Coconut-Fiber-Reinforced Thermosetting Plastics

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Synopsis

Thermosetting plastic composites have been prepared with phenol–formaldehyde resins as well as unsaturated polyesters as binders and coconut hair as fibrous reinforcement. Using resole-type phenol–formaldehyde resins, the effect of coconut fiber pretreatment by NaOH, the precondensation time of the impregnated fibrous press material, the resin–fiber ratio, and pressing parameters have been studied. Especially advantageous press-material has been obtained using 60–65 wt % linear novolac type phenol-formaldehyde resin as binder and 35–40 wt % of coconut hair. Applying unsaturated polyester (UP) as binder, BMC (bulk molding compound)-type press material can be prepared using coconut fiber reinforcement instead of glass fibers. To achieve better coupling between coconut fiber and UP matrix, coconut fiber was pretreated by NaOH and/or gamma-preirradiation. It has been found that in glass-fiber-reinforced UP press materials a significant part of glass fiber could be changed for short-cut coconut fiber.

INTRODUCTION

A significant effort is made recently to apply natural fiber reinforcement in synthetic-polymer-bonded composite materials. These synthetic-natural composites offer a better utilization for the renewable fibrous biomass. Particular interest is concentrated to produce and apply such composites in developing countries.

Belmares and his co-workers[1] have utilized some typical natural fibers of tropical America: sisal, henequen, and palm fibers for composite plastics. First, nonwoven fabrics (mats) were made from the natural fibers, using polyvinylacetate dispersions for coating and binding of the fibers. Then unsaturated polyester laminates were made using the mats by hand lay-up techniques. It has been found that natural hard fibers give good reinforcement for composites, and such fibers can be used as replacement in part of the glass fiber.

Usmani and his collegues[2–4] used bagasse for different composite materials on the basis of phenolic resin, rubber, or thermoplastic binders. Bagasse can be grafted with acrylonitryle[5] before bringing it in composites.

Jute fiber has attracted growing attention recently. It is applied not only with unsaturated polyesters[6,7,9] but also in reinforced natural rubber composites.[8]

Coconut fiber (coconut hair, or coir) is produced in the order of 5 million tons per year in the tropical countries of the world.[10,11] Beside the conventional utilization of coir for mats, rugs, carpets, and ropes a significant amount is used for "rubberized coconut hair,"[11,12] which is a random mat binded with synthetic and/or natural latex, used as upholstery material.

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Recently coir has been used in plastic composites as well.[10,13–16] A copolymer of styrene, methyl methacrylate, and divinylbenzene has been used as binder for coconut hair composite board.[13] Particle boards have been prepared utilizing coir fiber and urea–formaldehyde resin.[14] Similar sheets were made by Mitsubishi of coir and phenolic resin binder, containing some polyethylene fiber.[15] According to a Sumitomo patent,[16] coconut fiber sheets can be prepared using an ethylene–vinyl acetate–vinyl chloride copolymer binder.

Continuing our work in applying natural fiber reinforcement in plastics,[17] the aim of the present work was to apply short cut coconut hair as reinforcement in thermosetting press materials.

EXPERIMENTAL

Materials

The origin of the coconut hair used in the present experiments was Sri Lanka (Ceylon). It is imported in form of coarse-fiber rope. After loosening the rope, the dark-brown fibers showed the following average characteristics: fiber length 10–20 cm; fiber diameter 0.28 ± 0.17 mm; tensile strength 160 ± 80 MN/m^2; modulus of elasticity 2.40 ± 0.62 GN/m^2; elongation at break $21 \pm 14\%$.

Two different types of conventional phenol–formaldehyde (PF) resins were used: a resole-type PF resin of 40°C softening temperature, which readily undergoes crosslinking (in about 2 min at 160°C) without any crosslinking agent. This resin was used in a 65% alcoholic solution for impregnation of 1–2 cm long coconut fiber. After evaporating the solvent, the composition (parts by weight) of typical resole–PF press material was the following: Resole-type PF resin 40; chopped coconut fiber 58; MgO 1; Zn–stearate 1.

The other PF resin was a novolac-type, which has a lower degree of condensation and is of linear-chain character. For the crosslinking of such a PF resin, some crosslinking agent is used (e.g., 5–10% hexamethylene–tetramin).

So, a typical composition (parts by weight) of a novolac–PF press material was the following: novolac-type PF resin 58; chopped coconut fiber 35; MgO 1; Zn–stearate 1; hexamethylene–tetramine 5.

Methods

Phenol-Formaldehyde-Bonded Coconut Fiber Composites. The resole–PF-impregnated, chopped coconut hair was loosened by short-milling in a hammer mill after complete drying. The press material was then preheated for some time to achieve precondensation, as will be described in more detail in the next chapter.

The novolac–PF-based composition was mixed in a twin-roll laboratory mill (two horizontal cylinders of 20 cm diameter and 40 cm length, 1:1.5 friction). The material was homogenized without hexamethylene–tetramin at 85–95°C, for about 5 min. After that the crosslinking agent was added

and temperature elevated to 110°C. After 20 min of milling, the material was taken off, cooled, and treated in a hammer mill to produce filtered, coarse press powder of grain diameter below 2 mm.

The press molding of PF-resin-bonded coconut fiber composites was performed on a laboratory press working at 29 bar and 145–155°C, a complete molding cycle being 15 min. Standard testing bars of 15 × 10 × 150 mm^3 were thus produced, six pieces in a mold.

Unsaturated Polyester-Bonded Coconut Fiber Composites. Bulk molding compound (BMC)-type press materials were produced on the basis of the following typical recipe (parts by eight):

unsaturated polyester binder		100
$CaCo_3$ filler	forming a paste	75
MgO		3
styrene monomer		12
Zn–stearate		2.5
tert-butyl perbenzoate		1.25
chopped fibrous reinforcement		100

In that basic recipe we changed the type and quantity as well as pretreatment of the last component from glass fiber to (a different amount of) coconut fiber.

To achieve a better coupling between the natural fiber and the synthetic polymer we pretreated the coconut fiber in some cases in one of the following two ways. In the first method we treated the fiber with a dilute (20 g/L) NaOH solution at 100°C for 1.5 h. After that, the fibers were thoroughly washed and dried completely. The second method was preirradiating the coconut fibers in air in a Co-60 gamma source of 1.85 × 10^{13} Bq (500 Cu), at room temperature with an average dose of 10 kGy (1.0 Mrad) at a dose rate of 0.2 kGy/h (20 krad/h). Finally a combined method of NaOH treatment and preirradiation was also applied.

The ingredients of the press material were processed for about 5 min in a Brabender-type kneader at room temperature to ensure proper homogeneity. The resulting doughlike material—BMC—can be stored between polyethylene foils for several weeks. The press molding of test plates of 2 mm thickness was done at 130°C with 30 bars pressure for 10 min, cooling afterwards to room temperature under the same pressure.

RESULTS AND DISCUSSION

PF-Bound Coconut Fiber Composite Materials

The resole-type PF resin impregnated, chopped coconut fiber was pretreated before molding to advance the polycondensation process. The thermal pretreatment was performed in dry state at 90°C in a drier oven. The effect of the precondensation time on the mechanical properties of the molded test specimens is shown on Table I. Molding of the test bars of 150 × 15 × 10 mm^3 was performed at 145°C, 29 bar, and 15 min pressing time.

TABLE I
Effect of Precondensation Time on Mechanical Properties of PF (Resole)-Bound Coconut Fiber Composites

Precondensation time (h)	Compressive strength (N/mm^2)	Flexural strength (N/mm^2)	Impact strength (kJ/m^2)	Loss (g) during molding[a]	Quality of the surface
3.5	118.3	62.3	12.3	13	Uncovered with resin
4.0	118.7	—	11.6	10	Uneven
4.5	114.2	62.6	9.2	5	Smooth, perfect
5.0	130.6	66.4	9.9	6	Fiber pulls out
5.5	136.9	63.9	9.1	6	Uncovered with resin

[a] From 150 g of charge.

As it is seen on Table I, the quite high compressive strength of the molded sample is growing, while the flexural strength remains almost the same, as precondensation time is increased. On the other hand, impact strength has an opposite trend: It decreases with increasing time of thermal pretreatment of the press material.

To find a compromise and considering the quality of the surface of the samples, 4.5 h are advisible for precondensation thermal treatment at 90°C of the coir–PF (resole) molding compound.

In the following the effect of chemical pretreatment of the coconut fiber has been studied. Two different types of PF (resole) resin were used to impregnate untreated coconut fiber as well as fiber treated with NaOH as described above. The precondensation time of the dry molding compound at 90°C was 4.5 h, the resin/fiber ratio was 42/58, and the molding conditions were 145°C, 29 bar, 15 min cycle.

As it is seen on Table II, the NaOH treatment of the natural coconut fiber enhances the bonding between fiber and resin matrix. Almost in all cases the molded samples showed better properties if coconut fiber was alkali-pretreated.

In the next step we tried to vary the resin/fiber ratio of the composite as it is seen on Table III. In these experiments NaOH-pretreated fiber was impregnated with resole I (commercial product, type PC 111), preconden-

TABLE II
Effect of Pretreatment of Coconut Fiber on Mechanical Properties of PF (Resole)-Bound Composites

Binder resin	Coconut fiber	Compressive strength (N/mm^2)	Flexural strength (N/mm^2)	Impact strength (kJ/m^2)
Resole I	Untreated	114.2	62.6	9.2
Resole I	NaOH-treated	115.0	53.0	19.1
Resole II	Untreated	116.8	62.3	7.1
Resole II	NaOH-treated	138.5	98.0	9.3

TABLE III
Effect of Resin/Fiber Ratio on Mechanical Properties of PF (Resole)-Bound Coconut Fiber Composition

Coconut fiber (wt % of the total mass)	Compressive strength (N/mm^2)	Flexural strength (N/mm^2)	Impact strength (kJ/m^2)
49	110.0	30.5	10.9
58	115.0	53.0	19.1
62	90.5	45.2	13.7

sation time and molding conditions maintained as by Table II. No improvement has been found by increasing or lowering significantly the fiber content, so that the 58/42 weight ratio between fiber and matrix seems to be around optimum.

Table IV shows the effect of molding (pressing) parameters on mechanical properties of PF (resole)-bound coconut fiber composites. In that series untreated coconut fiber has been used for resin impregnation. Precondensation of the molding compound was performed at 90°C for 4.5 h, the resin/fiber ratio was 42/58, and a molding pressure of 29 bars was applied.

As is seen, best results can be achieved in a somewhat slow molding cycle of 15–20 min, pressing 150 × 15 × 10 mm^3 test bars.

In all of the experiments described above medium-long cut coconut fibers (1–2 cm long) has been used. We tried to use short-cut coir too, the length of which was 1 mm in average. Impregnation and molding is much easier if short-cut coconut fibers are applied; molded specimens are more homogeneous and of better surface shine. However, the impact strength of that latter composite is lowered to about the half of the composites containing cm-long coconut fibres.

Finally, composites were made using novolac-type PF resin binder. The molding compound containing 35 wt % of short cut (mm) coconut fiber (untreated) results in a very good press material, which can be molded (155°C, 29 bar, 15 min) into homogeneous pressed products of high surface gloss. The flexural strength of 71.4 N/mm^2, and the impact strength of 5.3 kJ/m^2 have been measured for this product. Apart from these mediocre values, the novolac–PF-bound coir composite has an extremely high compressive strength over 220 N/mm^2.

TABLE IV
Effect of Molding Conditions on Mechanical Properties of PF (Resole)-Bound Coconut Fiber Composites

Pressing		Compressive strength (N/mm^2)	Flexural strength (N/mm^2)	Impact strength (kJ/m^2)
Temp (°C)	Time (min)			
145	15	114.2	62.6	9.2
160	15	135.5	40.9	6.7
145	12.5	118.9	54.7	12.8
145	20	120.0	66.0	10.1
145	25	120.0	54.4	9.2

Considering all these results obtained with PF molding compounds, one can state that coconut fiber is a very suitable reinforcement for resole type as well as novolac-type PF-bound thermosetting press materials. Its molding parameters as well as mechanical properties can be compared with several conventional PF-bound thermosets (Table VII, see later).

BMC Press Materials on the Basis of Unsaturated Polyester and Coconut Fiber

Bulk molding compound (BMC) is produced actually in large quantities using chopped glass fiber as reinforcement, unsaturated polyester (UP) as binder, and different fillers. the doughlike press material, which can be stored before molding during several weeks or months, is applied mainly for electric insulators, technical parts, and household appliances as well.

Starting from a conventional BMC formula described above—which con-

TABLE V
Tensile Strength of Coconut-Hair-Reinforced, Unsaturated Polyester-Bonded BMC Press Material

No.	Reinforcement (g) for 100 g UP		Tensile strength (N/mm^2)	Elongation at break (%)	E modulus (kN/mm^2)
	Untreated coconut hair				
1	40		23.9 ± 6.4	0.4	7.29 ± 1.09
2	60		24.0 ± 2.1	0.3	8.43 ± 1.64
3	80		13.8 ± 4.2	0.2	6.28 ± 1.23
4	100		20.4 ± 9.0	0.4	6.82 ± 1.40
5	120		20.3 ± 7.2	0.3	6.78 ± 1.04
	Preirradiated coconut hair				
6	40		31.0 ± 3.5	0.6	7.98 ± 1.60
7	60		28.5 ± 1.6	0.5	4.30 ± 1.4
8	100		23.0 ± 5.3	0.4	6.02 ± 1.32
9	120		24.8 ± 2.7	0.4	7.71 ± 0.93
	NaOH-treated coconut hair				
10	40		33.3 ± 2.6	0.6	8.09 ± 0.75
11	60		31.6 ± 2.3	0.6	8.21 ± 1.23
12	100		29.0 ± 0.6	0.5	7.33 ± 0.58
	NaOH treated and preirradiated coconut hair				
13	40		29.6 ± 5.0	0.5	15.69 ± 2.39
14	60		30.6 ± 2.8	0.6	7.52 ± 1.26
15	100		26.5 ± 3.8	0.4	8.67 ± 0.82
	Glass fiber				
16	40		31.5 ± 4.6	0.4	12.36 ± 3.17
17	60		22.6 ± 3.6	0.3	12.07 ± .86
18	100		30.4 ± 6.2	0.4	16.30 ± 1.31
19	116		29.5 ± 3.0	0.3	13.96 ± 1.95
	Coconut hair +	*Glass fiber*			
20	25	75	23.9 ± 3.4	0.4	7.15 ± 1.96
21	50	50	27.1 ± 2.0	0.5	7.92 ± 0.84
22	75	25	27.8 ± 3.4	0.3	14.00 ± 5.93
23	87.5	12.5	22.1 ± 3.1	0.3	9.12 ± 1.1

tains relatively high amount of fillers—the glass-fiber reinforcement has been changed for growing amount of coconut fiber. Mechanical properties of the molded composites are shown in Tables V and VI.

Interestingly enough, tensile strength of molded BMC doesn't decrease very much, if glass fiber is changed at growing extent to coconut fiber. The corresponding modulus of elasticity remains, however, well below that of glass-fiber-reinforced BMC. Similar decrease is observed for impact tensile strength and for Dynstat impact strength if glass fiber is changed to coconut fiber. On the other side, very good results have been obtained in static flexion for coir composites. Although the flexural strength of BMC made with untreated coconut fiber is below that of glass fiber, this flexural strength was increased significantly when coconut fiber was pretreated by NaOH and/or gamma-irradiation. This is shown clearly in Figure 1.

TABLE VI
Flexural and Impact Strength of Coconut-Hair-Reinforced, Unsaturated-Polyester-Bonded BMC Press Material

No.	Reinforcement (g) for 100 g UP		Flexural strength (N/mm^2)	DYNSTAT impact strength (kJ/m^2)	CHARPY impact strength (kJ/m^2)
	Untreated coconut hair				
1	40		22.2 ± 0.8	3.08 ± 1.37	3.2 ± 1.1
2	60		19.6 ± 2.0	2.91 ± 0.54	2.92 ± 0.43
3	80		18.5 ± 1.4	8.77 ± 4.71	4.69 ± 0.66
4	100		21.8 ± 3.9	5.87 ± 1.41	7.9 ± 2.6
5	120		20.7 ± 2.9	9.30 ± 1.78	10.7 ± 3.2
	Preirradiated coconut hair				
6	40		49.5 ± 3.4	2.13 ± 0.54	2.48 ± 0.63
7	60		56.3 ± 7.4	2.53 ± 0.79	4.83 ± 1.21
8	100		45.1 ± 5.0	6.47 ± 2.25	6.83 ± 1.6
9	120		—	5.68 ± 1.28	4.68 ± 2.3
	NaOH-treated coconut hair				
10	40		51.1 ± 2.3	2.19 ± 0.54	2.99 ± 0.49
11	60		44.5 ± 5.0	2.94 ± 0.89	3.77 ± 0.6
12	100		47.6 ± 4.4	4.85 ± 1.03	6.18 ± 0.81
	NaOH-treated and preirradiated coconut hair				
13	40		47.8 ± 2.0	3.22 ± 0.84	4.63 ± 1.55
14	60		50.9 ± 2.1	3.65 ± 0.90	3.53 ± 0.62
15	100		52.0 ± 6.2	5.67 ± 0.87	5.79 ± 1.6
	Glass fiber				
16	40		33.9 ± 7.9	7.23 ± 2.78	6.85 ± 1.54
17	60		31.0 ± 14.3	9.81 ± 3.33	9.33 ± 4.3
18	100		41.8 ± 6.6	7.49 ± 1.91	12.7 ± 3.9
19	116		36.5 ± 3.8	7.79 ± 1.40	6.7 ± 1.6
	Coconut hair +	*Glass fiber*			
20	25	75	20.5 ± 1.7	3.97 ± 1.03	5.28 ± 1.52
21	50	50	24.7 ± 6.6	3.49 ± 0.85	7.79 ± 0.99
22	75	25	25.2 ± 0.6	5.49 ± 1.86	3.59 ± 0.64
23	87.5	12.5	19.2 ± 1.7	5.42 ± 1.05	3.39 ± 0.72

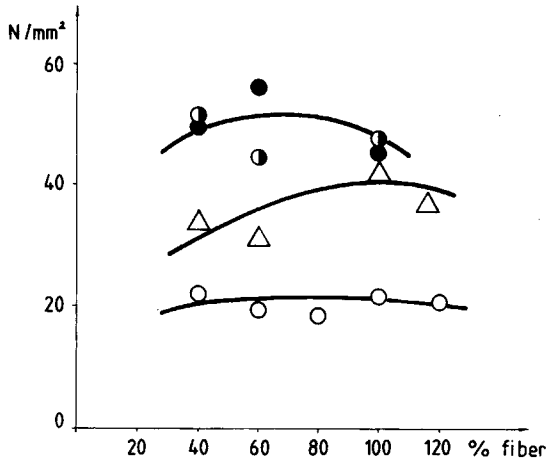

Fig. 1. Flexural strength of BMC press-materials in function of the fiber-content /% fiber = g fiber/100 g UP resin/ (○) untreated coconut fiber; (△) chopped glass fiber; (◑) NaOH-treated coconut fiber; (●) gamma preirradiated coconut fiber.

It should be noted here that a relatively high scattering of data concerning all of mechanical properties was observed. This is due above all to the uneven quality and length of the natural fibers.

The trends on Figure 1 indicate that NaOH-treated or preirradiated coconut fiber imparts a relatively high flexural strength for that highly filled BMC press material that is higher than in the case of chopped glass fiber. The role of the NaOH treatment is mainly a surface activation: NaOH, removing natural and artificial impurities from the waxy surface of the natural coconut fiber, improves the wettability. Such a treatment can facilitate the accessibility of synthetic resin (UP and styrene monomer together with) to the complex lignocellulosic structure of coconut fiber.

Graft copolymerization methods onto natural fibers, initiated by (mutual or previous) gamma-irradiation are well known. We obtained interesting results coupling wood[18] or wood fiber[17] with unsaturated polyester resin by radiation methods. Grafting of bagasse by chemical initiation was also reported earlier.[5] Gamma preirradiation of coconut fiber in the presence of air produces R—OO· peroxy radicals or R—OOH hydroperoxy groups on the radiation-sensitive sites of the lignocellulosic backbone of the natural polymer. The styrene-containing UP resin gets in close contact with the natural fiber during the kneading and storage of the BMC press materials, during which a swelling of the fibers can also be observed. And finally—if not before—in the last step: by press molding of BMC at high temperature (130°C for 10 min) the peroxy compounds will decompose initiating polymerization and/or crosslinking in the unsaturated synthetic resins around.

The benefit of the gamma preirradiation of coconut fiber is comparable with NaOH treatment, as it is seen in Figure 1. Interestingly enough, no synergistic effect has been found if both method of NaOH treatment and preirradiation were used successively.

TABLE VII
Comparison of Natural-Fiber-Reinforced Plastics with Conventional Composites

Binder	Reinforcement	Flexural strength (N/mm^2)	Compressive strength (N/mm^2)	Ref. no.
Phenolic resin	Glass mat	70–420	120–180	19
Phenolic resin	Paper	70–210	140–280	19
Phenolic resin	Nylon cloth	60–150	200–250	19
Phenolic resin	Wood flour	60–70	—	20
Phenolic resin	Bagasse	51	—	3
UP resin	Glass mat	180–280	100–350	19
UP resin	Paper	90–200	140–180	19
Resol PF	Untreated coir	62	116	Present work
Resol PF	NaOH treated coir	98	138	Present work
Novolac PF	Untreated coir	71	220	Present work
UP (in BMC)	Untreated coir	18–22	—	Present work
UP (in BMC)	Irradiated coir	45–50	—	Present work

CONCLUSIONS

Similarly to the conventional fibrous reinforcements of biomass origin (paper, wood flour, cotton cloth, etc.) and coarse natural fibers of recent interest (sisal, henequen, palm fiber, bagasse, or jute) coconut fiber can also be used in reinforced thermosetting plastics. Table VII offers some comparison of different fiber-reinforced thermosets. It can be predicted that with coconut fiber reinforcement the best properties of glass-fiber-reinforced plastics cannot be achieved, above all because of the big difference between the modulus of elasticity of the glass and natural fibers. However, in certain filled and fiber-reinforced molding compounds very good mechanical properties can be obtained. Press molding "powder" was prepared using phenolic resin binders and 35–58 wt % coconut fiber, the mechanical properties as well as surface qualities being comparable with wood-flour-reinforced phenolics. Bulk molding compound on the basis of unsaturated polyester binder was produced, in which a part or all of the chopped glass fiber was changed for coconut fiber. Significantly better coupling achieved in cases when coconut fiber was pretreated by NaOH or gamma-irradiation.

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