Lignocellulose - Polymer Composites

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SUMMARY: Water hyacinth and its mechanical pulps were used as lignocellulose to produce composites together with polystyrene or urea-formaldehyde resins. The bending strength of the composites increased with increasing concentration of the resin. The temperatures of the treatment of water hyacinth to obtain the pulps affect the strength and densities of the composites. This may be attributed to the behavior of lignin at temperatures higher than 135 °C. The composites produced using urea-formaldehyde resins showed slight increase in bending strengths compared with those produced using polystyrene, which may be attributed to the ability of formaldehyde to make crosslinks with the free OH groups of cellulose and hemicellulose. Contrary to water hyacinth, the use of ground palm leaves together with 10 % urea-formaldehyde resin produced composite with high density and low bending strength, while the ground water hyacinth failed. The pulp from palm leaves when processed into composites using 10 % urea-formaldehyde resin show bending and densities affected by its preparation and by the amount of the composite mixture to be pressed. Hence the type of the substrate defined the type of the polymers or resin used to obtain composites with proper mechanical properties. The effect of the pressure used to produce composites from ground palm leaves or their pulp together with polystyrene was investigated. Linear relationships between the bending strength and pressure were obtained, the bending strength and densities increasing with increasing pressure. Thus, the increased pressures enhance mechanical properties of the composites.

Introduction

The interest in forming lignocellulose-polymer composites has increased in recent years. Emphasis is put on the agro-based fibers such as wood, pulp, bagasse, and jute as major components of these composites because of low cost and high performance characteristics of these fibers.

Other large sources of fibers can be obtained by recycling agro-fiber-based products such as paper, waste, wood, rice hulls from a rice-processing plant, and sunflower seed hulls from an oil-processing unit (1). New fibers, which cause environmental pollution, can be used, such as water hyacinth containing a high percentage of holocellulose (60 %). The previous papers of this series (2-5) dealt with different raw materials used as substrates to produce lignocellulose-polymer composites of good performance. The variables affecting the performance and mechanical and physical properties of the composites were investigated.

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Different treatments were applied to different raw materials to improve properties of the composites.

In the paper (5), palm leaves as a wood lignocellulose together with polystyrene were used to produce composites. Chemothermal mechanical pulps (CTMP) from palm leaves obtained by the treatment with alkali, acid or water were processed into composites together with polystyrene. It has been found that chemical constituents of the CTMP as well as the yields of the pulps play a certain role in mechanical and physical properties of the composites. Therefore, the type of the substrate of the composite and its weight fraction were important factors in determining properties of the composites.

In this part, water hyacinth, which is a wild plant growing in the streams of rivers, preventing sailing, absorbing more than 60 % of water and causing high pollution, was qualified as lignocellulose to produce composites. The ground water hyacinth and its CTMP were used together with polystyrene on the one hand and urea-formaldehyde resin on the other to produce lignocellulose-polymer composites. The influence of increasing the proportion of the polymer or resin in the composites on their properties has been investigated.

Materials and methods

CTMP from palm leaves were produced as in (5). Composites from CTMP pulps were produced using 10 % of urea-formaldehyde resin for the sake of comparison. The effect of pressure on properties of the composites prepared from CTMP together with 10 % polystyrene was monitored.

Preparation of composites

Water hyacinth or its CTMP produced by water treatment at 120 or 170 °C for 1.5 h were fluffed using a Pfeiffer shredder for 20-25 min, then dried at 45 °C for 24 h and ground to pass mesh size 20. Composites were prepared by impregnating the ground mass with polystyrene or urea-formaldehyde resin solution together with 2 % of ammonium chloride. The mixtures were then left to dry. 100 g of the dried mixture was pressed under 4.7 MPa at 160 °C for 10 min. Untreated palm leaves or CTMP were processed into composites by the same method as in paper (5) using 10 % polystyrene under 2.4, 3.5, 4.7, and 5.9 MPa at 160 °C for 10 min. In another series, 10 % of urea-formaldehyde resin together with 2 % of ammonium chloride were used to prepare the composites from palm leaves and their CTMP pulps.

Measurements of composites

Composites were subjected to the following measurements.

Thickness was measured using a dial micrometer. The density was calculated using the well-known relation.

Water uptake. Small pieces of the composite, uniform in shape, were placed in water for 24, 48, 72 h or 7 days, at room temperature (≅ 25 °C). After each period, a piece was centrifuged at 5000 r.p.m. for 10 min, then weighed and dried at 105 °C for 24 h. The water uptake was calculated by the formula:

$$\text{water uptake (\%)} = [(B - A) / A] \times 100$$

where B is the weight of the centrifuged sample and A is the weight of the sample dried at 105 °C.

Bending strength (kg/cm^2) was determined on an Instron 1/28 as the weight at which the composite specimen breaks.

Results and Discussion

Water hyacinth composites

Water hyacinth was analyzed for holocellulose, α-cellulose, hemicellulose, lignin and ash contents (Table 1). The results showed that the percentage of holocellulose increased from 60 to 65 or 66.7 % on treating water hyacinth with water at 120 or 170 °C, respectively. The hemicellulose content decreased from 28 to 23 or 24.2 % respectively, while α-cellulose increased similarly from 32 to 42 or 42.5 %. The lignin content decreased from 19.1 to 18.3 or 16.8 %.

Table 1. Chemical analysis of raw materials and pulps

Pulping condition	Holocellulose %	Hemicellulose %	Lignin %	Ash %	α-cellulose %
Water hyacinth					
Untreated	60	28	19.1	18.6	32
Water-treated (120 °C, 1.5 h)	65	23	18.3	17.9	42
Water-treated (170 °C, 1.5 h)	66.7	24.2	16.8	19.2	42.5
Palm leaves					
Untreated	71.85	40.22	19.51	7.57	31.63
CTMP (water)	74.30	42.33	16.32	8.38	32.01
CTMP (NaOH)	82.29	23.45	6.44	12.45	58.84
CTMP (NaOH, Na_2S)	78.81	22.92	5.34	12.35	55.89
CTMP (Na_2SO_3)	84.00	33.20	5.2	5.7	50.10

Untreated or treated water hyacinth was processed into composites using different concentrations of polystyrene or urea-formaldehyde resin by pressing 100 g of the mixture under 4.7 MPa at 160 °C for 10 min.

The bending strengths of these composites were collected in Tables 2 and 3. Other properties of the composites were also investigated.

Table 2. Effect of urea-formaldehyde resin on properties of composites made from water hyacinth

Pulping conditions	Urea-formaldehyde resin (%)	Thickness cm	Density g/cm^3	Bending strength kg/cm^2	Water absorption			
					24 h	48 h	72 h	7 days
Water-treated	10	0.31	0.96	59	23	23.8	26	27.3
(120 °C, 1.5 h)	20	0.34	0.93	69.2	18	19	21	23
	30	0.36	1.03	80.3	15	15.7	17.3	18.5
Water-treated	10	0.30	0.98	57.6	25	25.5	28	30
(170 °C, 1.5 h)	20	0.33	0.95	68.3	20	20.7	24	25
	30	0.34	1.05	79	18	18.6	21	22

It is worth mentioning that the untreated ground water hyacinth could not be processed into composites using 20 % of polystyrene or 20 % of urea-formaldehyde resin. Therefore, their properties are absent from Tables 2 and 3. Composites from CTMP of water hyacinth obtained at 120 or 170 °C showed an increased bending strength if 10 % of urea-formaldehyde resin was used in the processing. The bending strengths still increased using 20 % of the resin but no longer with 30 % of the resin. However, the bending strengths of the CTMP composites obtained at 120 °C are slightly higher than those obtained at 170 °C (Table 2).

Using polystyrene instead of urea-formaldehyde resin, the bending strengths increased in the same order for the composites obtained from CTMP water treated at 120 or 170 °C. This means that the increase in the concentration of polystyrene from 10 to 20 to 30 % increased the bending strength from 57.1 to 66.5 and 79.4 kg/cm^2 for the CTMP obtained at 120 °C. For the CTMP obtained at 170 °C, the bending strength increased from 56 to 66 to 78 kg/cm^2 (Table 3).

Table 3. Effect of polystyrene percentage on water-hyacinth composite properties

Pulping condition	Polystyrene %	Thickness cm	Density g / cm^3	Bending strength kg /cm^2	Water absorption			
					24 h	48 h	72h	7 days
Water-treated	10	0.30	0.97	57.1	21.6	22	24.2	26
(120 °C, 1.5 h)	20	0.32	0.97	66.5	16	16.7	18	19.2
	30	0.33	1.04	97.4	12.2	12.8	14.3	15.1
Water-treated	10	0.29	0.99	65	22	23.2	25.8	27
(170 °C, 1.5 h)	20	0.31	0.99	66	20	20.5	23.2	24
	30	0.32	1.05	78	17	18	20.1	21.3

However, the use of polystyrene for processing composites from water hyacinth CTMP led to slightly decreased bending strengths for all experiments compared with those obtained using urea-formaldehyde resin (Tables 2 and 3).

For both polymers, the bending strengths of the obtained composites are slightly higher for those obtained from CTMP at 120 °C rather than for those obtained at 170 °C (Tables 2 and 3). The densities of the composites from urea-formaldehyde resin or polystyrene and CTMP obtained at 120 or 170 °C showed decreased values on increasing the percentage of the polymers from 10 to 20 % but then increased. However, the densities of composites produced from CTMP at 170 °C showed a slight increase with respect to the values obtained for composites produced from CTMP prepared at 120 °C. The thicknesses of the CTMP composites obtained at 170 °C are lower than those obtained at 120 °C.

The water absorption of composites produced using 10, 20 or 30 % of urea-formaldehyde resin or polystyrene decreased even after impregnation in water for 7 days. Also, the water uptakes of the composites obtained from CTMP at 120 °C are lower than those obtained from CTMP at 170 °C even after impregnation for 7 days (Tables 2 and 3).

The difference in properties of the composites produced from CTMP obtained at 120 °C and those obtained at 170 °C can be explained using the concepts stated by Badwin et al (6) who found that at temperatures higher than 135 °C, lignin behaves as a semiglassy solid. Above this temperature, the fiber regions high in lignin are more susceptible to rupture than the regions high in cellulosics. At higher temperatures, fiber separation occurs predominantly in zones of higher lignin core nutrition, i.e., in the middle of the lamella region. Thus, the defibering process at high temperatures produces fibers with high lignin contents on the surface (5). On the basis of this concept, in CTMP produced at 170 °C, though lower in lignin

than CTMP produced at 120 °C (16.8 and 18.3 % respectively, Table 1), lignin is concentrated at the surface of the fiber leaving the fiber core more plasticized.

Therefore, the internal bonding and, consequently, the compression strength of the composites produced from the higher-temperature CTMP are high, which is manifested by their increased densities.

On the other hand, the decreased bending strengths for the composites produced from higher-temperature CTMP (170 °C), compared with those obtained at 120 °C, contributed to the increased susceptibility of the fiber to rupture at this high temperature and thus the bending strength depends more or less on the fiber length in the composites.

It is worth noting that the bending strength values obtained for the water hyacinth - urea-formaldehyde resin composite are slightly higher than those produced using polystyrene. The increase with the former composites can be attributed to the ability of formaldehyde to crosslink free OH groups of cellulose and hemicellulose leading to more internal bonds and, consequently, to high compression strengths (7,8).

Palm leaves composites

Ground palm leaves of mesh size 20 were processed into composites using 10 % of urea-formaldehyde resin and 2 % of ammonium chloride. Palm leaves CTMP were also processed into composites using the same resin. The results obtained are in Table 4.

Table 4. Effect of the pretreatment of palm leaves on the composite properties

Pretreatment	Density g /cm^3	Water uptake %	Bending strength kg /cm^2
A	1.12	47.21	10.5
B	1.11	86.59	55.3
Water, 170 °C, A	1.17	40.62	33.5
Water, 170 °C, B	0.99	42.75	78.3
NaOH, 170 °C, A	1.08	56.95	23.8
NaOH, 170 °C, B	1.13	43.01	75.5
Na_2S/NaOH, 170 °C,A	1.05	59.17	13.3
Na_2S/NaOH, 170 °C, B	1.10	44.44	34.5
Na_2SO_3, 170 °C, A	0.88	47.55	-
Na_2SO_3, 170° C, B	0.98	43.13	-

A 50 g of palm leaves + 10 % of urea-formaldehyde resin + 2 % of ammonium chloride
B 100 g of palm leaves + 10 % of urea-formaldehyde resin + 2 % of ammonium chloride

The composites obtained from untreated palm leaves showed certain properties (Table 4) Increasing the amount of the mixed untreated palm leaves in urea-formaldehyde resin from 50 to 100 g, the thickness increased while the density remained virtually the same. The bending strength significantly increased from 10.5 to 55.3 kg/cm^2 and the water uptake also increased.

Alternatively, CTMP obtained by the water treatment at 170 °C was used for the formation of composite at 100 °C leading to the bending strength of 33.5 kg/cm^2 (Table 4). The density of the composite was 1.17 g/cm^3, the thickness being lower than that of the composite in Table 4. The water uptake was practically the same.

When the NaOH treatment of the palm leaves to obtain CTMP was carried out at 170 °C, the bending strength decreased to 23.8 and 75.5 kg/cm^2, respectively for the 50-g and 100-g composite mixture. The density of the former composite decreased to 1.08 g/cm^3, while for

the latter composite, it increased compared with CTMP (water). Water uptakes of both composites slightly increased (Table 4).

Using sodium hydroxide and sodium sulfide (kraft process) for the treatment of palm leaves to obtain CTMP, the composites prepared showed decreased bending strengths for both the 50-g and 100-g mixture. Their densities decreased to 1.05 and 1.1 g/cm^3, respectively (Table 4). The water uptake correspondingly increased. The bending strengths of the two composites prepared from sulfite CTMP could not be detected on the bending tester used. The water uptake, however, decreased. The densities of the composites for both mixtures (50-g and 100-g) made from sulfite CTMP are low compared with those of the preceding ones (Table 4).

Comparing the composites prepared from water-treated CTMP (170 °C) from water hyacinth (Table 2) using 10 % urea-formaldehyde resin with those prepared under the same conditions from palm leaves (Table 4), one finds that the bending strength for the former (57.6 kg/cm^2) was significantly lower than that for the latter (78.3 kg/cm^2) (Tables 2 and 4). The densities of both are nearly the same. Using polystyrene and CTMP (water-treated) from water hyacinth and palm leaves at polymer concentration of 10 %, the thickness of the composites were 0.2 cm for the former (Table 3) and 0.65 cm for the latter (Table 5). The densities were 0.99 and 1.03, respectively.

Thus, treatment of either water hyacinth or palm leaves with water at relatively low temperatures leads to composites with better mechanical properties owing to the concepts mentioned before.

Table 5. Effect of pressure on physical properties of composites based on palm leaves using 10 % polystyrene

Substrate	Pressure MPa	100 g pressed		50 g pressed	
		Thickness cm	Density g/cm^2	Thickness cm	Density g/cm^2
Ground palm leaves	2.4	0.59	0.91	0.34	0.96
	3.5	0.68	0.91	0.31	0.98
	4.8	0.67	0.94	0.28	1.17
	5.9	0.64	0.97	0.26	1.17
Palm-leaves CTMP	2.4	0.67	0.90	0.27	1.14
(H_2O at 170 °C, 1.5 h)	3.5	0.67	1.14	0.25	1.34
	4.8	0.65	1.03	0.24	1.39
	5.9	0.65	1.06	0.24	1.41
Palm-leaves CTMP	2.4	0.60	1.03	0.30	1.02
(Na_2SO_3,155 °C, 1.5 h)	3.5	0.60	1.11	0.28	1.21
	4.8	0.59	1.13	0.28	1.18
	5.9	0.58	1.16	0.27	1.26

Effect of pressing pressure

Ground palm leaves or their CTMP obtained with water at 170 °C or 10 % Na_2SO_3 at 155 °C for 1.5 h were mixed with 10 % of polystyrene. 50 g or 100 g of the mixture was processed into composite using the pressures 2.4, 3.5, 4.8 or 5.9 MPa. Their mechanical and physical properties are collected in Table 5. The relation between the bending strengths and the compression pressures are illustrated in Figs 1 and 2 for pressed 50-g and 100-g mixtures.

From Table 5, it is evident that the amount of the mixtures to be pressed affected the thicknesses and densities. The increased density means an increase in the number of internal bonds and hence in the compression strength of the composite. Also an increase in the applied

pressures from 2.4 to 5.9 MPa increased the density. However, no relation was found between the increase in the pressures and in the densities (Table 5).

Regarding the bending strength (Figs 1 and 2), linear relationships were obtained, where the bending strength increased with increasing pressure. The slopes of the lines corresponding to the relation between the pressure and the bending strength for the composites prepared from untreated ground palm leaves showed the highest values followed by those for CTMP (water or sulfite). This order parallels that of the densities, where the densities of the composites prepared from untreated ground palm leaves showed the lowest values followed by those of composites prepared from CTMP (Table 5). These results emphasize that the type of substrates affects the performance of the composites.

The increased pressing pressure enhanced mechanical properties, the bending strength and compression strength.

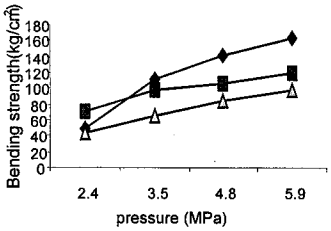

Fig. 1 Effect of pressure on bending strength of composite based on palm leaves (50-g pressed mixture); ◆ untreated, ▩ CTMP (water), Δ CTMP (sulfite)

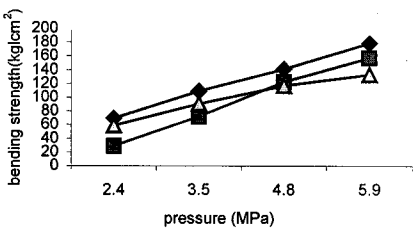

Fig. 2 Effect of pressure on bending strength of composite based on palm leaves (100-g pressed mixture); ◆ untreated, ▩ CTMP (water), Δ CTMP (sulfite)

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