

# The Effect of Chemical Treatment of Wood and Polymer Characteristics on the Properties of Wood-Polymer Composites

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## Synopsis

The physical-mechanical properties and the microscopic structure of caixeta (*Chrysophyllum viride*) and slash pine (*Pinus elliottii*) impregnated with polystyrene (PS) were investigated. The influence of a pretreatment with hydrogen peroxide ( $H_2O_2$ ) solutions utilized in the production of the wood-polymer composites (WPC) and the characteristics of polystyrene formed *in situ* on the properties of WPC were analyzed. The incorporation of polystyrene improved the compression and static bending properties of slash pine and caixeta. The micrographies confirmed that there were distinct but continuous phases of polymer and wood cell wall which granted the composites a better physical-mechanical behavior. The sensibilizing treatment with dilute hydrogen peroxide solution led to an increase in the viscosity average molecular weight ( $\bar{M}_v$ ) of polystyrene, and to the graft polymerization of the monomer, which, in turn, enhanced the stress properties of caixeta-polystyrene composites. Concentrated  $H_2O_2$  solutions degraded caixeta wood, decreasing its tensile properties. Lower initiator concentration favoured higher molecular weight of polystyrene formed in pine wood. A fivefold increase in  $\bar{M}_v$  of PS, however, had little effect on the compression properties of pine-polystyrene composites.

## INTRODUCTION

Wood-polymer composites (WPC) are obtained by impregnating wood with liquid monomers, and then polymerizing those monomers *in situ*, using catalyst-heat or radiation process.<sup>1-4</sup> A wide range of properties for WPC is possible by varying the monomer or the oligomer with crosslinking agent, the wood, the monomer filling method, and the polymerization process.<sup>1-7</sup>

WPC have been subject of many researches since 1960. Their physical-mechanical properties, water and humidity absorption, as well as their dimensional stability, have been extensively analyzed as a function of the parameters listed before. Generally, WPC show fairly improved properties compared with the untreated wood, independently of the materials and the way it is obtained.<sup>3-11</sup>

Most of the researchers have tried to improve especially the dimensional stability of woods and WPC, using various techniques.<sup>5-11</sup> The two most widely used methods for those purposes are the solvent exchange techniques of impregnation and the graft polymerization of monomers onto cellulose.

Taneda et al.<sup>12</sup> used hydrogen peroxide to initiate the graft polymerization of styrene onto woody substance. They succeeded in promoting both graft

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polymerization and crosslinking of styrene. Subramanian and Hofmann<sup>13</sup> verified that an oxidizing treatment of wood with nitric acid resulted in the formation of carboxylic acid groups chemically bonded to wood. Those acid groups initiated the polymerization reaction of a polymerizable monomer. Based on those results, some investigations have been made in this laboratory, using  $H_2O_2$  solutions as oxidizing agent to possibly promote the initiation of graft polymerization of styrene onto cellulose.

The present article has been directed to microstructure analysis, characteristics of the polymer formed *in situ*, and to the possibility of correlations between WPC microstructure and WPC properties. The characteristics of polystyrene obtained in different conditions, and then extracted from the wood, have been determined. The influence of polystyrene molecular weight on the mechanical properties of WPC has also been analyzed. We report those results, presenting scanning electron and optical micrographies that clarified several aspects of microstructure–property relationships of WPC.

## EXPERIMENTAL

### Materials

Caixeta (*Chrysophyllum viride*) and slash pine (*Pinus elliottii*) were used as the wood species. Boards of  $2.5 \times 5.0 \times 120.0 \text{ cm}^3$  were air-dried to 14 wt % moisture content. Specimens were cut from those boards, into sticks with appropriate dimensions for each test, and then conditioned to 7.0–9.0 wt % moisture content. The specimens selected were those presenting density within the range of 0.54–0.64  $\text{g/cm}^3$  for caixeta and 0.36–0.52  $\text{g/cm}^3$  for pine.

Commercial styrene used in the treatment of wood was distilled before each impregnation. As the initiator of catalyst–heat polymerization, azoisobutyronitrile was primarily used, although in some preliminary tests benzoyl peroxide was also used.

The extraction of polystyrene from wood was performed using chloroform. The solvent for determining  $\bar{M}_v$  was a solution of solvents, toluene–methanol, in the proportion of 75.2 : 24.8 in volume, respectively.

### Preliminary Tests

In the preliminary tests, some conditions in the production of WPC were investigated, particularly the efficiency of benzoyl peroxide (BPO) and azoisobutyronitrile (AIBN) as initiators of styrene polymerization in the wood cells. The main reason for that study was the fact that it was expected AIBN would favor reactions at lower temperatures in shorter periods of time compared with BPO. Lower temperatures and shorter periods mean lower energy costs and a way to prevent or at least to minimize the evaporation of monomers during the polymerization process.

Wood samples with 7–9 wt % moisture content were impregnated using vacuum/pressure method. The impregnated samples were wrapped in aluminum foil just after wiping off the excess monomer from their surface. Some variables such as type and concentration of initiator, and polymerization temperature, were varied in order to find the appropriate conditions (Table I).

TABLE I  
Impregnation and Polymerization Conditions Used in the Preliminary Tests for Obtaining  
Wood-Polymer Composites

Vacuum time (min)	Pressure (MPa)	Impregnation time (min)	Initiator	Initiator concentration (wt %)	Polymerization temperature (°C)
30	196	20	BPO	0.1	60
90	196	20	BPO	0.1	60
30	196	20	BPO	0.1	70
30	196	20	BPO	1.0	60
30	196	20	BPO	1.0	70
30	196	20	BPO	2.0	70
30	196	20	AIBN	1.8	60
30	196	20	AIBN	1.6	70
30	196	30	AIBN	1.6	70
30	196	20	AIBN	0.9	70
30	245	20	AIBN	0.1	60
30	245	20	AIBN	0.5	60

Based on the initiator at minimum concentration which provided the lowest time and temperature of polymerization, and the highest polymer retention (lowest monomer evaporation), as well as the best aesthetic appearance, the treating conditions considered appropriate were: vacuum, 30 min; pressure,  $24.5 \times 10^4$  Pa, 20 min; initiator, AIBN 0.2 wt %; temperature of polymerization, 60°C; time of polymerization, 48 h.

### Testing Methods

Mechanical testings were carried out using Instron universal tester Model 1127, at room temperature. Compression test (parallel to the grain) was determined according to COPANT<sup>†</sup> 30:1-008 standard. Sample dimensions were  $2 \times 2 \times 8$  cm<sup>3</sup>. The strain rate used was 0.6 mm/min.

According to the COPANT 30:1-006 standard for evaluation of static bending properties, test samples with dimensions of  $2 \times 2 \times 30$  cm<sup>3</sup> were used. The strain rate in this test was 1.0 mm/min. The tensile test was performed following the ASTM D638 standard (parallel to the grain, type 1).

Moisture content was determined according to the COPANT 30:1-003. The ASTM D570 standard was used for determining water absorption, and ASTM D2395 for determining density.

### Pretreatment with H<sub>2</sub>O<sub>2</sub> Solutions

In this study, solutions of H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O, 1.65 and 16.5 wt %, have been used. Dry wood samples were treated in a vacuum/pressure chamber in the following manner: vacuum for 30 min; immersion in the treating solution under pressure of  $24.5 \times 10^4$  Pa for 15 min. The treated samples were air dried for 48 h, and then oven-dried at 40°C for 72 h. Impregnation with styrene using

<sup>†</sup>COPANT—Comisión Panamericana de Normas Técnicas.

the same procedure described before was accomplished, subsequent to the pretreatment.

### Molecular Weight Determination

The extraction of styrene from wood was performed using a Soxhlet extractor with chloroform. The samples,  $2 \times 2 \times 1 \text{ cm}^3$ , were continuously extracted for different periods depending on the purpose of the experiment. A period of 48 h was used to investigate the effect of AIBN concentration—0.2 and 0.6 wt % AIBN in styrene—on the  $\bar{M}_v$  of polystyrene formed *in situ*. The other periods, 7 days or 168 h and 30 days or 720 h, of continuous extraction were used to verify the possibility of extracting all the polymer formed in wood.

The material extracted was first dissolved with toluene/methanol, and subsequently diluted to concentrations of 0.25, 0.10, and 0.05 wt %. Dilute solution viscometry was accomplished using an Ostwald–Fenske viscometer. Both Huggin's and Kraemer's equations were used for calculating the viscosity average molecular weight.

### Microstructure Analysis

Samples for microstructure analysis using a scanning electron microscope were obtained by fracturing longitudinally the test samples. Then they were machined into dimensions of  $2 \times 1 \times 1 \text{ cm}^3$ .

Slices of  $2 \times 2 \text{ cm}^2$  cross section and  $5 \mu\text{m}$  thick were used as the samples for optical microscopy. They were obtained by cutting test samples with microtome, followed by a wetting with glycerin/water solution.

## RESULTS AND DISCUSSION

The results of mechanical properties for the different test materials are presented in Table II. Those values correspond to the average of measurements made in 10–17 test pieces. Test series are labeled CPS, CTCPS, DTCPS, PPS, 2PPS, and 6PPS. CPS refers to samples of caixeta–polystyrene composite. Preceding the impregnation with styrene, a pretreatment using  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  solutions was applied in the CTCPS and DTCPS series. High concentrations of 16.5 wt % (concentrated) and low concentrations of 1.65 wt % (dilute) were used in CTCPS and DTCPS samples, respectively. Pine wood was impregnated with polystyrene in the PPS series.

The two series labeled 2PPS and 6PPS refer to slash pine–polystyrene composites obtained from pine impregnated with styrene containing 0.2 and 0.6 wt % of AIBN, respectively. Those samples were used to investigate the effect of initiator concentration on the molecular weight of polystyrene as well as on the compression properties of pine–polystyrene composites.

The results of the different test series are compared in Table III. The significance of the differences between those values was obtained based on the *t*-test.

The incorporation of 34–38% of polystyrene in caixeta increased, as was expected, the compression and static bending strengths. Improved values were also expected for treated slash pine, whose polymer content was much higher:

TABLE II  
Mechanical Properties for Different Test Materials

Test	Material	Pps <sup>a</sup> (wt %)	Strength $\sigma$ (MPa)	Modulus $E$ (GPa)
Compression parallel to the grain	Caixeta	—	49.1	4.45
	CPS	38.6	62.7	5.08
	CTCPS	41.0	56.7	5.79
	DTCPS	41.6	66.5	5.91
	Slash pine	—	32.0	2.57
	PPS	132.0	74.4	5.95
	2PPS	113.5	89.6	5.87
	6PPS	118.8	76.2	5.75
Static bending perpendicular to the grain	Caixeta	—	108.2	10.33
	CPS	35.7	145.4	11.76
Tensile parallel to the grain	Caixeta	—	96.2	2.89
	CPS	30.5	96.4	3.02
	CTCPS	41.1	66.7	2.99

<sup>a</sup>Pps = relative retention of polystyrene in wood.

136%. An interesting feature can be observed when compression strengths of those two different composites are compared. A product, pine-polystyrene (PPS), 13.8% denser than caixeta-polystyrene (CPS) is obtained with pine 52.4% less dense than caixeta. Untreated pine shows compression strength ( $\sigma_c$ ) 53.4% lower and elastic modulus in compression ( $E_c$ ) 73.4% lower than those of untreated caixeta. However, PPS shows  $\sigma_c$  18.8% higher and  $E_c$  17.2% higher than those of CPS. Compression properties of caixeta-polystyrene reach the values of those of pine-polystyrene composites only when pre-

TABLE III  
Differences between Results of Mechanical Tests for Each Pair of  
Test Series and Their Respective Significances

Test	Control $\times$ sample	Difference between the values of the pair (%)	
		Strength ( $\sigma$ )	Signifi- cance (%)
Compression parallel to the grain	C $\times$ CPS	27.7/99.9	14.2/99.0
	CPS $\times$ CTCPS	-10.6/90.0	14.0/98.0
	CPS $\times$ DTCPS	6.1/80.0	16.3/99.0
	CTCPS $\times$ DTCPS	17.3/99.0	2.0/not sign.
	CPS $\times$ PPS	18.8/99.0	17.2/99.0
	P $\times$ PPS	132.5/99.9	131.8/99.9
	2PPS $\times$ 6PPS	-17.6/95.0	-2.2/not sign.
Static bending perpendicular to the grain	C $\times$ CPS	34.4/99.9	13.9/99.9
Tensile parallel to the grain	C $\times$ CPS	0.2/not sign.	4.6/80.0
	C $\times$ CTCPS	-30.7/95.0	3.6/not sign.

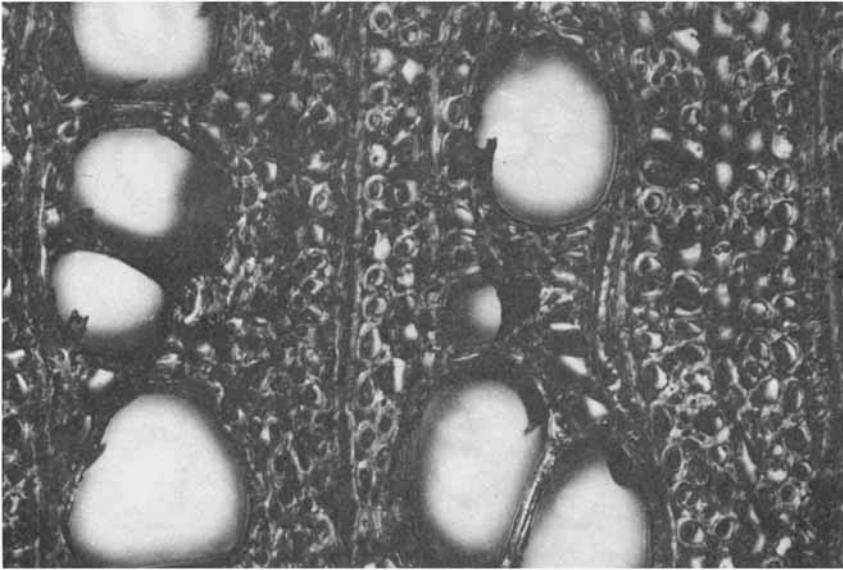


Fig. 1. Polarized light micrograph of caixeta wood (100  $\times$ ).

treated caixeta is used, as will be seen later. That is one of the advantages of using low density soft wood for the production of WPC.

Optical micrographies of untreated caixeta and caixeta-polystyrene composite are presented in Figures 1 and 2, respectively. Untreated pine and pine-polystyrene composite micrographies are shown in Figures 3 and 4, respectively.

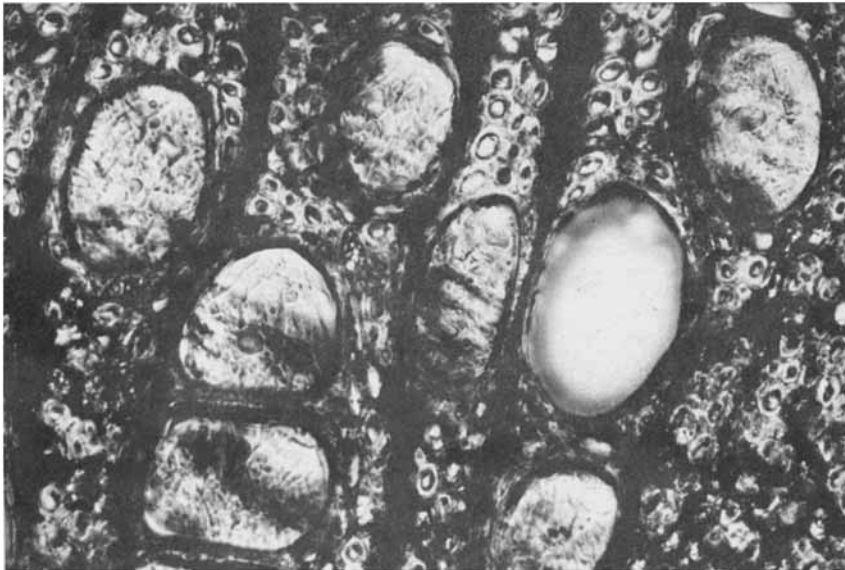


Fig. 2. Polarized light micrograph of caixeta-polystyrene composite. Not all the cell lumens are filled with polymer (100  $\times$ ).

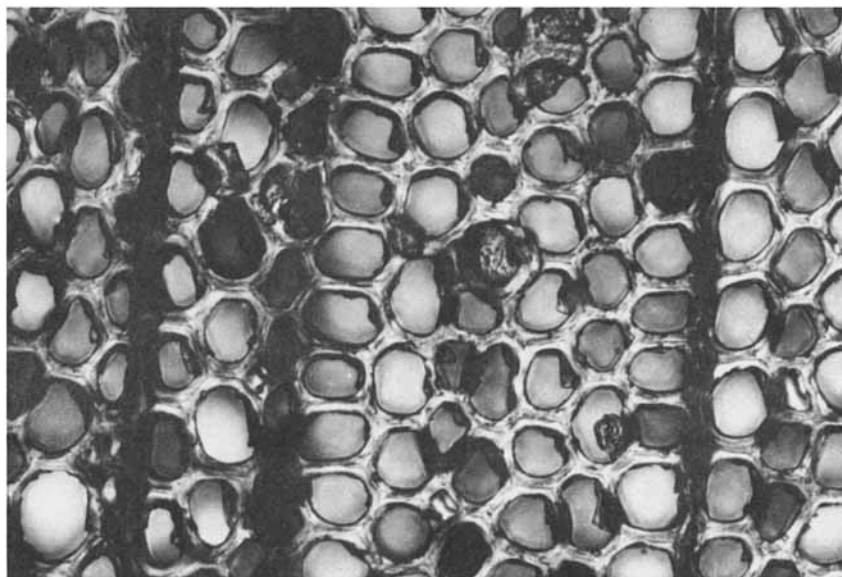


Fig. 3. Polarized light micrograph of slash pine wood (100  $\times$ ).

Those figures show that almost all the cell lumens are filled with polystyrene in PPS composites, and partially in CPS composites. They also show that the shrinkage of styrene monomer is negligible in this polymerization reaction. In an experiment using pure cellulose and styrene, it was verified a high wettability of cellulose with styrene, which would indicate some compatibility be-

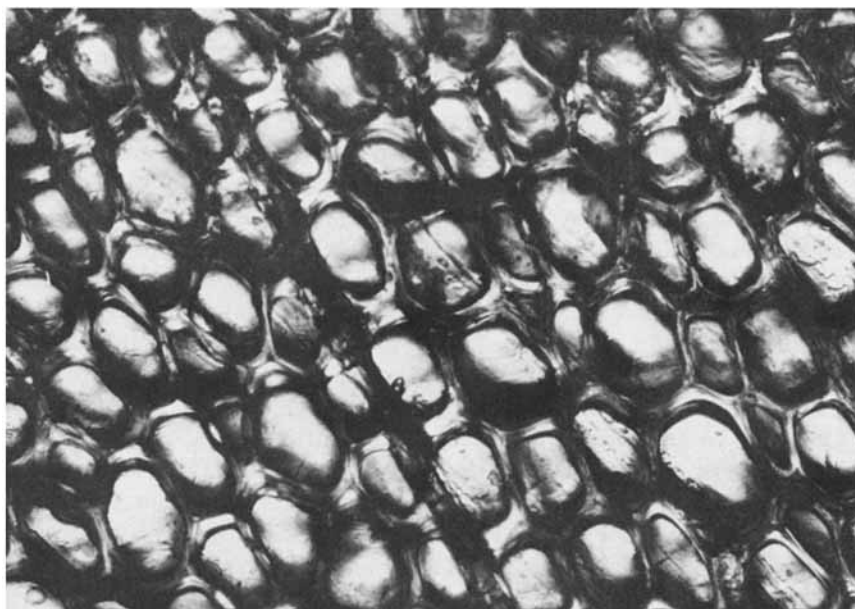


Fig. 4. Polarized light micrograph of slash pine-polystyrene. All the cell lumens are filled with polymer (100  $\times$ ).

tween the two materials. Therefore, it is probable that, in the impregnation process, the monomer wets the cell wall, and polymerizes on its surface and in the cell lumen. That would lead to the formation of distinct but continuous polymer-cell wall phases, which, in fact, is verified in the micrographies.

The results of the test for analyzing the influence of initiator concentration, and, consequently, of polystyrene molecular weight, are shown in Table II. The  $\bar{M}_c$  of polystyrene in 2PPS is fivefold that of PS in 6PPS. The effect of that drastic increment in PS molecular weight on compression properties is little: 17.6% in  $\sigma_c$  (significant) and 2.2% in  $E_c$  (not significant).

Tensile test was carried out only for caixeta, CPS, and CTCPS, which the results are presented in Table II. Even though the tensile strength and the modulus of CPS compared with those of untreated caixeta are slightly higher, those values cannot be considered significantly different.

It has been proposed in the literature that tensile strength and dimensional stability as well as the physical and mechanical properties of WPC, in general, would be improved if chemical bonds between the polymer and the cellulose molecules were promoted.<sup>8</sup> It has also been proposed that the oxidation of wood with nitric acid would favor the formation of carboxylic acid chemically bonded to wood, which is capable of initiating the polymerization of monomers.<sup>13</sup> Expecting the same tendency, in the present study, the highly oxidant hydrogen peroxide was used as the possible promoter of graft polymerization of styrene onto cellulose.

The results in Table II show a positive effect of the sensitizing treatment only for DTCPS series, in the compression test. When high  $H_2O_2$  concentration is used, CTCPS series, both compression and tensile strengths are depressed. Although a significant increase of 14.1% in  $E_c$  of CTCPS compared to that of CPS has occurred, an equally significant decrease of 10.6% in  $\sigma_c$  has been observed.

The effect of the sensitizing treatment was pronounced for tensile properties, having the CTCPS series show tensile strength  $\sigma_t$  30.7% even lower than that of the untreated caixeta. This might have been due to the existence of two competing reactions in treating wood with  $H_2O_2$  solutions: initiation of graft polymerization and oxidegradation. Taking in consideration the fact that the pretreatment with concentrated  $H_2O_2$  solution would have caused an extensive degradation of wood constituents, electron micrographies of CTCPS were examined. The comparison between Figures 5(a) and 5(b) confirms that the caixeta has been severely attacked by hydrogen peroxide. The holes in the degraded caixeta are totally filled with polymer after impregnation and polymerization of styrene, as shown in Figure 5(c). The bulking of the degraded structure with polystyrene is not efficient for recovering the original mechanical properties of caixeta wood.

Opposite to the effect of concentrated solution,  $H_2O_2$  dilute solution affected quite positively the compression properties of WPC, as can be seen in Table II. Since there were difficulties in concluding about the microstructure of caixeta treated with  $H_2O_2/H_2O$ , 1.65 wt %, using electron microscope, it was decided to use light microscope and analyze the transversal views of that material. Figures 6(a) and 6(b) show those micrographies where it is clear that the microstructure of untreated and treated wood differs from each other. It





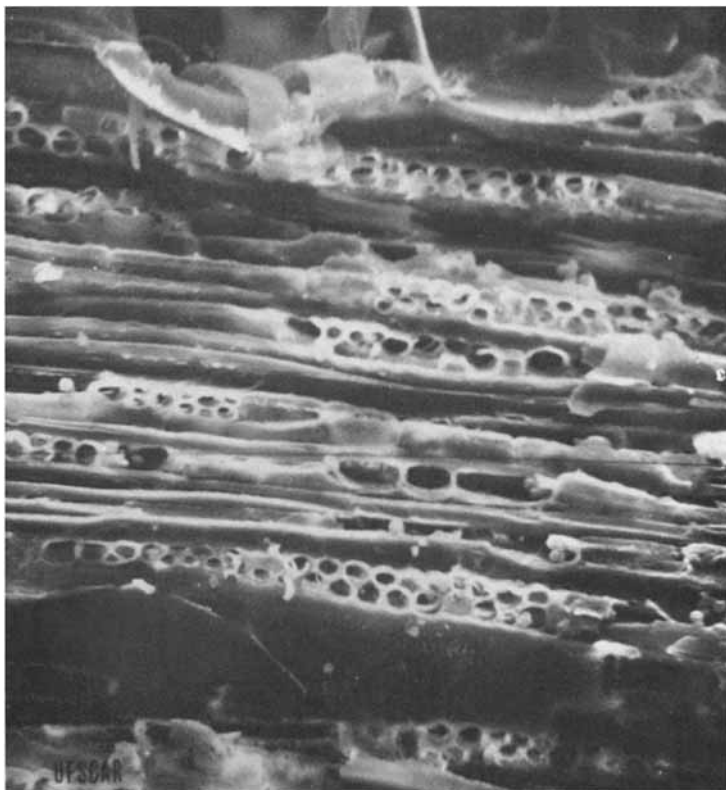
(a)

Fig. 5. Scanning electron microographies: (a) caixeta wood ( $220\times$ ); (b) caixeta sensitized with  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ —16.5 wt %; note the wood degradation evidenced by the holes ( $190\times$ ); (c) caixeta-polystyrene composite obtained from degraded wood. The holes are completely filled with polymer ( $210\times$ ).

appears that treated caixeta has been washed up, so that some constituents and/or impurities have been eliminated.

A volume swelling of 11.4% in caixeta impregnated with dilute hydrogen peroxide solution is verified, which indicates penetration of the solution into the wood cell wall. Dried treated pieces recover their original dimensions, hence the monomer does not diffuse into the cell walls during the impregnation, making difficult an intimate monomer-cellulose and polymer-cellulose associations. Nevertheless, it does not prevent chemical bonds to occur on the wall surfaces. In addition, styrene monomer can fill those spaces left by wood constituents/impurities in the lumens and in the cell walls, making possible physical entanglements between polymer and cellulose molecules.

The fact that styrene monomer fills the excess spaces in caixeta when pretreatment is applied has been proved by its improved impregnability in those cases, as it can be seen in Table II. Higher polymer retention means better physical and mechanical properties, and that is an important factor contributing to the increased properties of WPC obtained from sensitized



(b)

Fig. 5. (Continued from the previous page.)

caixeta, though other factors must be considered. For instance, although CTCPS and DTCPS present the same polymer retention, compression properties are lower for CTCPS due to the degradation of wood structure.

The possibility of styrene grafting onto cellulose has been verified by continuous extraction with chloroform, which the results are presented in Table IV. It is interesting to note that three quarters of polymer formed in CPS are extracted after 168 h, while the same amount of that formed in DTCPS is extracted only after 720 h. Practically all polystyrene is dissolved from CPS and CTCPS, but the same is not true for DTCPS.

The viscosity average molecular weights of two different fractions of polystyrene from caixeta-PS composite, one extracted in the first 7 days and the other extracted in the last 23 days, are different: The fraction dissolved first shows lower  $\bar{M}_v$ , which means the lower  $\bar{M}_w$ , the easier polystyrene dissolution. Similar behavior is observed for PS extracted from the two test series of pine-polystyrene composites: 2PPS and 6PPS. Styrene containing lower concentration of initiator AIBN led to the formation of polymer with higher  $\bar{M}_v$ . As can be seen in Table IV, for the same period of extraction, i.e., 48 h, the fraction of PS dissolved was less for that with higher  $\bar{M}_v$ . Therefore, based on the values of molecular weights in Table IV, a higher difficulty is



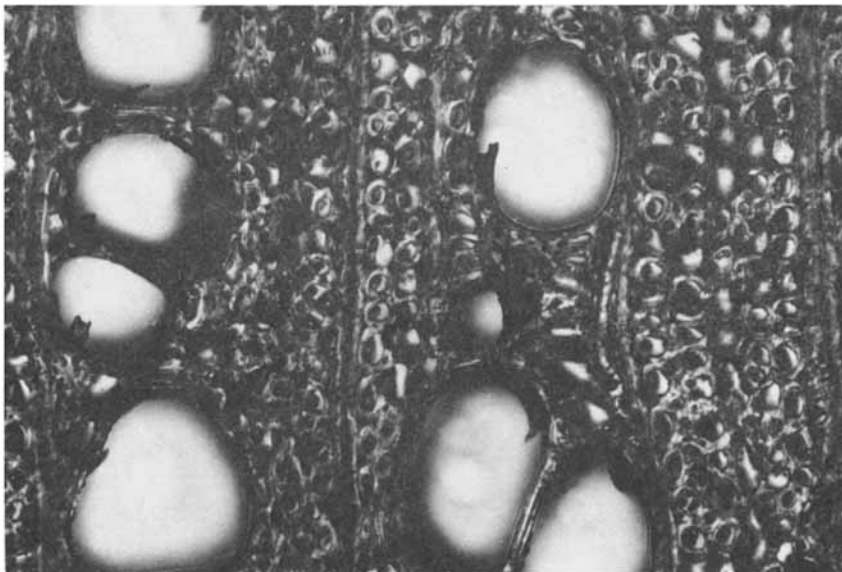
(c)

Fig. 5. (Continued from the previous page.)

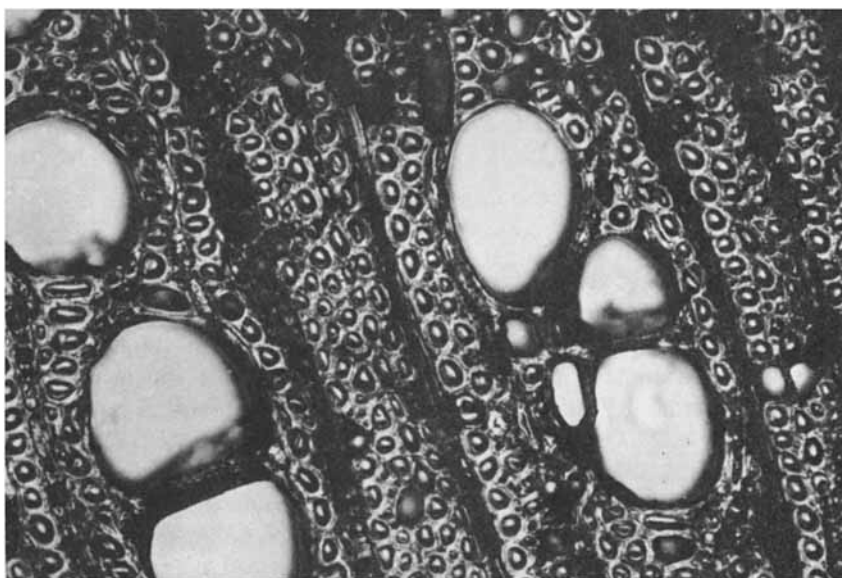
expected in extracting the polymer from DTCPS compared with any other composites. However, it cannot be considered definitely that the 23.5% of polystyrene did not dissolve exclusively due to the very high  $\bar{M}_v$ . Graft polymerization is another possibility considering that in the last 72 h the sample weight remained practically constant, indicating no further polystyrene dissolution.

The sensibilizing treatment with  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ , dilute solution, has affected not only caixeta impregnability but also the molecular weight of the *in situ* polymer, as shown in Table IV. The environment of polymerization reaction in this case must have been altered by the oxidation reaction. Wood constituents, such as lignin and those presenting polyalkyl ring-substituted phenols, have probably been eliminated. Those phenols act as free radical scavengers so that its presence in heat-catalyst polymerization decreases both the rate of polymerization and the polymer molecular weight, through chain transfer reactions.<sup>14</sup> The elimination of those substances by the pretreatment thus has granted the polymer in DTCPS the highest value of  $\bar{M}_v$ , which is probably one of the factors for the most improved compression properties.

Inaccessible polymer molecules in the wall layers could have contributed to the insolubility of polystyrene, making impossible its extraction from caixeta pretreated with  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  dilute solution. Timmons et al.<sup>15</sup> found that the



(a)



(b)

Fig. 6. Polarized light micrographies: (a) caixeta wood (100 × ); (b) caixeta sensibilized with H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O-1.65 wt %. Note that some impurities and/or constituents have been washed up (100 × ).

TABLE IV  
Viscosity Average Molecular Weight of Polystyrene Extracted from  
Caixeta-Polystyrene composite (CPS), Pretreated Caixeta-Polystyrene  
Composites (TCPS), and Pine-Polystyrene Composites: 2PPS and 6PPS

		$\bar{M}_v$ (g/mol)	Fraction of PS extracted (wt %)
CPS			
7-day extraction		48,000	73.0
30-day extraction		53,000	94.4
TCPS, 30-day extraction	Treated with $H_2O_2$ —16.5 wt % (CTCPS)	97,000	95.4
	Treated with $H_2O_2$ —1.65 wt % (DTCPS)	434,000	76.5
PPS, 48-h extraction	Pine impregnated with styrene + 0.2 wt % AIBN	152,000	78.5
	Pine impregnated with styrene + 0.6 wt % AIBN	29,000	83.4

ovendried cell wall of white pine and basswood was initially impermeable, and after soaking 100 h, methyl methacrylate penetration was detected, but only into the outer  $S_2$  layer. They also found that the pentane-dried cell wall, which was partially swollen, was more permeable to the monomer than the ovendried wall. Soaking white pine in monomer for 12 h, insignificant penetration occurred. In our work, the pressure impregnation for 30 min of pretreated ovendried caixeta, which presented no swelling, certainly has not induced styrene diffusion into the cell walls. So, physical absorption of monomer on the wall surface is more likely to occur.

If monomer diffusion is improbable, the presence of inaccessible polymer molecules will be equally improbable. The surface physical absorption of polystyrene with high  $\bar{M}_v$  would not prevent at all its dissolution after 720 h in Soxhlet extractor, unless there were complex physical entanglements. Therefore, we are inclined to conclude that the majority of the remaining 23.5% of polystyrene has been grafted to cellulose molecules located on the wall surface, and that in turn has led the DTCPS to show the highest compression properties compared with those of other composites studied in this work.

## CONCLUSION

Microscopy with polarized light and scanning electron microscopy were proved to be useful tools for the analysis of correlations between WPC microstructure and WPC properties. They showed that there was an intimate polystyrene-cellulose association at the wall surface, leading to the formation of continuous polymer-cell wall phases. They also showed two different microstructures for caixeta pretreated with dilute and concentrated hydrogen

peroxide solutions, which were responsible for the differences in the mechanical properties of the correspondent composites.

Lower initiator concentration contributed to higher compression properties for pine-polystyrene composites. That was attributed to the higher viscosity average molecular weight in this case.

The sensibilizing treatment of caixeta wood with dilute hydrogen peroxide solution was considered to be an efficient method for improving the composite properties. That pretreatment favored the graft polymerization of styrene onto cellulose, higher polymer retention, and higher polymer molecular weight. The graft polymerization was thought to be the main factor contributing to the highest compression properties showed by the DTCPs samples, compared with any other caixeta-polystyrene composites.

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