

Polypropylene–Wood Fiber Composites: Effect of Treatment and Mixing Conditions on Mechanical Properties

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ABSTRACT: Polypropylene/wood fiber composites were prepared at three different temperatures: 170°C, 180°C, and 190°C. The surface of wood fibers was modified through the use of silane coupling agents and/or coating with polypropylene or maleated polypropylene. The fiber coating was performed by propylene polymerization in the presence of wood fibers or by immersion in an *o*-dichlorobenzene polypropylene (or maleated polypropylene) solution. Tensile and three-point bending tests were performed in order to evaluate the adhesion between matrix and wood fibers. Evidence shows that 180°C is the best mixing temperature, while the use of vinyl-tris (2-methoxy ethoxy) silane with or without maleated polypropylene coating is the best surface treatment. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1227–1235, 1997

Key words: wood fibers; polypropylene; composites; mechanical properties

INTRODUCTION

The use of wood fibers in polymeric composites shows advantages as they are inexpensive, derive from renewable sources, present lower density than mineral fibers, undergo little damage during processing, and their disposal causes minor ecological impact.^{1,2–6}

Cellulosic fibers used for reinforcement in non-polar thermoplastics, such as polypropylene (PP), have to be modified because effective wetting of fibers and strong interfacial adhesion are required in order to obtain composites with optimized mechanical properties.^{1,7,8} Several methods for improvement in the adhesion between polymer and cellulosic fibers have been developed. The use of maleated polypropylene (MAPP) and the addition of silane coupling agents has been reported to improve bonding between the cellulose and polypropylene matrices.^{1,9,10}

In this article, the use of silanes as coupling agents as well as coating of the fibers with poly-

mer through immersion in an *o*-dichlorobenzene polypropylene solution is reported. Also, an attempt of chemical coating of wood fibers with polypropylene was made through *in situ* propylene polymerization. In olefin polymerization, silica is sometimes used as catalyst support because of its high surface area and good morphology. Silica reacts with the Ziegler–Natta catalyst through hydroxyl groups forming different active sites for olefin polymerization. Wood fibers also present hydroxyl groups which, similarly to silica, can react with a titanium catalyst, forming active centers so that a thin layer of the forming polymer on the wood fibers surface would be produced, as low activity should be expected for the system.^{11,12} A thin polypropylene coating on wood fibers can facilitate the filler dispersion into the polypropylene matrix and also improve adhesion between polymer and cellulosic fibers.

Besides poor dispersion characteristics in the thermoplastic melt and limited compatibility with the polypropylene matrix, unsatisfactory final properties of wood fibers/PP composites are due to limited thermal stability during processing.⁸ Therefore, it is also the aim of this article to search for mixing

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Table I Tensile Properties of Composites of PP/Silane-Treated Wood Fibers Composites

Type of Silane	Silane w/w (%)	Fiber w/w (%)	Stress at Maximum Load (MPa)	Elongation at Yield (%)	Modulus (MPa)
—	—	—	37.5	14.2	1055
—	—	20	29.1	4.4	1386
A1100	2	20	34.0	4.0	1452
A1100	2	30	33.9	3.0 ^a	1676
A1100	4	10	34.5	5.6 ^a	1336
A174	4	20	34.0	5.5	1235
A172	2	10	31.6	5.0	1208
A172	6	10	34.6	5.4	1226

Mixture conditions: 10 min, 60 rpm, 190°C.

^a Not all specimens exhibited yield.

conditions that optimize the performance of the modified wood fiber composites.

EXPERIMENTAL

Materials

Polypropylene (Espheripol H206) and maleated polypropylene (MAPP) were supplied by OPP Petroquímica S/A, molecular weight (M_w) 68000 and 106000, respectively.

Wood fibers were received from Centre de Recherche en Pâtes et Papiers (Université du Québec à Trois-Rivières) in the form of chemithermo-mechanical (CTMP) aspen air dried pulp (impregnation solution used was of 8% Na_2SO_3 and it was steam-cooked at 128°C for 10 min).

Dicumylperoxide (DCUP) was supplied by Atochem–Pennwalt S/A and the silane coupling agents used, A172 vinyl-tris(2-methoxy ethoxy) silane, A174- γ -methacryloxy propyltrimethoxy silane, and A1100- γ -aminopropyl triethoxy silane were supplied by Union Carbide and donated by Osi Specialities Ltd. TiCl_3 was synthesized as described elsewhere.¹³

The solvents employed were Iso-octane, hexane, and *o*-dichlorobenzene of research grade, donated respectively by Polibrasil S/A, CENPES/Petrobrás, and Hoechst do Brasil.

Wood Fiber Treatment

Silane Coupling Agents

CTMP aspen pulp oven dried (60°C) for 24 h was refluxed for 3 h in a methanol coupling agent solu-

Table II Flexural Properties of Composites of PP/Silane-Treated Wood Fibers

Type	Silane		Fiber w/w (%)	Stress at Yield ^a (Maximum Load) (MPa)	Modulus (MPa)
	w/w (%)				
—	—	—	—	31.3	3011
—	—	—	20	36.1	3113
A1100	2	—	30	51.0	4803
A1100	4	—	10	33.4	3265
A174	4	—	10	40.1	4003
A174	4	—	20	43.7	4703
A172	2	—	10	33.2	2961
A172	6	—	10	36.9	3360

Mixture conditions: 10 min, 60 rpm, 190°C.

^aStress at maximum load (at yield) occurs at 2.5% elongation.

Table III Tensile Properties of Composites of Wood Fibers Treated with A172 (4% w/w)/PP or MAPP

Matrix	Stress at Maximum Load (MPa)				Elongation at Yield (%)				Modulus (MPa)			
	0	10	20	30	0	10	20	30	0	10	20	30
	(fiber w/w %)				(fiber w/w %)				(fiber w/w %)			
PP	33.1	35.0	nd	43.8	14.8	7.0	nd	5.8	1096	1198	nd	1496
MAPP	36.7	41.9	46.6	48.6	12.6	10.2	8.8	8.4	1030	1186	1269	1450

Mixture conditions: 10 min, 60 rpm, 180°C; nd, not determined.

tion containing 2% w/w dicumylperoxide in a glass reactor. At the end of the reaction, methanol was eliminated by vacuum and the pulp was thoroughly washed with methanol and oven dried (60°C) for 24 h. The treated pulp was ground and screened to 60-mesh size. The silane coupling agents A172, A174, and A1100 were used as 2, 4, or 6% w/w methanol solutions.

Polypropylene Coating

Through Solution. 50 g (10% w/v coating) or 10 g (2% w/v coating) of polypropylene (PP or MAPP) was mixed with 500 mL of *o*-dichlorobenzene in a 1-L glass reactor, and after 24 h of swelling the mixture was heated to 180°C until complete dissolution. When the temperature of the viscous solution reached 130°C, the wood fibers (60-mesh size) were added. The mixture was then cooled to room temperature, thoroughly washed with toluene and hexane, and finally dried at 60°C for 24 h. The resultant solid mixture was finally ground (60 mesh).

Through Propylene Polymerization. The reaction with propylene in the presence of 60 g of 60-mesh size wood fibers, previously refluxed with methanol (as described previously but without

coupling agent or DCUP), was carried out in a pilot plant in iso-octane (2 L) at 70°C for 30 min under a propylene pressure of 0.098 MPa and using 2.58 mmol of a TiCl₃ Ziegler-Natta-type catalyst and triethylaluminum (TEA) as cocatalyst in a TEA/Ti ratio of 50. The coated fibers were thoroughly washed with hexane and dried at 60°C for 24 h.

Composite Preparation

The mixtures of polypropylene and wood fibers were compounded in a Haake Rheomix 600 equipped with a roller blades rotor at 170, 180 or 190°C for 10 or 15 min at 60 rpm. After the addition of polypropylene, the filler was added as soon as the registered torque indicated that the polymer melt had reached a steady state (~ 2 min).

Tensile and flexural specimens were obtained by compression molding in a Carver press at 188°C under a pressure of 4 MPa followed by cooling in another press equipped with refrigeration facilities. Rectangular specimens were cut from the pressed sheets to size (~ 100 × 8 × 0.9 mm). They were measured with the aid of a micrometer for tensile (ASTM D882-83) and flexural tests (ASTM D790M-84 three-point bending, adapted to the available support span). The mechanical

Table IV Flexural Properties of Composites of Wood Fibers Treated with A172 (4% w/w)/PP or MAPP

Matrix	Stress at Yield (Maximum Load) (MPa)				Modulus (MPa)			
	0	10	20	30	0	10	20	30
	(fiber w/w %)				(fiber w/w %)			
PP	25.0	45.6	nd	62.1	3227	5042	nd	5770
MAPP	42.1	48.5	58.1	64.0	3759	4989	5291	6345

Mixture conditions: 10 min, 60 rpm, 180°C; nd, not determined.

Table V Tensile Properties of Composites of PP/Wood Fibers Coated Through *in situ* Propylene Polymerization

Mixture Temperature (°C) ^a	Stress at Maximum Load (MPa)				Elongation at Yield (%)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
170 ^b	31.2	35.0	34.1	34.6	13.6	10.5	7.3	6.7	857	1259	1272	1344
190	37.5	34.5	32.5	33.7	14.2	8.7	7.9	6.9	1055	1246	1267	1325

Mixture conditions: 10 min, 60 rpm.

^a Fiber w/w % does not consider polymer coating.

^b Specimen presented agglomerated particles.

property measurements were carried out in an Instron Tester (model 4204) with a load cell of 1 kN, crosshead speed of 5 mm/min in tensile tests, and 6.5 mm/min in flexural tests. A minimum of four samples were tested.

RESULTS AND DISCUSSION

Tables I–XII present tensile and flexural properties of PP/wood-fiber composites prepared at 170, 180, or 190°C. Almost all samples prepared at 170°C were light yellow and presented a heterogeneous appearance with agglomerated particles, while the samples prepared at 190°C were deep yellow but presented a more uniform appearance. Figure 1 present torque data of some mixtures which show that differently from composites prepared at 170°C, which do not present a torque decay after 8-min processing (curve 1A), the same composite prepared at 190°C (curve 1B), indicate wood-fiber degradation. That suggestion is also supported by the deep yellow color developed at this temperature. Curve 1C shows torque data of

PP/20% untreated wood-fiber composite prepared at 180°C in 15 min. It can be seen that a torque decay after 10-min processing may indicate that the best mixture conditions are 180°C, 10 min, and 60 rpm (curve 1D). The poor mechanical properties presented by the curve 1C composite (stress at max load 23.9 MPa (tensile)/30.38 MPa (flexural), elongation at yield 4.6%, modulus 1038 MPa (tensile), and 3296 MPa (flexural) supports wood fiber degradation visualized by a torque decay even when the mixture temperature is 180°C, but it used the mixture time of 15 min instead of 10 min.

Tables I and II present tensile and flexural properties of composites of silane-treated wood fibers prepared at 190°C. Compared to pure polypropylene, the addition of silane-treated wood fibers (Table I) caused a decrease in the tensile strength. The increase in modulus was mainly influenced by the proportion of fiber reinforcement in the polymer.

Wood fiber contains bound moisture which could hydrolyze the coupling agent that may be represented by the formula $YRSiX_3$, where X is

Table VI Flexural Properties of Composites of PP/Wood Fibers Coated Through *in situ* Propylene Polymerization

Mixture Temperature (°C) ^a	Stress at Yield (Maximum Load) (MPa)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
170 ^b	34.9	29.9	31.9	31.6	3377	2567	3070	3073
190	29.3	27.3	31.2	38.2	3011	2732	3243	3297

Mixture conditions: 10 min, 60 rpm.

^a Fiber w/w (%) does not consider polymer coating.

^b Specimen presented agglomerated particles.

Table VII Tensile Properties of Composites of PP/Untreated Wood Fibers Coated Through Polypropylene Solution

Mixture Temperature (°C) ^a	Stress at Maximum Load (MPa)				Elongation at Yield (%)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
170 ^b	31.2	34.1	31.9	31.0	13.6	9.1	8.0	6.6	857	1167	1190	1238
190	37.5	34.3	32.3	31.7	14.2	8.7	8.0	6.0	1055	1066	1142	1172

Mixture conditions: 10 min, 60 rpm.

^a Fiber w/w % does not consider polymer coating.

^b Specimen presented agglomerated particles.

Table VIII Flexural Properties of Composites of PP/Untreated Wood Fibers Coated Through Polypropylene Solution

Mixture Temperature (°C) ^a	Stress at Yield (Maximum Load) (MPa)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
170 ^b	34.9	33.8	32.9	32.6	3377	3192	3214	3276
190	31.3	29.2	32.1	31.8	3011	2970	3153	3352

Mixture conditions: 10 min, 60 rpm.

^a Fiber w/w (%) does not consider polymer coating.

^b Specimen presented agglomerated particles.

Table IX Tensile Properties of Composites of PP/Miscellaneous Treated Wood Fibers

Fiber Treatment	Stress at Maximum Load (MPa)				Elongation at Yield (%)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
untreated	33.1	31.0	25.5	25.6	14.8	9.7	4.8	4.1	1096	1090	1276	1414
untreated + ^a	33.1	30.6	32.7	35.3	14.8	8.5	5.1	5.1	1096	1112	1254	1425
silane A172 4% w/w + ^b	33.1	36.8	40.4	40.2	14.8	10.4	9.0	9.1	1096	1074	1208	1336

Mixture conditions: 10 min, 60 rpm, 180°C.

^a Fibers coated through maleated polypropylene solution (2% w/v).

^b Fibers coated through polypropylene solution (10% w/v).

a hydrolyzable alkoxy group, *Y* is a functional group, and *R* is a small aliphatic chain. The hydrolyzed product, silanol, may develop either covalent or hydrogen bonds with the hydroxyl-rich wood fiber, improving interfacial adhesion at the fiber–matrix interface.⁷ However, as suggested by the deep yellow color of samples prepared at 190°C, composites of Table I probably have been

submitted to temperatures that caused fiber degradation.

Tables III and IV present tensile and flexural properties of composites of wood fibers treated with A172, 4% w/w prepared at 180°C using PP or MAPP as matrix. Compared to pure polypropylene, the addition of A172 (4% w/w)-treated wood fibers caused a significant increase in the strength

Table X Flexural Properties of Composites of PP/Miscellaneous Treated Wood Fibers

Fiber Treatment	Stress at Yield (Maximum Load) (MPa)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
Untreated	25.0	40.2	44.2	49.5	3227	3949	4766	5588
Untreated + ^a	25.0	27.3	33.5	37.3	3227	4035	4408	4837
Silane A172 4% w/w + ^b	25.0	45.0	46.1	50.1	3227	4287	4846	5612

Mixture conditions: 10 min, 60 rpm, 180°C.

^a Fibers coated through maleated polypropylene solution (2% w/v).

^b Fibers coated through polypropylene solution (10% w/v).

Table XI Tensile Properties of Composites of MAPP/Miscellaneous Treated Wood Fibers

Fiber Treatment	Stress at Maximum Load (MPa)				Elongation at Yield (%)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
Untreated	36.7	36.8	42.2	44.1	12.6	4.8	8.1	7.2	1030	1132	1316	1425
Silane A172 4% w/w + ^a	36.7	41.4	45.0	47.9	12.6	12.9	9.7	9.2	1030	1106	1418	1502
Silane A172 4% w/w + ^b	36.7	40.9	41.6	45.4	12.6	17.0	10.3	13.2	1030	1095	1120	1452

Mixture conditions: 10 min, 60 rpm, 180°C.

^a Fibers coated through maleated polypropylene solution (2% w/v).

^b Fibers coated through polypropylene solution (10% w/v).

Table XII Flexural Properties of Composites of MAPP/Miscellaneous Treated Wood Fibers

Fiber Treatment	Stress at Yield (Maximum Load) (MPa)				Modulus (MPa)			
	0	10 (fiber w/w %)	20	30	0	10 (fiber w/w %)	20	30
Untreated	42.1	31.7	49.2	67.5	3759	2468	4291	6445
Silane A172 4% w/w + ^a	42.1	45.7	55.4	57.7	3759	4359	5236	5051
Silane A172 4% w/w + ^b	42.1	37.6	47.0	49.2	3759	4292	4396	5206

Mixture conditions: 10 min, 60 rpm, 180°C.

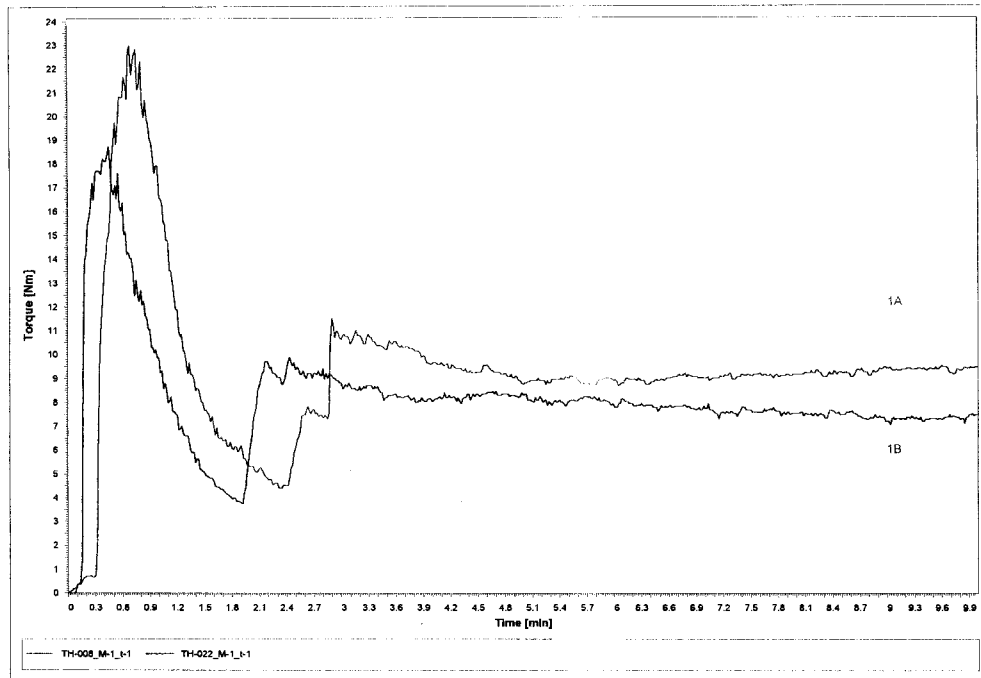
^a Fibers coated through maleated polypropylene solution (2% w/v).

^b Fibers coated through maleated polypropylene solution (10% w/v).

and modulus, and an expected decrease in the elongation at yield suggesting that satisfactory interfacial adhesion was developed with both types of matrix (PP or MAPP). The best results of the composites prepared with MAPP as matrix are due to the polar characteristics of the polymer.

Tables V and VI present tensile and flexural properties of composites of PP/wood fiber-coated through *in situ* propylene polymerization prepared at 170 or 190°C. Although compared to pure polypropylene there is an increase in the strength and modulus of composites prepared at 170°C, the

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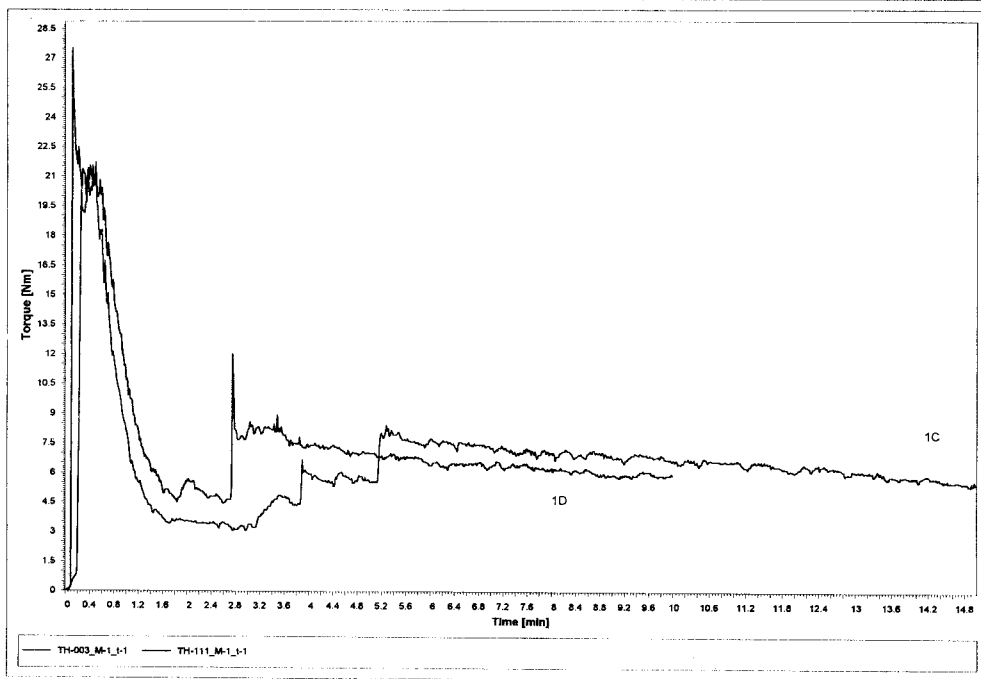
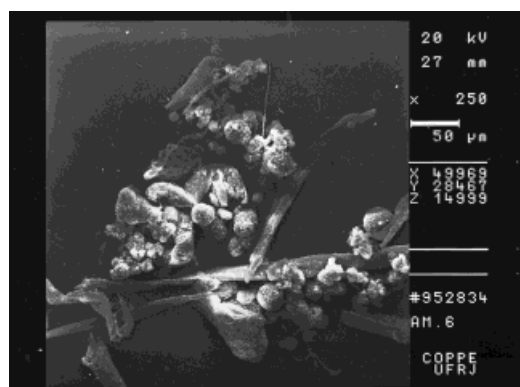


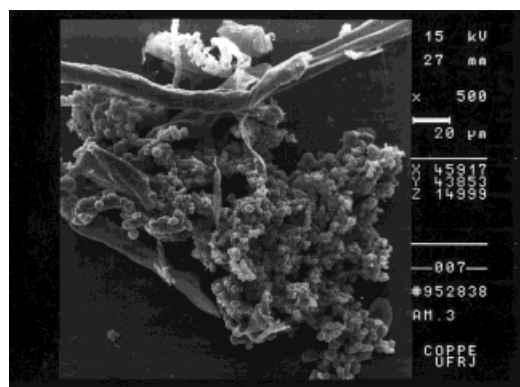
Figure 1 Torque (Nm) \times time (Min). Curves 1A and 1B, PP/20% wood fibers coated through *in situ* propylene polymerization prepared at 170°C and 190°C, respectively. Curves 1C and 1D, PP/20% untreated wood fibers prepared at 180°C in 15 and 10 min, respectively.

SEM micrographs [Fig. 2(a)] show that instead of polypropylene surface coating, polypropylene agglomerated around the wood fibers, which does not justify this laborious type of coating to be repeated in the composites prepared at 180°C.

Tables VII and VIII present tensile and flexural properties of composites of PP/wood fibers coated through the polypropylene solution. The SEM micrographs [Fig. 2(b)] of the modified wood fibers used in these composites show that the polypropylene coating also produced agglomerated polymer particles other than the surface fiber coating. Diversity in flexural modulus and strength between PP/silane-coated fiber composites (Tables II and IV) and PP/polypropylene-coated fiber composites (Tables VI and VIII) may suggest that the lower values of the later composites are due to morphology and viscosity differences between polypropylene of the matrix and of the coating. Since 180°C is an optimal temperature of mixture, a thinner coating through polypropylene solution could prevent the formation of agglomerated polymer particles, and Tables III and IV showed a

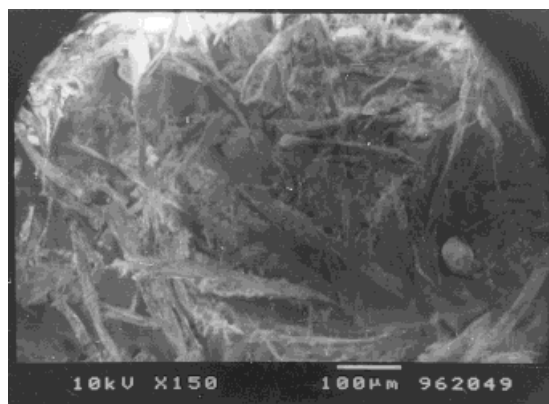


(a)

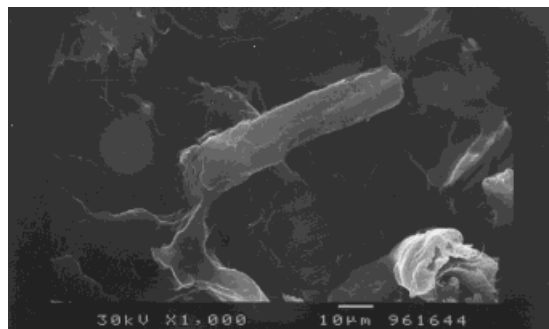


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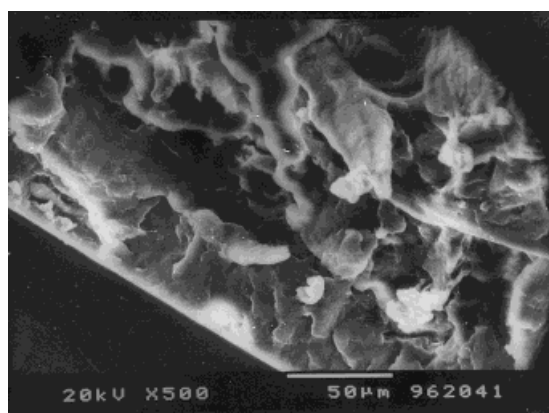
Figure 2 SEM micrographs. (a) Fibers coated through *in situ* propylene polymerization. (b) Fibers coated through polypropylene solution (10% w/v).



(a)



(b)



(c)

Figure 3 SEM micrographs. (a) Fibers treated with A172 4% w/w and coated through maleated polypropylene solution (2% w/v). (b) Fracture of MAPP/20% untreated wood fibers prepared at 180°C. (c) Fracture of PP/20% A172 (4% w/w) treated wood fibers and coated through MAPP solution (10% w/v).

significant increase in mechanical properties when A172 or maleated polypropylene was used. Supported by these results we made an attempt to obtain still better composites; therefore, Tables IX and X present tensile and flexural properties of miscellaneous treated wood fibers in composites prepared at 180°C with polypropylene, and Tables XI and XII present data of miscellaneous wood

fibers in composites of MAPP matrix. Figure 3(a) shows a SEM micrograph of wood fibers treated with A172 4% w/w and coated through maleated polypropylene solution (2% w/v). Figure 3(b) presents a SEM micrograph of a fracture of the composite MAPP/20% untreated wood fibers prepared at 180°C, which show adhesion between fiber and matrix. Figure 3(c), which also shows adhesion between fiber and matrix, presents a SEM micrograph of a fracture of the composite PP/20% A172 (4% w/w) treated wood fibers plus MAPP coating (10% w/v), prepared at 180°C.

CONCLUSION

The optimal mixture conditions of polypropylene/wood fiber composites are 180°C for the mixture temperature and 10 min for the time of mixture. The best wood fibers surface treatment is A172 (4% w/w) coated with MAPP through solution (2% w/v), since mechanical properties of these composites were optimized. Although the use of MAPP matrix with untreated wood fibers produce composites which develop adhesion between fibers and matrix [Figure 3(b)], the use of A172 silane treatment produce still improved adhesion.

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