers with functional groups, yielding different cellulose derivatives. The modification of cellulose can take place in heterogeneous and homogeneous phases.^{6–8}

The surface treatments of bagasse fiber (BF) with benzoic acid as a surface/interface modifier and the mechanical properties of BF/poly(vinyl chloride) (PVC) composites were studied.⁹ The interface modifier improved the tensile strength of the composite significantly and the impact strength of the composite a little; for example, the tensile strength changed between 42 and 52 MPa in comparison with the tensile strength of an untreated BF/PVC composite

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(38 MPa), and the impact strength changed between 8.3 and 9.2 kJ/m² in comparison with the impact strength of an untreated BF/PVC composite (7.5 kJ/m²), when the content of benzoic acid changed between 3 and 10%. Biodegradable composites reinforced with BF before and after alkali treatments were prepared; the mechanical properties of the composites made from alkali-treated fibers were superior to those of the untreated fibers, and composites of 1% NaOH solution treated fibers showed the maximum improvement. Scanning electron microscopy (SEM) observations of the fracture surfaces of the composites showed that surface modification of the fiber occurred and improved fiber–matrix adhesion.¹⁰

Novel cationic hemicelluloses from sugarcane bagasse were synthesized by quaternization with 3-chloro-2-hydroxypropyltrimethyl ammonium chloride with sodium hydroxide as a catalyst in an aqueous ethanol solution; the extent of quaternization was measured by the yield and degree of substitution. The chemical modification of sugarcane bagasse cellulose with phthalic anhydride with 1-butyl-3-methylimidazolium chloride ionic liquid as the reaction medium was studied. A series of phthalated cellulosic derivatives were prepared with a degree of substitution ranging from 0.12 to 2.54. The degree of substitution increased with the reaction temperature increasing from 85 to 100°C.¹¹

The acetylation of lignocellulosic materials with acetic anhydride has been used to improve the properties of products, such as the hydrophobic properties.¹² In this study, the reaction of heterogeneous acetylation was applied to sugarcane bagasse. The product of heterogeneous acetylation was characterized with (1) Fourier transform infrared (FTIR) spectroscopy based on the presence of the C=O stretching band of the carbonyl group (ca. 1740 cm⁻¹), (2) wide-angle X-ray scattering based on the presence of a maximum in the 2 χ region of 5–10°, and (3) differential scanning calorimetry based on the presence of an endothermic peak at approximately 300°C.¹³

Previously, our group studied the effect of untreated sugarcane bagasse of different particle sizes on the retained values of the mechanical properties of natural and styrene–butadiene rubber (SBR) vulcanizates. Bagasse with a particle size less than 75 nm showed good retained values of the mechanical properties for both natural and SBRs in comparison with other commercial fillers such as calcium carbonate, hisil, and carbon black.¹⁴ The aim of this work was to improve the physicochemical properties of SBR by increasing the degree of distribution of bagasse in the SBR matrix. This could be achieved by chemical modification of purified BF by acetylation or by stearic acid adsorption to increase its

hydrophobic character. The stearic acid modified bagasse and acetylated bagasse were incorporated into SBR formulations with concentrations of 20, 30, 50, and 70 phr. The retained values of the physicochemical properties of the rubber vulcanizates were measured and compared with those containing carbon black, hisil, and untreated bagasse.

EXPERIMENTAL

Materials

The following materials were used: SBR from Bayer EG (SBR-1502) (Cairo, Egypt), 2-mercaptobenzothiazole as an accelerator, isopropylphenylenediamine as an antioxidant, stearic acid and zinc oxide as activators, elemental sulfur as a curing agent, naphthene processing oil as a plasticizer, stearic acid modified bagasse and acetylated bagasse with a particle size less than 75 nm as the investigated materials (in comparison with untreated bagasse with the same particle size, carbon black and hisil as commercial fillers used in industry).

Experimental techniques

Purification of sugarcane bagasse¹⁵

Seventy-six milliliters of 0.25M NaOH was added to a 4.0-g sample of dried and ground bagasse maintained at room temperature for 18 h, and this was followed by filtration and a pH adjustment to 4.5–5.0 with HCl. Seventy-six milliliters of 4.2M ethylenediamine was added, and the pH was readjusted. The bagasse was refluxed with 20% EtOH/HNO₃ (v/v) for 3.0 h, and this was followed by washing with distilled water and oven drying at 105°C for 3 h.

Modification of sugarcane bagasse

Stearic acid modification. To prepare stearic acid modified sugarcane bagasse, different concentrations (20, 30, 50, and 70 g) of purified bagasse with a particle size less than 75 nm were mixed with a 0.07M stearic acid solution in toluene at room temperature for 48 h, and then they were filtered and oven-dried at 105°C for 3 h.

Modification by the acetylation method. The purified bagasse was mixed with 16 mL of glacial acetic acid, 24 mL of toluene, and 0.4 mL of perchloric acid for 10 min by shaking; 15 mL of acetic anhydride was added. The reaction was left for 48 h, and this was followed by filtration, washing with absolute ethanol and distilled water, and drying in the oven at 105°C for 3 h. The acetylated bagasse was characterized by FTIR with a Nexus 670 FTIR spectrophotometer

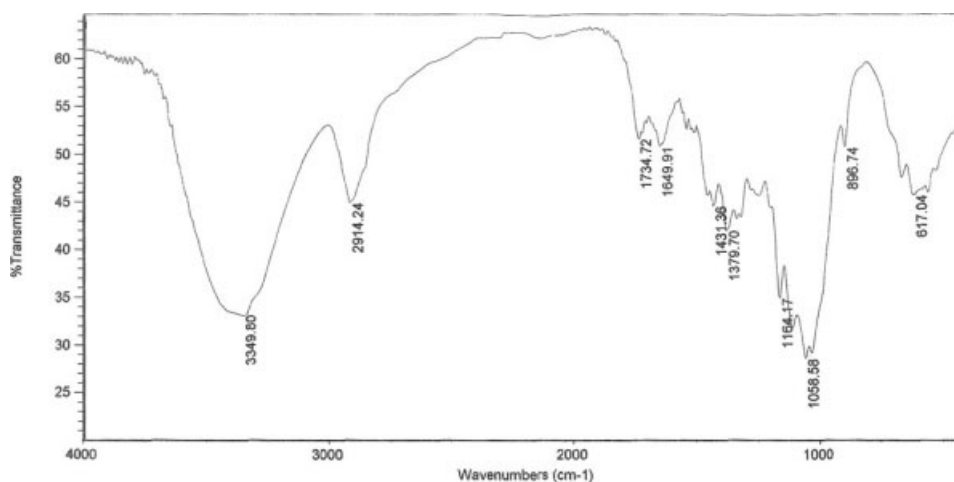


Figure 1 FTIR spectrum of acetylated sugarcane bagasse.

(Nicolet) [Madison, USA] with a resolution of 4 cm^{-1} from 4000 to 400 cm^{-1} .

Preparation and aging of the rubber mix vulcanizates

The mixes were prepared on a two-roll mill (diameter, 470 mm; width, 300 mm; speed of the slow roll, 24 rpm; and gear ratio, 1:1.4). The compounded SBR was vulcanized in a hydraulic press at $152 \pm 1^\circ\text{C}$ and 4 MPa. The mechanical characteristics (tensile strength and elongation at break) were determined with a fully computerized Instron 5586 (Zwick, Germany) tensile testing machine according to standard methods [ASTM D 412-98a (1998)]. The rubber vulcanizates containing different amounts of modified bagasse with a particle size less than 75 nm were subjected to thermal oxidative aging in an electric oven at 90°C for different time periods [ASTM D 1330 (1998)]. The aging data were compared with those of vulcanizates containing carbon black, hisil, and untreated bagasse. The equilibrium swelling was determined in toluene [ASTM D 471-97 (1998)]. It was possible to make use of the swelling data to calculate the molecular weight between two successive crosslinks (M_c) by the application of the well-known Flory–Rehner equation¹⁶ (crosslinking density = $1/2M_c$):

$$-\frac{1}{2}M_c = \frac{1}{2}\rho V_0 \left\{ \ln(1 - V_R) + V_R + \mu V_R^2 \left[V_R^{1/3} - \left(\frac{1}{2}\right)V_R \right] \right\} \quad (1)$$

where ρ is the density of rubber, V_0 is the molar volume of the swelling solvent absorbed (V_0 for toluene = $106.3\text{ cm}^3/\text{mol}$), μ is the interaction parameter constant, and V_R is the volume fraction of the rubber

in the swollen material. V_R is calculated as $1/(1 + Q_m)$, where Q_m (equilibrium swelling) is equal to V/W_d [weight difference between swelled and dry samples.] (ρ_1), V is the volume of the solvent absorbed by the rubber, and ρ_1 is the density of the solvent. μ is 0.446 for SBR.

The fracture surface of some tested specimens was analyzed by SEM with a JEOL JXA-840A electron probe microanalyzer (Tokyo, Japan) on gold–palladium-coated specimens. The SEM observation was carried out with secondary electron imaging and acceleration of the electron beam at 10 kV.

RESULTS AND DISCUSSION

FTIR

Figure 1 presents the spectrum of the acetylated sugarcane bagasse after 48 h (complete acetylation). There is an absorption band around 1734 cm^{-1} , which is characteristic of the stretching vibration of the carbonyl group.⁹

Effect of thermal aging on the retained physicochemical properties of the SBR vulcanizates

Stearic acid modified bagasse and acetylated bagasse with a particle size less than 75 nm and with concentrations of 20, 30, 50, and 70 phr were incorporated into SBR mixes; these were compared with those containing untreated bagasse with the same particle size and with those containing carbon black and hisil as commercial fillers used in industry. The mixing process was carried out with a laboratory mill according to the usual method, and the rubber formulations are given in Table I.

The physicochemical properties of the SBR vulcanizates (the equilibrium swelling, M_c , and $1/2M_c$)

TABLE I
SBR Formulations Containing Carbon Black, Hisil, Untreated Bagasse, and Different Ratios of Modified Bagasse with a Particle Size Less than 75 nm

Ingredient ^a	Formula											
	S ₀	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀	S ₁₁
Carbon black	—	30	—	—	—	—	—	—	—	—	—	—
Hisil	—	—	30	—	—	—	—	—	—	—	—	—
UB	—	—	—	30	—	—	—	—	—	—	—	—
SB1	—	—	—	—	20	—	—	—	—	—	—	—
SB2	—	—	—	—	—	30	—	—	—	—	—	—
SB3	—	—	—	—	—	—	50	—	—	—	—	—
SB4	—	—	—	—	—	—	—	70	—	—	—	—
AB1	—	—	—	—	—	—	—	—	20	—	—	—
AB2	—	—	—	—	—	—	—	—	—	30	—	—
AB3	—	—	—	—	—	—	—	—	—	—	50	—
AB4	—	—	—	—	—	—	—	—	—	—	—	70

The base recipe was as follows: SBR, 100 phr; stearic acid, 2 phr; zinc oxide, 5 phr; processing oil, 3 phr; 2-mercaptobenzothiazole, 0.8 phr; sulfur, 2.5 phr; and isopropylphenylenediamine, 1 phr.

^a AB = acetylated bagasse; SB = stearic acid modified bagasse; UB = untreated bagasse.

were determined, and the results are given in Table II. From this table, it can be concluded that the modification of bagasse improved the mechanical properties of the rubber vulcanizates in comparison with those of the rubber vulcanizates containing carbon black, hisil, and untreated bagasse. Therefore, the stress at yield, stress at rupture, strain at yield, and strain at rupture increased as the concentration of modified bagasse increased up to 50 phr and after that decreased.

The samples of SBR vulcanizates were subjected to thermal oxidative aging in an oven at 90°C for different time periods (2, 4, 6, and 7 days). The physicochemical properties of the aged samples were determined, and the retained values of each property were calculated. The effect of thermal aging on the retained values of the physicochemical properties of SBR vulcanizates containing modified bagasse, untreated bagasse, carbon black, and hisil was investigated, and the results are presented in Figures 2–7. As the concentration of modified bagasse increased, the retained values of the physicochemical properties increased until the concentration of

modified bagasse reached 50 phr and after that decreased. The retained tensile strength decreased beyond the modified bagasse concentration of 50 phr because of the agglomeration of the modified bagasse and dewetting of the SBR matrix at the interface, which generated a weak structure by creating stress concentration points. The incorporation of the filler caused an interruption in the alignment process of the chains; when the filler loading increased, more weak interfacial regions between the filler surface and rubber matrix were formed. As shown in Figures 2–7, the SBR vulcanizates containing modified bagasse showed retained physicochemical properties better than those of the vulcanizates containing untreated bagasse, carbon black, and hisil. The modified bagasse showed retained physicochemical properties better than those of the untreated bagasse. The improvement in the retained tensile strength was attributed to the interaction between the SBR matrix and modified bagasse, which caused more effective transfer of stress from the SBR matrix to the modified filler. The untreated bagasse had a hydrophilic nature and did not show good chemical compatibility with

TABLE II
Mechanical Properties of SBR Vulcanizates Containing Carbon Black, Hisil, Untreated Bagasse, and Different Ratios of Modified Bagasse with a Particle Size Less than 75 nm

Property	Formula											
	S ₀	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀	S ₁₁
Stress at yield (MPa)	2.11	8.6	11.2	21.5	69.3	77.4	90.5	17.6	76.5	98.2	102	19.2
Stress at rupture (MPa)	2.11	8.6	11.1	21.5	69.3	78	91	17.5	76.5	98.2	102	19.2
Strain at yield (%)	655.9	610.7	676.5	1655.7	1669.8	1681	1692	1220	1679.9	1687	1695.5	1134
Strain at rupture (%)	656	611	677	1656	1670	1681	1691.8	1220	1680	1687	1696	1134
Equilibrium swelling (%)	321	437	262	251	262	244	210	188	259	230	223	210
$M_c \times 10^{-4}$ (g/mol)	0.48×10^{-8}	0.0001	0.113	7×10^{-8}	3.58	5.51	7.18	9	28	4.03	6.22	11
$1/2 M_c \times 10^{-4}$	0.0103×10^5	2.22	0.0044	0.0007×10^5	1.79	2.75	3.59	7.7	14	2.01	3.11	5.5

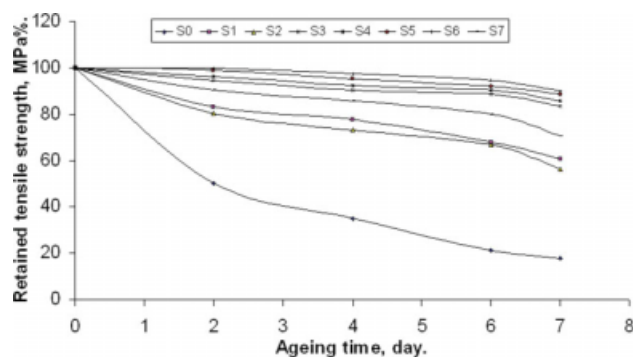


Figure 2 Retained tensile strength versus the aging time for SBR vulcanizates containing different ratios of stearic acid modified bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the SBR matrix, which was hydrophobic, and poor adhesion between the untreated bagasse and SBR matrix was confirmed by the large number of voids, as shown in Figure 8(a). In contrast, the modified bagasse was well dispersed and firmly embedded in the SBR matrix because of its good compatibility and large specific surface area; when the modifier was an organic carboxylic acid such as stearic acid or acetic anhydride, the reaction between the carboxylic acid of the modifier and the hydroxyl group of the natural fiber of the untreated bagasse resulted in the formation of hydrophobic groups, so the modified bagasse had high compatibility with the SBR matrix, and these interactions improved the filler dispersion and imparted good adhesion of the modified bagasse and SBR matrix. From these figures, it is also clear that the retained values of the tensile strength, elongation at break, and equilibrium swelling were slightly affected by time. Therefore, the retained values of the tensile strength of SBRs containing treated bagasse, untreated bagasse, carbon black, and hisil were

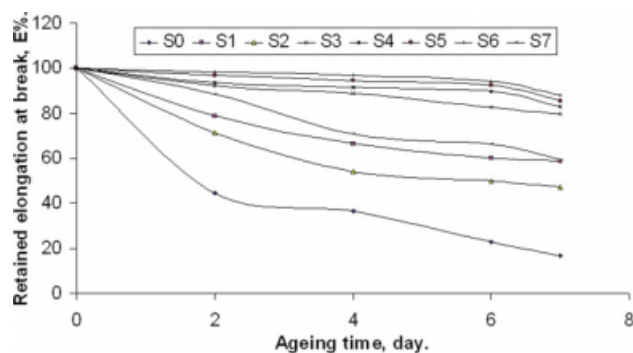


Figure 3 Retained elongation at break versus the aging time for SBR vulcanizates containing different ratios of stearic acid modified bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

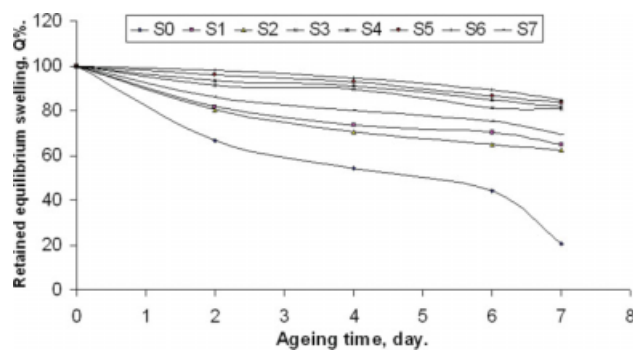


Figure 4 Retained equilibrium swelling versus the aging time for SBR vulcanizates containing different ratios of stearic acid modified bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

arranged in the order of $S_6 > S_5 > S_4 > S_3 > S_7 > S_2 > S_1 > S_0$ for stearic acid modified bagasse and in the order of $S_{10} > S_9 > S_8 > S_3 > S_{11} > S_2 > S_1 > S_0$ for acetylated bagasse. The stearic acid modified bagasse and acetylated bagasse with concentrations of 20, 30, 50, and 70 phr (particle size < 75 nm) could protect the SBR vulcanizates against thermal oxidative aging in comparison with the rubber vulcanizates containing 30 phr untreated bagasse (particle size < 75 nm), carbon black, and hisil. The optimum concentration of modified bagasse was 50 phr. The acetylated bagasse imparted better mechanical properties than stearic acid modified bagasse.

SEM

Figure 8 shows extensive interactions and good distribution between stearic acid modified bagasse [Fig. 8(b)] and acetylated bagasse [Fig. 8(c)] and rubber in comparison with a composite of rubber with untreated bagasse [Fig. 8(a)]. The distribution of bagasse into the

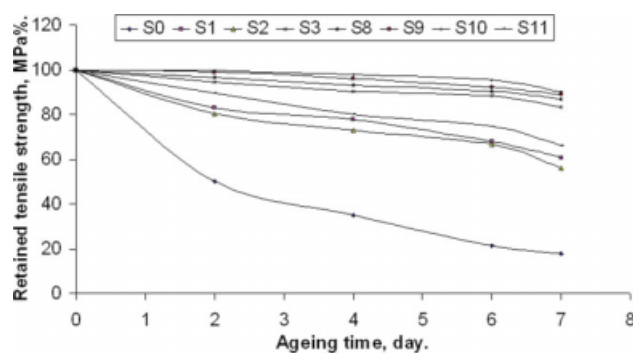


Figure 5 Retained tensile strength versus the aging time for SBR vulcanizates containing different ratios of acetylated bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

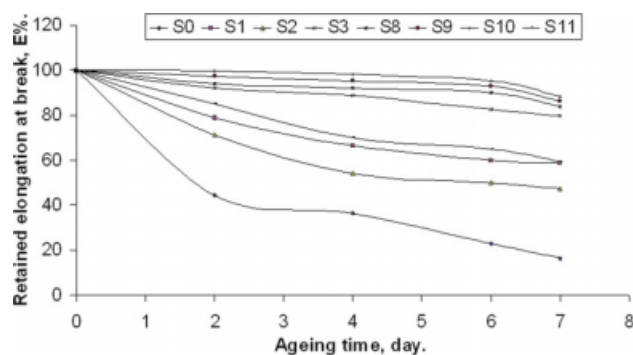


Figure 6 Retained elongation at break versus the aging time for SBR vulcanizates containing different ratios of acetylated bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

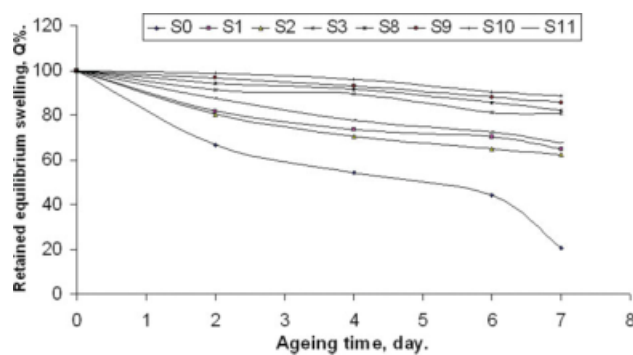


Figure 7 Retained equilibrium swelling versus the aging time for SBR vulcanizates containing different ratios of acetylated bagasse in comparison with a control, carbon black, hisil, and untreated bagasse. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymer matrix and the mechanical behavior greatly depended on the hydrophobic character of the modified bagasse; the modified bagasse introduced the highest mechanical properties and also showed good compatibility and adhesion with the rubber matrix in comparison with the untreated bagasse.

CONCLUSIONS

From the previous results, it can be concluded that

1. Stearic acid modified bagasse and acetylated bagasse fillers improved the mechanical properties

of SBR vulcanizates in comparison with carbon black, hisil, and untreated bagasse.

2. Rubber vulcanizates containing modified bagasse waste with a concentration of 50 phr showed better physicomechanical properties than those with concentrations of 20, 30, and 70 phr.
3. The physicomechanical properties of SBR increased as the concentration of modified bagasse increased up to 50 phr and after that decreased.
4. Acetylated bagasse showed physicomechanical properties better than those of stearic acid modified bagasse.

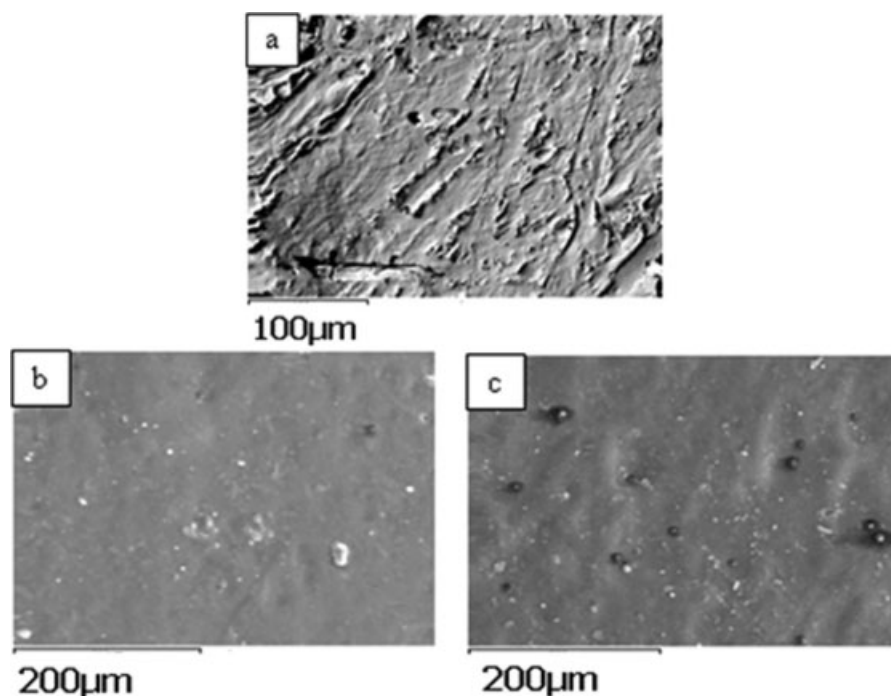


Figure 8 SEM micrographs of fracture surfaces of composites of SBR vulcanizates with (a) 30 phr untreated bagasse, (b) 50 phr stearic acid modified bagasse, and (c) 50 phr acetylated bagasse.

5. The SEM technique revealed good dispersions of the stearic acid modified bagasse and acetylated bagasse in the rubber matrix in comparison with untreated bagasse.

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