

# H<sub>2</sub>O<sub>2</sub> as a Modifier of Phenol–Formaldehyde Resin used in the Production of Particleboards

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**ABSTRACT:** The purpose of the research was to study the influence of H<sub>2</sub>O<sub>2</sub> on the properties of fluid phenolic (PF) resin, the curing process, the cured resin structure, and the properties of the particleboards produced with its use. The influence of added H<sub>2</sub>O<sub>2</sub> on resin usability at 20°C, on the gel time of the modified PF resin in the temperature range 110–140°C, and on the activation energy of the curing process were studied. Also, the structure of the cured resin was examined by Fourier transform infrared spectroscopy. Fi-

nally, the properties of the obtained particleboards were determined. The results indicate that the H<sub>2</sub>O<sub>2</sub> modification leads to greater reactivity of the phenolic resin and increases the mechanical properties of particleboards. In contrast, there is no significant influence of H<sub>2</sub>O<sub>2</sub> on the water resistance of the particleboards. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3084–3092, 2003

**Key words:** adhesives; resins; modification; FT-IR

## INTRODUCTION

The properties of particleboards greatly depend on the kind and amount of the bonding agent applied during their production. In the process of manufacturing boards for use in the building industry, phenol–formaldehyde (PF) resins are commonly used because they emit only slight amounts of phenol and formaldehyde and because the boards glued with them are characterized by good physical and mechanical properties. In the process of gluing, PF resins show little sensitivity to humidity of the glued wood, and the resultant adhesive-bonded joints are relatively flexible, vibration resistant, and thermally stable. However, during the curing process, high temperatures or long pressing times are required and the cost of manufacturing the resins is relatively high. For these reasons, researchers strive to improve the technological and economical aspects of the production process, mostly by increasing resin reactivity.<sup>1,2</sup> Most research on the activation of PF resins focuses on the production of water-resistant plywood. The scope of this research has only to a certain extent been concerned with polycondensation of resins in the technological process of producing particleboards. The process of resin activation should be conducted in such a way that, on the one hand, it does not decrease the usability of the mixed glue and, on the other hand, it shortens the polycondensation time at higher temperatures (i.e., during particleboard pressing).

Previous studies in which numerous groups of chemical compounds were tested for the production of plywood and laminated wood, showing that encouraging results can be obtained by introducing inorganic oxidizing agents into PF resins because they are capable of speeding the curing process.<sup>3–5</sup> Yet, it must be noted that many oxidizing agents are relatively expensive: assuming the oxidizing agents are mixed with glue in amounts up to 5% by weight in relation to the dry mass of the resin, a noticeable increase in the cost of manufacturing wood-based materials would result from their use. Also, oxidizing agents often contain heavy metals, which is a drawback from an ecological point of view. Therefore, for the purposes of this study, H<sub>2</sub>O<sub>2</sub> was selected as the accelerator of the reaction of PF resin polycondensation. Its availability, low price, and the fact that it does not contain any elements or functional groups that unfavorably affect the health issues associated with the particleboards are undeniable advantages of this compound. Moreover, resins produced with H<sub>2</sub>O<sub>2</sub> are characterized by long life. There are also sufficient grounds to assume that H<sub>2</sub>O<sub>2</sub> can act in a twofold manner; that is, as an accelerator of the curing process and as an activator of the wood surface, which assists the adhesion process.<sup>6–8</sup>

The purpose of the present work is to study the influence of H<sub>2</sub>O<sub>2</sub> on the properties of fluid and polycondensated phenolic resin as well as particleboards produced with its use.

## EXPERIMENTAL

### Materials

For research purposes, pure resol phenol–formaldehyde (PF) resin designed for use in the production of

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TABLE I  
Characteristics of PF Resin

| Characteristic               | Properties stated by the manufacturer | Actual properties     |
|------------------------------|---------------------------------------|-----------------------|
| Appearance                   | Dark red liquid                       | Clear dark red liquid |
| Density, g/cm <sup>3</sup>   | —                                     | 1.21                  |
| Dynamic viscosity, mPa·s     | 90–500                                | 465                   |
| Solids content, %            | 43–47                                 | 44.8                  |
| pH                           | —                                     | 11.63                 |
| Gel time at 120°C, s         | —                                     | 206                   |
| Life, days                   | 60                                    | 54                    |
| Free phenol content, %       | max. 0.10                             | 0.03                  |
| Free formaldehyde content, % | max. 0.100                            | 0.034                 |
| NaOH content, %              | max. 8.00                             | 7.47                  |

particleboards was used (Fenokol 43, manufactured by CHEMKO, a. s., Strážske, Slovak Republic). The properties of the PF resin are shown in Table I.

The PF resin was modified with a liquid solution of 30% H<sub>2</sub>O<sub>2</sub>, with a density of 1.11 kg/dm<sup>3</sup>. The reagent was analytically pure. The H<sub>2</sub>O<sub>2</sub> was produced by CHEMPUR, Piekary Śląskie, Poland.

Scotch pine (*Pinus silvestris* L.) flakes obtained under industry conditions were used to produce particleboards. The flakes were subjected to screen classification before being used for the production of particleboards. Dust and the fraction that was unable to pass through square mesh (2 mm on a side) were removed. Some of the flakes were ground in a vibratory ball mill. The resultant dust was used in preparing samples for analysis by Fourier transform infrared (FTIR) spectroscopy and determination of activation energy of the PF resin crosslinking. The cellulose used in the FTIR tests was manufactured by SERVA Feinbiochemika, Heidelberg, Germany. The reagent was analytically pure.

#### Influence of H<sub>2</sub>O<sub>2</sub> on PF resin at 20°C

The use of oxidizing agents that activate the curing process leads to significant changes in the viscosity of the prepared mixed glue. Thus, it was possible to determine the influence of H<sub>2</sub>O<sub>2</sub> added to the PF resin on the resin viscosity as a function of time. First,

immediately before the determination, solutions of mixed glue were prepared; the solutions contained 0, 1, 2, 5, 10, and 15 parts by weight of H<sub>2</sub>O<sub>2</sub> per 100 parts by weight of dry resin solids. Every hour, the dynamic viscosity of the solutions was determined with a Höppler rheoviscometer manufactured by VEB MLW Prüfgeräte-Werk Medingen, Dresden. The name Höppler rheoviscometer is a brand name used by the manufacturer. However, the referred viscometer is in fact a falling-weight viscometer. The measurements were repeated over a period of 12 h, and an addition measurement was made after 24 h.

#### Gel time of PF resin modified with H<sub>2</sub>O<sub>2</sub> and determination of the activation energy of crosslinking

The ability to activate the thermosetting resins with various additives is commonly estimated by measurements of the gel time of the mixed glue at temperatures of ≥100°C. Therefore, the gel times were examined at the temperatures of 110, 120, 130, and 140°C. The solutions of mixed glue were prepared by adding H<sub>2</sub>O<sub>2</sub> to the resin immediately before the determination. The mixtures consisted of 0, 1, 2, 5, 10, and 15 parts by weight of the H<sub>2</sub>O<sub>2</sub> modifier per 100 parts by weight of dry resin solids. The volume of the added H<sub>2</sub>O<sub>2</sub> solution was constant. The amount of the modifier was adjusted by changing its concentration in the

TABLE II  
Changes with Time in Viscosity of PF Resin Modified with H<sub>2</sub>O<sub>2</sub>

| H <sub>2</sub> O <sub>2</sub><br>fraction,<br>% | Dynamic viscosity, mPa·s         |     |     |     |     |     |     |      |      |      |      |      |      |      |
|---|----------------------------------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|
|   | Measurement time after mixing, h |     |     |     |     |     |     |      |      |      |      |      |      |      |
|   | 0                                | 1   | 2   | 3   | 4   | 5   | 6   | 7    | 8    | 9    | 10   | 11   | 12   | 24   |
| 0   | 423                              | 423 | 423 | 423 | 423 | 423 | 424 | 425  | 426  | 426  | 427  | 427  | 427  | 432  |
| 1   | 419                              | 423 | 428 | 429 | 436 | 441 | 448 | 458  | 468  | 512  | 546  | 567  | 587  | 756  |
| 2   | 415                              | 423 | 447 | 487 | 498 | 512 | 532 | 558  | 576  | 643  | 687  | 745  | 812  | 1456 |
| 5   | 404                              | 438 | 496 | 536 | 617 | 658 | 679 | 721  | 767  | 821  | 956  | 1056 | 1167 | 2954 |
| 10  | 387                              | 442 | 513 | 607 | 733 | 829 | 920 | 998  | 1081 | 1201 | 1254 | 1432 | 1589 | 5123 |
| 15  | 371                              | 456 | 523 | 638 | 791 | 876 | 945 | 1023 | 1199 | 1387 | 1676 | 1932 | 2130 | 7967 |

TABLE III  
Influence of H<sub>2</sub>O<sub>2</sub> on the Gel Time of PF Resin at Various Temperatures

| Curing temperature, °C | H <sub>2</sub> O <sub>2</sub> Fraction, % |     |     |     |     |     |
|------------------------|---|-----|-----|-----|-----|-----|
|                        | 0   | 1   | 2   | 5   | 10  | 15  |
|                        | Gel time, s                               |     |     |     |     |     |
| 110                    | 432                                       | 410 | 390 | 353 | 304 | 284 |
| 120                    | 220                                       | 208 | 180 | 164 | 159 | 143 |
| 130                    | 106                                       | 103 | 102 | 100 | 99  | 98  |
| 140                    | 73  | 73  | 72  | 71  | 71  | 70  |

solution. Moreover, to determine the possible influence of H<sub>2</sub>O<sub>2</sub> on the reaction of PF resin towards wood, the following mixtures were prepared and tested: resin and distilled water; resin and H<sub>2</sub>O<sub>2</sub>; resin and pine dust; resin, pine dust, and distilled water; and resin, pine dust, and H<sub>2</sub>O<sub>2</sub>. The amount of H<sub>2</sub>O<sub>2</sub> was 10 parts by weight. The amount of pine dust was 30 parts by weight of dry mass per 100 parts by weight of dry resin solids.

The gel times of mixed glue were used to assess the relative activation energy of the crosslinking process of the tested variants.<sup>9</sup> A preliminary assumption was made that the curve illustrating the curing process with time, for the temperatures of 110, 120, 130, and 140°C, was a linear function (until the curing point was reached). Because the reaction rate increases along with the rise of the temperature, it is possible to correlate it with the reaction temperature. The logarithmic curve of the curing rate is dependent on the inverse of the absolute temperature as shown by the very good linear correlation. In these conditions, the activation energy ( $E_a$ ) can be calculated on the basis of Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (1)$$

where  $k$  is the curing reaction rate constant,  $A$  is the pre-exponential factor,  $R$  is the gas constant, and  $T$  is the absolute temperature.

TABLE IV  
Gel Time of PF Resin with Various Additives at Various Temperatures

| Curing temperature, °C | Formulation |  |   |                                   |   |  |
|------------------------|-------------|--|---|-----------------------------------|---|--|
|                        | PF resin    | PF resin + H <sub>2</sub> O <sup>a</sup> | PF resin + H <sub>2</sub> O <sub>2</sub> <sup>b</sup> | PF resin + pine dust <sup>c</sup> | PF resin + pine dust <sup>c</sup> + H <sub>2</sub> O <sup>a</sup> | PF resin + pine dust <sup>c</sup> + H <sub>2</sub> O <sub>3</sub> <sup>b</sup> |
|                        | Gel time, s |  |   |                                   |   |  |
| 110                    | 403         | 430                                      | 301   | 171                               | 190   | 150  |
| 120                    | 206         | 215                                      | 149   | 103                               | 142   | 94   |
| 130                    | 100         | 104                                      | 99  | 75                                | 89  | 71   |
| 140                    | 68          | 73                                       | 71  | 60                                | 69  | 63   |

<sup>a</sup> Water was added in the amount corresponding to the amount of water added as diluent of H<sub>2</sub>O<sub>2</sub>.

<sup>b</sup> The amount of H<sub>2</sub>O<sub>2</sub> added was 10% in relation to dry mass.

<sup>c</sup> The amount of pine dust added was 30% of dry mass in relation to the dry mass of the resin.

### FTIR spectroscopic study of cured resin structure

FTIR spectroscopy was used to explain the influence of H<sub>2</sub>O<sub>2</sub> on the structure of the cured resin, the wood substance, and the character of interactions between the resin and wood. The analyses were made for pine wood, cellulose, and phenolic resin before and after the activation with H<sub>2</sub>O<sub>2</sub>; for nonactivated and activated pine dust; and for cellulose with resin. All the samples were cured at various temperatures. The curing processes took place in test tubes placed in a glycerol bath. Moreover, the samples intended for FTIR analysis were dried under vacuum in the presence of P<sub>2</sub>O<sub>5</sub> and later ground in a vibratory ball mill. Mixtures of these samples with KBr were prepared in the weight ratio 1:200 and homogenized in a ball mill. Then, 200 mg of the homogenized mixture were subjected to tableting in a hydraulic press under vacuum and a pressure per unit area of 100 MPa. The FTIR spectra were recorded with the Mattson Infinity FTIR spectrophotometer (Mattson Instruments, Madison, WI) at resolution of 2 cm<sup>-1</sup>. Estimates of the baseline were made between 4000 and 2940, 2940 and 1737, and 625 cm<sup>-1</sup>.

### Production of the laboratory particleboards and examination of their properties

To examine the influence of H<sub>2</sub>O<sub>2</sub> on the properties of particleboards glued with PF resin, single-layer boards with density of 700 kg/m<sup>3</sup> and dimensions of 450 × 450 × 12 mm were produced under laboratory conditions. The following pressing parameters were employed: pressure, 2.5 MPa; temperatures, 180, 200, and 220°C; time, 8–12 min. H<sub>2</sub>O<sub>2</sub> was added to the glue, and the resultant mixture was spread over the particles in a slow-speed laboratory blender. The amounts of H<sub>2</sub>O<sub>2</sub> were 0.0, 0.1, 0.2, 0.5, 1.0, and 1.5% in relation to the dry mass of the chip. The resin levels were 6, 8, 10, and 12%.

The properties of the particleboards were examined according to the relevant European Standards (EN):

**TABLE V**  
Curing Process Kinetic Parameters

| Formulation  | Activation energy, kJ/mol |
|--|---------------------------|
| PF resin   | 79.66                     |
| PF resin + H <sub>2</sub> O                          | 79.74                     |
| PF resin + H <sub>2</sub> O <sub>2</sub>             | 62.80                     |
| PF resin + pine dust                                 | 45.70                     |
| PF resin + pine dust + H <sub>2</sub> O              | 46.25                     |
| PF resin + pine dust + H <sub>2</sub> O <sub>2</sub> | 38.07                     |

modulus of rupture (MOR) and modulus of elasticity (MOE) according to EN 310;<sup>10</sup> internal bond (IB) according to EN 319;<sup>11</sup> swelling in thickness after 24 h according to EN 317;<sup>12</sup> and moisture resistance (test V 100) according to EN 1087-1.<sup>13</sup>

## RESULTS AND DISCUSSION

### Influence of H<sub>2</sub>O<sub>2</sub> on resin stability at 20°C and curing kinetics

The influence of H<sub>2</sub>O<sub>2</sub> on the stability of PF resin at 20°C is shown in Table II. The data show that as the amount of H<sub>2</sub>O<sub>2</sub> in the resin increased to 5% the dynamic viscosity after 8 h (i.e., in the period of time used in the production conditions) increased slightly. Yet, the resins containing 10 and 15% modifier were characterized by much higher viscosity. The latter result, however, does not exclude the possibility of using the resin in industrial conditions.

The influence of the amount of H<sub>2</sub>O<sub>2</sub> added to the resin on the gel time is illustrated in Table III. The data

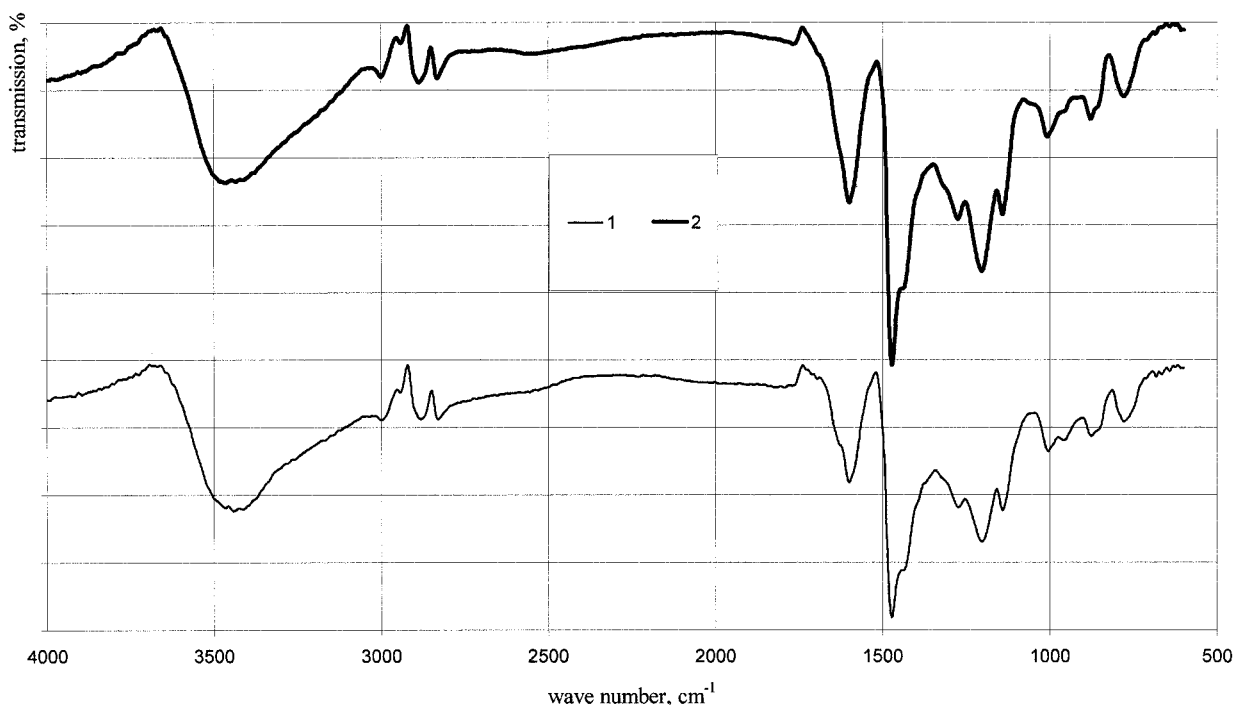
show that at 110 and 120°C, the gel time shortened as the amount of the added modifier increased. This process is less distinct at 130 and 140°C.

The influence of H<sub>2</sub>O<sub>2</sub> and other components present in the PF resin polycondensation process on its gel time is shown in Table IV. Water added to the resin in an amount that corresponds to that of H<sub>2</sub>O<sub>2</sub> did not significantly affect the gel time of PF resin. However, the addition of pine dust shortened this time considerably, especially at lower temperatures. The greatest reduction of the gel times was observed when both H<sub>2</sub>O<sub>2</sub> and pine dust were introduced to the resin.

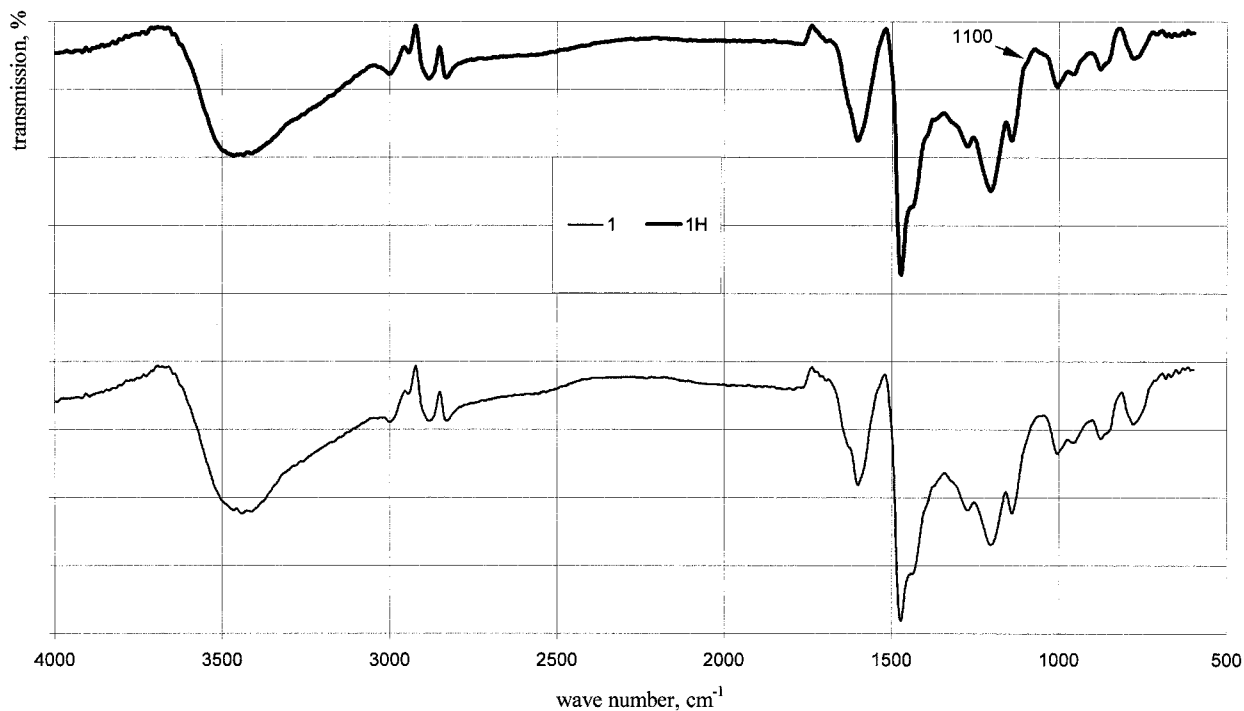
The influence of H<sub>2</sub>O<sub>2</sub> and other components present in the PF resin polycondensation process on the activation energy of this process, based on gel time measurements, is shown in Table V. The data confirm that H<sub>2</sub>O<sub>2</sub> introduced into the resin along with pine dust leads to a significant decrease in the activation energy of this process.

### FTIR spectroscopy

The FTIR spectra of the studied samples are shown in Figures 1–5. Qualitative analysis of spectra illustrated in Figure show that PF resins cured at 130 and 150°C are not significantly different. Other spectra, illustrated in Figures 2 and 3, show the influence of H<sub>2</sub>O<sub>2</sub> on the structure of the cured resin. The qualitative and quantitative changes featuring at 130°C were slight. The action of H<sub>2</sub>O<sub>2</sub> led to slight changes in the 1100



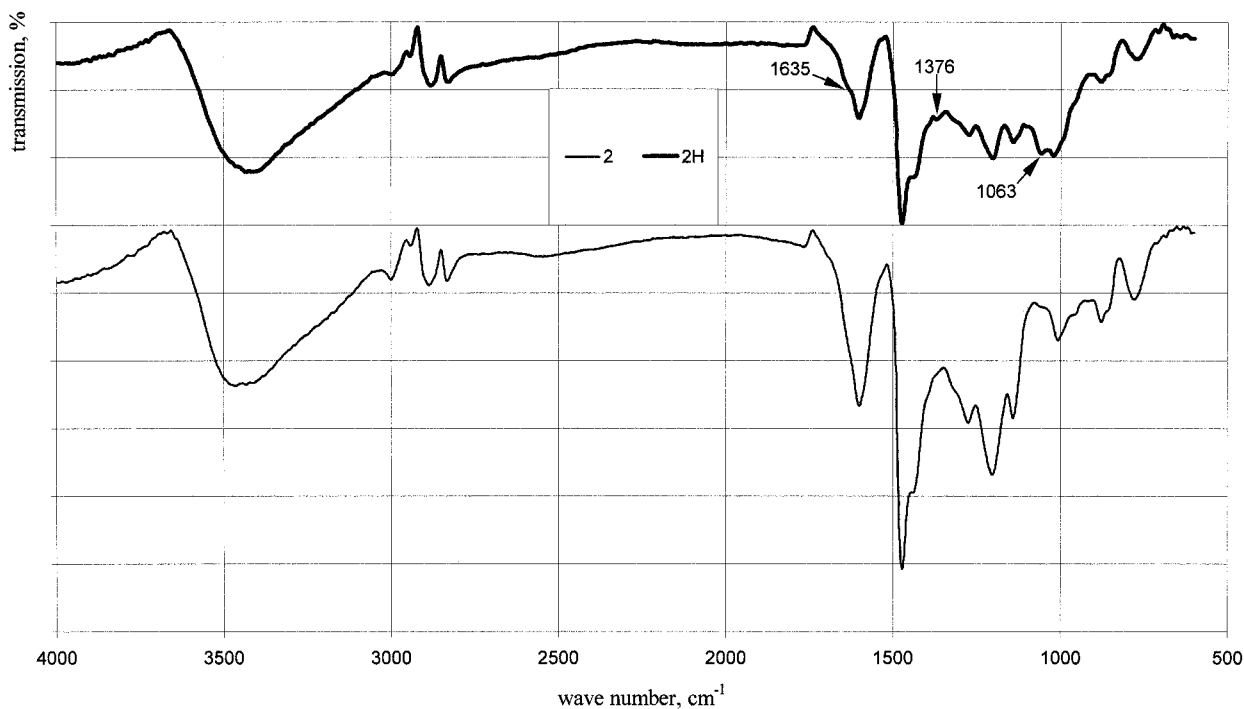
**Figure 1** FTIR spectra of PF resins cured at (1) 130°C and (2) 150°C.



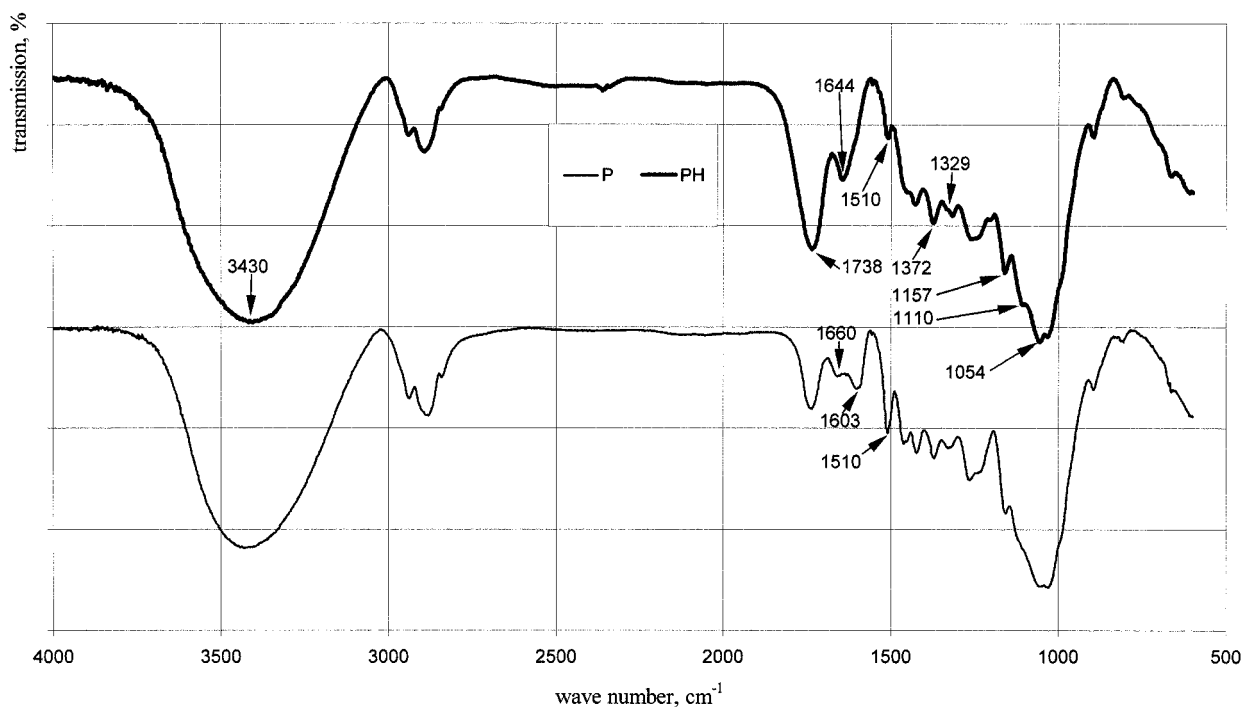
**Figure 2** FTIR spectra of PF resins cured at 130°C, with (1H) and without (1) the addition of H<sub>2</sub>O<sub>2</sub>.

cm<sup>-1</sup> band. The influence of H<sub>2</sub>O<sub>2</sub> on the structure of the cured resin was much more significant for the curing temperature of 150°C. In this case, under the influence of H<sub>2</sub>O<sub>2</sub>, peaks appeared at 1635, 1376, and 1063 cm<sup>-1</sup>. The latter is a counterpart of the weak peak at ~1100 cm<sup>-1</sup> in case of the resin cured with the addition of H<sub>2</sub>O<sub>2</sub> at

130°C. Taking into account the expected oxidizing effect of hydrogen peroxide on PF resin, the observed changes should be ascribed to the formation of carboxylic ion. The quantitative changes are characterized by the increasing number of OH groups in the 3460 and 1205 cm<sup>-1</sup> bands in case of the oxidized resin.



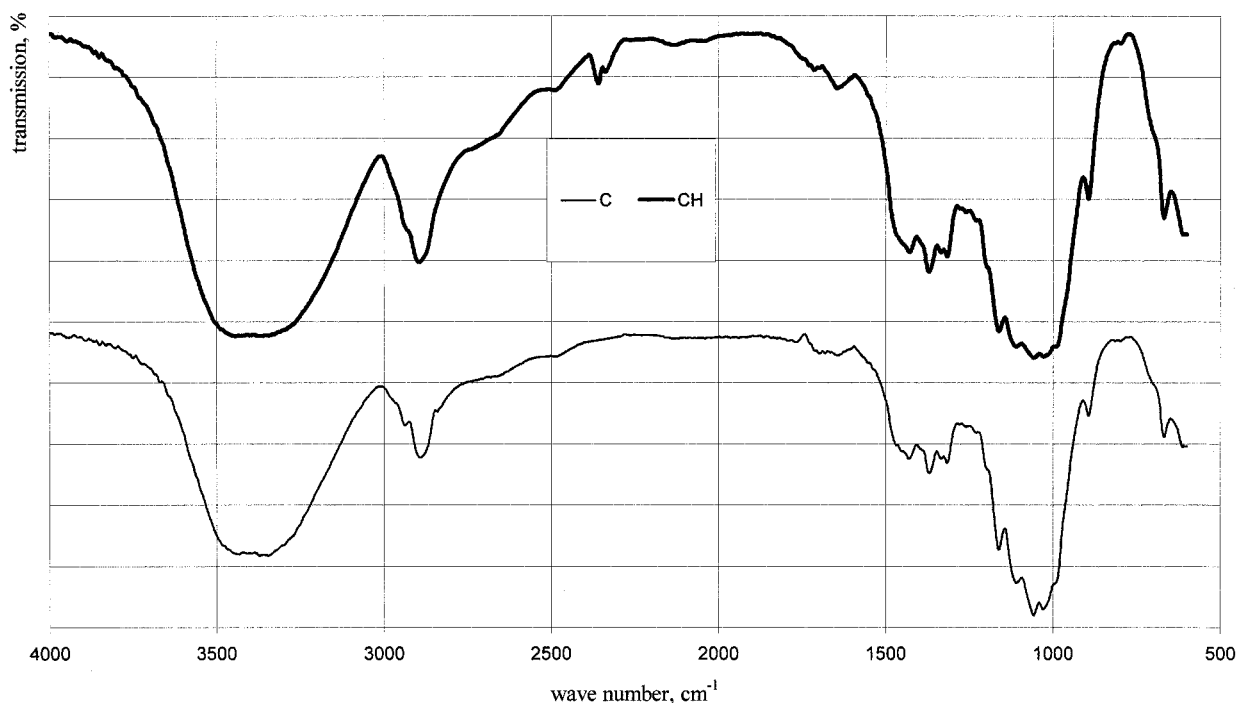
**Figure 3** FTIR spectra of PF resin cured at 150°C, with (2H) and without (2) the addition of H<sub>2</sub>O<sub>2</sub>.



**Figure 4** FTIR spectra of pine dust held at 100°C, with (PH) and without (P) the addition of H<sub>2</sub>O<sub>2</sub>.

The FTIR spectra of pine wood before and after the activation indicate that there were considerable changes in the structure of wood treated with H<sub>2</sub>O<sub>2</sub> (Figs. 4 and 5, respectively). The spectra vary in both a qualitative and a quantitative sense. The qualitative changes refer mainly to the “fingerprint” range (i.e.,

1740–600 cm<sup>-1</sup>). In the spectra of wood that was not treated with H<sub>2</sub>O<sub>2</sub>, it is possible to distinguish bands characteristic of vibrations of the lignin aromatic ring at 1603 and 1510 cm<sup>-1</sup>. However, in the spectra of wood activated with H<sub>2</sub>O<sub>2</sub>, there is no band at 1603 cm<sup>-1</sup> and the intensity of the band at 1510 cm<sup>-1</sup>



**Figure 5** FTIR spectra of cellulose held at 100°C, with (CH) and without (C) the addition of H<sub>2</sub>O<sub>2</sub>.







tively low pressing parameters were characterized by the decrease in swelling in thickness as the amount of  $H_2O_2$  added increased. The accelerator did not distinctly influence the moisture resistance of the particleboards in the boiling test.

The favorable changes connected with the increase in strength properties of the particleboards are unquestionably associated with the activation process of PF resin caused by the action of  $H_2O_2$ , which is illustrated by Tables II–V. Moreover,  $H_2O_2$  affects the wood structure, especially lignin (Fig. 4), which leads to the growth of reactive groups in the wood surface as confirmed by FTIR analyses.

### CONCLUSIONS

1. Introducing  $H_2O_2$  into the fluid phenolic resin shortens the gel time and pot life of the resin as measured by the increase in viscosity with time and the decrease in activation energy of the polycondensation process. The degree to which these effects occur increases with the increase of the amount of  $H_2O_2$  added. The observed changes of viscosity at 20°C do not limit the usability of obtained mixed glue in the industrial production of particleboards.
2. Under the influence of  $H_2O_2$ , the structure of the cured phenolic resin, determined by FTIR analysis, undergoes minor changes that are apparently due to the increased number of carboxyl groups, which are probably the result of oxidation of some hydroxymethylene groups.
3. The optimal fraction of  $H_2O_2$  with regard to both the reactivity of the resin and the production of particleboards is 2–5%. This amount makes it possible to produce particleboards of the required properties in a shorter time, at lower temperature, and at decreased resin levels.
4. Introducing  $H_2O_2$  into the mixed glue does not significantly influence the resistance of the particleboard to the action of water.

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