

Lignocellulose-Polymer Composite. I

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Synopsis

Bagasse grinded to different mesh sizes was used for the production of lignocellulose polymer composites. Samples of different polymer loads were prepared from crude-grafted bagasse with polymethyl methacrylate. A sodium bisulfite-soda lime glass system was used as an initiator for the grafting reaction. The properties of the resulting composites have been found to be affected by both the polymer load and the mesh size of the ground bagasse. Grafting in the absence of soda lime glass from the initiator system was successful, and the properties of the composite produced from the prepared samples differed greatly from those containing glass. Other oxides, namely, copper (cupric) oxide and iron (ferric) oxide, were used in replacing glass in the initiator system. Some of the properties of the composite containing the latter were deteriorated. A composite from the true-grafted sample (homopolymer free) showed improvement in some of the properties, while the others deteriorated. Composites prepared from impregnated bagasse with polymer or homopolymer behaved differently in their properties and from those from crude-grafted samples, depending on the mesh size of the ground bagasse they are made from.

INTRODUCTION

A composite is a system that is created by the synthetic assembly of two or more materials, namely, a selected filler or reinforcing element and a compatible resin binder, to obtain specific characteristics and properties. Cellulose in the form of timber and wood pulp or cotton is cheap, relatively abundant, provides a suitable substrate to which improved properties can be given by the use of chemicals, and hence can be compressed into composite.¹

Many variations of mechanical and physical properties can be developed through appropriate compounding of polymers with fibers and fillers (Ref. 2, p. 200).

Wood et al.³ have noted that maximum property improvements are usually achieved with maximum polymer content.

Regarding the properties of wood-plastic composites, it has been mentioned by some investigators⁴ that composites are more dense than untreated wood, and their specific gravities usually fall below 0.85 and 1.15. The hardness is increased, as are the bending, compression, and shear strengths. Their abrasion resistance is particularly good. Because of the water uptake is reduced, dimensional stability is increased and ant swell efficiencies of up to 70% have been recorded. High stabilities are observed in centrally heated atmospheres. Composites also resist decay and attack by fungi and insects. The materials can be sewn, machined, planed, drilled, and jointed by conventional woodworking techniques.

In the present work, our aim was to prepare composites from ground bagasse

through grafting with polymethyl methacrylate using a sodium bisulphite–soda lime glass system as initiator. The influence of the particle size of the ground bagasse, polymer load, homopolymer, and the absence, presence, or replacement of glass in the initiator system with other metal oxides on the properties of the composites was studied.

It was also our aim to prepare composites from bagasse impregnated with the polymer or homopolymer polymethyl methacrylate and to study their properties in comparison with those obtained from the grafted ones.

EXPERIMENTAL

Bagasse ground to 20, 40, and 60 mesh was grafted or impregnated with polymethyl methacrylate to be used for the preparation of the composite samples.

Grafting was carried out using a sodium bisulfite–soda lime glass system as initiator.⁵ In some experiments the glass was either omitted or replaced by copper or iron oxide.

In 500-ml glass bottles stoppered with a ground joint, 10 g of air-dried ground bagasse, pre-extracted with methanol–benzene (1:1) for 8 hr, was placed together with 0.3-g sodium bisulfite, 5-g soda lime glass, and with a calculated amount of water. Soda lime glass may be omitted or replaced with ferric or cupric oxide. Different liquor ratios, as well as different periods of reaction time, were used in order to obtain different polymer loads. Purified nitrogen was passed through the mixture for 10 min, then 5-ml methyl methacrylate monomer was added. The reaction bottle was placed in a water bath at 40°C and shaken occasionally. The product was washed thoroughly with water, left in a drying oven at 60°C until complete dryness was achieved, and then weighed for determination of the crude-grafting yield. True-grafting yield is obtained through extraction of the crude product with benzene for 72 hr for the removal of the homopolymer polymethyl methacrylate. Thorough washing with water follows, and the sample is dried and weighed.

$$\text{Crude-grafting yield: } C\% = (F-S) - Z/Z$$

$$\text{True-grafting yield: } A\% = (G-S) - Z/Z$$

S is the weight of glass, Z is the weight of cellulose, F is the weight of crude-grafted cellulose (before extraction), and G is the weight of grafted cellulose (after extraction).

Impregnation of bagasse takes place either with the polymer or homopolymer of methyl methacrylate dissolved in benzene. The homopolymer is obtained through soxhlet extraction of crude polymethyl methacrylate grafted bagasse with benzene for 72 hr. Impregnation is followed by drying.

About 10 g of the grafted or impregnated bagasse are placed in a disk form, heated to 170°C, and then pressed under 160 kg/cm² for 10 min.

The composite samples were subjected to the following measurements:

1. Compression strength: determined as the weight at which the composite sample is deformed or breaks (in tons/cm²).
2. Percent deformation: calculated from the difference between the length before and after compression divided by the first length:

$$\frac{l_1 - l_2}{l_1} \times 100$$

where l_1 and l_2 are the lengths before and after compression, respectively.

3. Hardness: measured by an HPK hardness testing machine (Ball K6gel, Leipzig).

4. Compression strength to percent deformation:

$$\frac{\text{Compression strength (tons/cm}^2\text{)}}{\text{Deformation (\%)}}$$

calculated by the Poisson ratio obtained for the composite (Ref. 2, p. 127). Increased compression strength to percent deformation means the suitability of the design made of these composites in making supporting structures.

5. Compressibility K : calculated according to the following equation (Ref. 2, p. 30):

$$K = - (1/V)(dV/dP)$$

in which V is volume and P is pressure.

RESULTS AND DISCUSSION

Composite from Grafted Bagasse

Effect of Particle Size and Polymer Load

Among the samples of crude graftings containing glass, Table I shows that improved properties, namely, higher compression strength, lower percent deformation, higher compression strength to percent deformation, and lower compressibility are found in the sample with the lower polymer load, 12.5%, obtained from bagasse ground to mesh size 20, as compared with the corresponding one of higher polymer load, 29.2%. For bagasse ground to mesh 40, however, we find such properties in the sample with higher polymer load, 25.5%, as compared with the corresponding one with lower polymer load, 23.3%. Higher hardness was only achieved at lower polymer loads for both mesh sizes.

Table I also reveals that among the samples of crude graftings containing glass, the least deformation and highest compression strength and compression strength to percent deformation are obtained from bagasse of mesh size 60 with intermediate polymer loads, 15.3%, followed by bagasse of mesh size 40 with high polymer load, 25.5%, and finally by bagasse of mesh 20 with low polymer load, 12.5%. As regards the hardness, the highest value was due to bagasse ground to mesh size 40, followed by mesh 60, and then mesh 20.

The results achieved may relate to either or both of the following:

1. Differences in the mesh size of the bagasse used.
2. There is a limit, i.e., maximum or minimum, for the change in the properties with increasing of the polymer loads.

Table I also shows that the density of the composites made from crude-grafted samples increases as the mesh size of the bagasse decreases, whereas the water uptake increases with increasing particle size. However, samples from bagasse of the same particle size possessed practically the same density, irrespective of the polymer load, while the water uptake decreases with increasing polymer. The extent of decrease depends on both the difference in the polymer loads and the time of soaking. The greater the difference in the polymer loads and the longer

TABLE I
Influence of Particle Size, Polymer Load, Homopolymer, and Presence and Absence of Glass on Composites from Grafted Bagasse^a

Property	20 Mesh+ Glass		True ^c	40 Mesh		60 Mesh + Glass + Crude
	Crude ^b	Crude		+ Glass Crude ^d	No Glass Crude ^d	
Polymer load (%)	12.5	29.2	14.3	16.6	23.3	15.3
Density (g/cm ³)	1.14	1.17	1.34	1.24	1.23	1.42
Compression strength (tons/cm ²)	1.03	0.88	1.75	1.43	0.97	1.53
Deformation (%)	11.3	15.0	44.9	13.0	12.0	7.7
Compression strength to percent deformation	0.09	0.06	0.04	0.11	0.08	0.20
Compressibility (K)	0.021	0.034	0.050	0.016	0.024	0.010
Hardness (HPK)	350	120	540	210	510	430
Water uptake (%) after						
24 hr	43.9	40.7	—	31.4	—	24.9
72 hr	51.6	42.2	67.5	34.1	—	—
96 hr	59.1	48.2	—	37.9	—	—
240 hr	66.5	50.3	80.4	47.7	34.5	27.2

^a Grafting reactions were carried out under the following conditions: liquor to total solid ratio, 10:1; liquor to lignocellulose ratio 15:1; monomer to lignocellulose ratio, 1:2; sodium bisulfite to lignocellulose ratio, 3:100; glass to lignocellulose ratio, 1:2; reaction time, 24 hr.

^b Reaction time, 4 hr.

^c True-grafted bagasse was prepared from the crude-grafted sample with polymer load of 29.2% by the removal of the homopolymer by extraction with benzene for 72 hr.

^d In these experiments the liquor to total solid ratio was 20:1 and the liquor to lignocellulose ratio was 30:1.

the time of soaking, the greater is the decrease in the water uptake. In this connection, it is worth mentioning that decreased values for the water uptake showed increased resistance to water decay and fungus attack.

Effect of Homopolymer

Crude-grafted bagasse with a polymer load of 29.2% was subjected to soxhlet extraction with benzene for 72 hr for the removal of the homopolymer. The resulting true-grafted sample thus obtained, having a polymer load 14.3%, was pressed into composite.

From Table I it is clear that the composite formed from true-grafted bagasse is of highly improved compression strength and hardness, while the percent deformation, compression strength to percent deformation, compressibility, and water uptake deteriorated, as compared with the samples from crude-grafted bagasse. The density was higher than the composites of crude graftings obtained from bagasse of mesh 20 and 40 but less than that from bagasse of mesh 60.

Effect of Glass

A scheme dealing with the mechanism of initiation for the initiator system sodium bisulfite-soda lime glass has been proposed that assumes the trapping of the bisulfite radical inside the glass framework to form a so-called sulfur-impregnated solid. Such a solid has paramagnetic properties and acts on the vinyl monomers and cellulose as any free-radical-producing source, thus leading to polymerization and graft polymerization onto cellulose.⁵

In the same work it was also shown that sodium bisulfite in the absence of soda lime glass did not initiate graft polymerization onto pure cellulose, namely, cotton linter.

In the present work it was possible to graft polymerize polymethyl methacrylate onto methanol-benzene pre-extracted bagasse in the absence of the glass in the initiator system, i.e., in presence of sodium bisulfite alone. However, a lower polymer load of 16.6% was obtained compared with 25.5% for the similarly prepared sample containing glass (Table I). Therefore, one may conclude that lignin, with its network structure, and the incrustants present in the bagasse act, though to a lesser efficiency, as the glass of the initiator system.

In order to reveal the influence of glass on the properties of the composites, one may take into consideration what has previously been observed regarding the effect of polymer load on the properties of the composites obtained from bagasse ground to mesh 40. Accordingly, Table I reveals that among the composites prepared from bagasse ground to this mesh size, the one containing no glass showed improved compression strength, compression strength to percent deformation, and compressibility, whereas the hardness deteriorated.

The density was practically unaffected, while the water uptake followed the polymer load, i.e., increased with increases of the latter, irrespective of the presence or absence of glass.

Effect of Oxides

It has previously been shown that replacing the soda lime glass of the initiator system by pure silica sharply decreases the grafting yield.⁵

In the present work, cupric and ferric oxides replaced the soda lime glass of the initiator system in the graft polymerization reaction of polymethyl methacrylate onto bagasse ground to mesh 40. The polymer load obtained with cupric oxide was 23.5%, while with ferric oxide 4.4% (Table II). This shows the high catalytic effect of cupric oxide in this polymerization process.

From all the above, we see that the differences in the catalytic efficiency of the various oxides may relate to differences in their lattice structure.

From Tables I and II it is clear that the composite containing cupric oxide showed improved properties (with the percent deformation excepted) over that containing soda-lime glass of practically the same polymer load, 23.3%. The density was slightly higher, while the water uptake was practically equal.

Again, from Tables I and II composites containing ferric oxide showed deteriorated properties compared with those containing cupric oxide or soda-lime glass, probably due to its distinctly low polymer load.

Composite from Impregnated Bagasse

From Tables I and III it is clear that composites from impregnated ground bagasse of mesh size 20 show highly improved properties compared with those from crude-grafted samples. Thus the former samples showed lower compressibility, higher compression strength, lower percent deformation, and higher compression strength to percent deformation than the latter samples. Taking into consideration what has previously been observed, i.e., decreased hardness accompanies increases in the polymer load, we see that the hardness was also strongly improved on impregnation.

The density was practically the same for both types of composite, while the water uptake, at sufficiently soaked times, namely, 96 and 240 hr, decreased as the polymer load increased from 12.5% to 18.0% to 29.2%, irrespective of the type

TABLE II
Effect of Cupric and Ferric Oxides on Composites from Grafted Bagasse^a

Property	Cupric Oxide	Ferric Oxide
Polymer load (%)	23.5	4.4
Density (g/cm ³)	1.31	0.82
Deformation (%)	13.9	13.6
Compression strength (tons/cm ²)	1.55	0.43
Compression strength to percent deformation	0.11	0.03
Compressibility (<i>K</i>)	0.020	0.062
Water uptake (%) after		
24 hr	31.1	174.0
72 hr	32.6	—
96 hr	35.7	—
240 hr	37.6	—

^a Bagasse was ground to mesh size 40. Grafting was carried out under the following conditions: liquor to lignocellulose ratio, 30:1; monomer to lignocellulose ratio, 1:2; oxide to lignocellulose ratio 3:10; and sodium bisulfite to lignocellulose ratio 3:100; reaction time, 24 hr.

TABLE III
Composites from Impregnated Bagasse

Property	Mesh Size		
	20 ^a	20 ^b	40 ^a
Polymer load (%)	18.0	45.0	18.0
Density (g/cm ³)	1.18	1.14	1.0
Compression strength (tons/cm ²)	1.26	1.38	0.69
Deformation (%)	7.3	8.1	15.3
Compression strength to percent deformation	0.17	0.17	0.04
Compressibility (<i>K</i>)	0.011	0.011	0.040
Hardness (HPK)	—	355	150
Water uptake (%) after			
24 hr	45.5	31.1	58.6
72 hr	55.5	44.4	169.1
96 hr	56.9	46.9	—
240 hr	61.7	49.7	—

^a Impregnation in 2% polymer solution.

^b Impregnation in homopolymer.

of the composite. The water uptake then remained practically constant as the polymer load was further increased to 45.0%.

On the other hand, composites from impregnated ground bagasse of mesh size 40 showed deteriorated properties, i.e., increased percent deformation, compressibility, and water uptake and decreased compression strength, compression strength to percent deformation, and hardness as compared with the samples from crude graftings (Tables I and III). However, the density was lower for the impregnated than for the grafted samples.

Composites from impregnated samples showed improved properties (lower compressibility, percent deformation, and water uptake) but higher compression strength, compression strength to percent deformation, and hardness when obtained from bagasse ground to mesh size 20 rather than 40. Only the density of the former was higher than the latter (Table III).

Regarding the change of the properties with the polymer load for composites obtained from impregnated bagasse, Table III shows only a slight increase in the compression strength and percent deformation, while the compression strength to percent deformation, as well as the compressibility, remained practically the same as the polymer load was increased from 18.0% to 45.0%.

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