

# Properties of Phenol–Formaldehyde Resin Modified with Organic Acid Esters

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**ABSTRACT:** Properties of liquid and cured phenol–formaldehyde (PF) resin modified with esters were analyzed in this study. Esters with different carbon chain lengths, both in the acid and alcohol groups, were applied in the experiments. It was found that the modification of phenolic resin with applied esters does not deteriorate its pot life at the temperature of 20°C. It results in an increase of its reactivity at higher temperatures, manifested in the shortening of gel time at 130°C

and a decrease of activation energy. Results of FTIR tests of polycondensed modified PF resin showed that products of alkali hydrolysis of esters not only catalyze the curing reaction of resin, but also become embedded in its structure. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3358–3366, 2008

**Key words:** PF resin; modification; esters; viscosity; infrared spectroscopy

## INTRODUCTION

Till now, phenol–formaldehyde (PF) resins have been the dominant bonding agents in the production of OSB, LVL, HB boards, and exterior plywood.<sup>1</sup> The application of these resins makes it possible to obtain adhesive bonded joints exhibiting high mechanical properties and high moisture resistance. Moreover, obtained joints are relatively elastic, shock-resistant, and thermally stable, which contributes to increased service life of wood-based materials resinated with PF resins.<sup>2</sup> However, considerable amounts of thermal energy are required in the curing process, i.e. long pressing times or high pressing temperatures need to be applied. For this reason, studies are undertaken aiming at the improvement of technological and economic indexes of the manufacturing process of reconstituted products resinated with PF resins by increasing resin reactivity through its modification.

The method preferred by many researchers and producers of wood-based materials is the modification of ready-to-use resins with added substances accelerating curing and/or reducing the temperature of this process. This direction of increasing PF resin reactivity seems to be more promising due to the

considerable number of compounds triggering this process.

It results from a review of literature that promising results were obtained when using esters as compounds accelerating PF resin curing. Pizzi and Stephanou hypothesized that the rate of resin curing remains dependent on the dissociation constant of the organic acid forming the ester.<sup>3</sup> The lower the  $pK_a$  value of the acid, i.e. the stronger the acid, the bigger its effect on the PF resin curing process. The detailed mechanism of curing PF resin modified with esters was presented by those authors on the basis of propylene carbonate, showing that a considerable effect of this compound on the curing process of PF resin results from its high reactivity.<sup>3</sup> It acts as a catalyst, facilitating the formation of crosslinkage between individual chains of phenolic polymers, which leads to the formation of strongly crosslinked structures of PF resin.<sup>4</sup> In turn, investigations conducted by Park and Riedl showed that propylene carbonate increases the reactivity of phenolic chains, which may considerably accelerate PF resin curing.<sup>5</sup> In contrast, Conner et al. stated that the application of esters considerably accelerates the reaction of PF resin crosslinking, but these compounds may not be treated solely as catalysts, since they participate in the reaction entering the resin structure.<sup>6</sup> Also Tohmura and Higuchi did not agree with the mechanism of the reaction proposed by Pizzi and Stephanou.<sup>3,7</sup> They were of the opinion that propylene carbonate after being introduced to the alkali PF resin undergoes fast hydrolysis to propylene glycol and hydrogen carbonates. Thus, the accelerating action of propylene carbonate is the

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result of the catalytic effect of the hydrogen carbonate ion and changes in the NaOH/P ratio in the resin.<sup>7,8</sup>

It seems, based on the presented review of bibliography, that the problem of reactivation of phenolic PF resins using esters has been thoroughly investigated. However, the mechanism of the activating action of esters as modifiers of polycondensation of these resins has not been fully clarified, and there is no explicit assessment of the testing results. The cited interpretations of results did not take into consideration the possible participation of alcohol, formed as a result of alkali ester hydrolysis, in PF resin polycondensation, whereas in view of the investigations conducted by the authors of this study it results that alcohols, especially polyols, significantly accelerate this process.<sup>9</sup> It may be assumed that the participation of glycerol formed as a result of hydrolysis of its triacetate made this ester a more effective activator than ethyl acetate.<sup>3</sup> Results of a study by Park and Riedl seem to confirm this claim, as they showed that the addition of propylene carbonate to PF resin reduces the stiffness of cured resin.<sup>5</sup> In turn, Conner et al. in model tests showed that particularly the hydroxymethyl group in the ortho position of resol PF resin is especially susceptible to esterification, which in case of the acid radical of monocarboxylic acid may cause—as a result of the chain termination reaction—a reduction of the degree of crosslinking in PF resin.<sup>6</sup> This phenomenon seems to be the cause for the lowering of strength, found by Hong, in cured PF resin when salicylic acid was applied in its modification.<sup>10</sup> However, there are no studies on the effect of esters of polycarboxylic acids on the activation of PF resin.

In view of such a situation, it was advisable to undertake studies aiming at the explanation of the effect of both the type of organic acid and alcohol formed as a result of hydrolysis of the ester, occurring in the process of pressing wood-based materials, on the increase of reactivity of PF resin used in their manufacture.

## MATERIALS AND METHODS

### Applied materials

Pure phenol-formaldehyde resin, designed for use in the production of moisture resistant plywood, was applied for experimental purposes. The used PF resin was manufactured by Plastic Works "Erg" Pusków, Poland. The PF resin was characterized by the following parameters: dry matter = 45.7%, density = 1.112 g/cm<sup>3</sup>, free phenol content = 0.02%, free formaldehyde content = 0.026%, dynamic viscosity = 520 mPa s, gel time at 130°C = 156 s, and pH = 12.52.

The type of modifiers and their amounts added to PF resin were selected on the basis of a review of literature and investigations conducted on this problem by the authors of this study. The basic criterion for the selection of modifying agents was the effect of their addition on pot life of PF resin at 20°C and gel time at 130°C.

Selected esters of organic acids were divided into two groups, in terms of

- the type of the acid radical of the organic acid at the preservation of the stable alkyl group coming from alcohol. Esters selected from this group included ethyl acetate, ethyl propionate, ethyl butyrate, ethyl heptanate, and in case of esters of dicarboxylic acids—diethyl malonate and oxalate,
- the type of the alkyl group coming from alcohol, at the preservation of the stable acid radical of the organic acid. Esters selected from this group included ethyl acetate, butyl acetate, amyl acetate, and from among esters of dihydric alcohols—ethylene and propylene glycol diacetate.

Moreover, to determine the participation of individual components of esters in phenolic resin polycondensation, it was also decided to conduct tests using acetic acid and malonic acid, ethanol, butanol, pentanol (amyl alcohol), ethylene glycol, 1,3-propylene glycol, and butanediol as modifiers of PF resin. All chemicals were purchased from Sigma-Aldrich, Germany and used as received.

Selected modifiers were added to resin in the amounts of 0, 0.01, 0.025, 0.05, 0.10, and 0.15 moles per 100 g dry matter of resin (d.m.) resin. The resin and modifiers were mixed together by means of a mechanical stirrer.

### Testing pot life of modified PF resin

Pot life of modified PF resin at a temperature of 20°C was determined on the basis of measured viscosity of glue solutions with the use of a Brookfield viscosimeter type DV-II +. For this purpose, mixed glues were prepared, containing 0, 0.01, 0.025, 0.05, 0.10, and 0.15 moles of respective modifiers per 100 g d.m. resin, for which viscosity was measured initially every 4 h for 12 h, and next every 12 h. Measurements were completed after 48 h, and in case of alcohols after 72 h.

### Testing gel time of modified PF resin

Measurement of gel time of mixed glues makes it possible to assess the activation capacity of thermo-setting adhesive resins. Mixed glues were prepared by adding respective modifiers to PF resin directly

before the onset of analyses, at 0, 0.01, 0.05, and 0.15 moles per 100 g d.m. resin. Analyses of gel time were conducted at 130°C. Modified PF resin samples (1 g) were put into test tubes and maintained in a constant temperature oil-bath with stirring. A glass rod was used as a probe, determining resin viscosity by pulling it straight upward from the resin mass. As the resin sample became viscous, a resin string line was formed when the glass rod moved upward. Gel time was determined as the time when the solidified resin string line was broken.<sup>11</sup>

### Testing gelation kinetics of modified PF resin

Results of gel time testing of respective mixed glues, between 120 and 150°C at 10°C intervals, were used to determine relative activation energy of PF resin gelation. It results from a review of bibliography that this method was successfully used to determine activation energy of phenolic resins.<sup>12</sup> In the calculations, it was assumed that the curve presenting gelation in time for individual temperatures is a linear function to reach curing point. Since the reaction rate increases with an increase in temperature and the curing rate curve depending on the reciprocal of absolute temperature shows a linear dependence, thus activation energy may be calculated from the Arrhenius equation:

$$k = k_0 \exp(-E_a/RT)$$

where  $k$  = constant reaction rate at temperature  $T$  (kg/min),  $k_0$  = frequency factor (kg/min),  $E_a$  = activation energy (kJ/mol),  $R$  = gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  = absolute temperature (K).

### Determination of pH in PF resin

The effect of added modifiers on the course of PF resin polycondensation may be indirectly inferred on the basis of changes in pH occurring in it after the introduction of modifiers. The range of pH in the resin was analyzed in samples of PF resin, to which 0.15 mole of a modifier was added per 100 g d.m. Changes in pH were determined after 2, 4, and 24 h using a MERA-ELWRO type NS17 pH-meter.

### Analyses of polycondensed PF resin structure in infrared spectroscopy

Infrared (IR) spectroscopy was applied to analyze the effect of modifiers on the structure of cured PF resin.

These tests were conducted for PF resin before and after modification. The following compounds were selected as modifiers for analyses: ethanol, 1,3-propylene glycol, ethyl acetate, propylene glycol diacetate, and diethyl oxalate. Spectroscopic analyses

were conducted for samples with the following composition:

- PF resin cured at 90°C, and next at 120°C,
- PF resin with modifiers added in the amount of 0.1 mole per 100 g d.m. resin cured at 90°C, and next at 120°C.

Samples cured in the manner described above were ground in an impact mill and screened through sieves with mesh sizes of 0.25, 0.2, and 0.125 mm. Further analyses were conducted on the fraction left on a sieve with mesh size of 0.2 mm. To eliminate the effect of NaOH on the spectrum, a portion of ~ 2 g ground resin was watered with 250 mL water and left for 2 h. After that period, resin was drained, washed with water until neutral reaction was obtained, and dried at 40°C for 24 h. Prior to analyses, all samples were dried in a desiccator under vacuum over P<sub>2</sub>O<sub>5</sub>.

To prepare samples for infrared analyses, the KBr pelletizing technique was used, which is one of the best and most commonly used methods of solid sample preparation. Infrared spectra were recorded using a Mattson Infinity Fourier transform spectrophotometer (MATTSON INSTRUMENTS) at 4000–500 cm<sup>-1</sup>.

## DISCUSSION AND RESULTS

### The effect of the type and amount of modifiers on PF resin pot life

The effect of the type and amount of esters added to PF resin on its pot life at 20°C, depending on the type of the ester-forming acid, is presented in Table I. Data contained in the table showed that the bigger the amount of a modifier introduced to the PF resin and the longer the alkyl acid chain forming the ester, the bigger the reduction of apparent viscosity of prepared mixtures, caused initially by introduced esters of monocarboxylic acids. The initial decrease of viscosity in modified PF resin may be explained by the introduction to the resin of compounds with a much lower viscosity. After 8 h, i.e. after the time required for applications at commercial scale production, analyzed solutions of modified PF resin generally exhibited viscosity only slightly higher than nonmodified resin. Only in case of ethyl acetate and propionate, added in the amount of 0.1 mole/100 g d.m. resin, a considerable increase in viscosity was observed after that time. Thus, for resin modified with ethyl acetate an over 8-fold and for that modified with ethyl propionate a 5-fold increase in viscosity was recorded in relation to unmodified resin. In successive testing times, a marked effect was recorded for the addition of all analyzed esters on an increase of PF resin viscosity. The intensity of the increase in viscosity was

**TABLE I**  
**Pot Life of Ester-Modified PF Resin Depending on the Length of Carbon Chain in Acids Forming the Esters**

Kind of modifier	Amount (mole/100 g d.m. resin)	Dynamic viscosity (mPa s)				
		0 <sup>a</sup>	4	8	12	24
PF	0	530	530	530	530	535
Ethyl acetate	0.01	530	750	815	875	900
	0.05	485	910	1480	1920	2380
	0.10	400	2710	4670	5875	–
	0.01	510	670	730	845	1000
Ethyl propionate	0.05	430	835	1415	1735	1920
	0.10	390	1155	3960	5060	8460
	0.01	550	610	640	805	880
Ethyl butyrate	0.05	395	575	625	850	1050
	0.15	360	590	630	885	1185
	0.01	405	450	495	625	765
Ethyl heptanate	0.05	385	430	475	625	775
	0.15	350	420	475	645	815
	0.01	475	535	590	640	680
Diethyl malonate	0.05	460	565	600	650	785
	0.15	420	625	650	715	885

<sup>a</sup> 0, 4, 8, 12, and 24 are the measurement times (in hour).

proportional to the amount of introduced modifier and inversely proportional to the length of the ester acid radical chain, i.e. to the strength of monocarboxylic acid forming the ester. In turn, the scale of the increase in the viscosity of PF resin, recorded in successive testing times for PF resin modified with ethyl malonate, much smaller than that it would result from the strength of malonic acid, may be explained by the fact that in comparison to the previously analyzed esters it constitutes a relatively large molecule and a certain role may be played by the so-called steric hindrance.

In turn, studies on pot life of liquid PF resin, depending on the type of ester-forming alcohol, showed that also in this case initially apparent viscosity decreased, as a result of system dilution (Table II). However, in successive testing times, a slow increase of viscosity was observed in case of esters of monohydric alcohols, which was proportional to their amounts introduced to PF resin. Also, in this case, the elongation of the carbon chain of the ester-forming alcohol resulted in the increase of viscosity of modified resin being slowed down in time. The fact that the fastest increase in viscosity in time

**TABLE II**  
**Pot Life of Ester-Modified PF Resin Depending on the Length of Carbon Chain in Alcohols Forming the Esters**

Kind of modifier	Amount (mole/100 g d.m. resin)	Dynamic viscosity (mPa s)				
		0 <sup>a</sup>	4	8	12	24
PF	0	530	530	530	530	535
Ethyl acetate	0.01	530	750	815	875	900
	0.05	485	910	1480	1920	2380
	0.10	400	2710	4670	5875	–
	0.01	525	540	550	575	630
Butyl acetate	0.05	510	540	590	650	755
	0.15	440	565	680	735	965
	0.01	525	530	545	555	595
Amyl acetate	0.05	480	525	550	585	690
	0.15	450	535	630	650	765
	0.01	495	940	1065	1100	1140
Ethylene glycol diacetate	0.025	465	2120	2515	2510	2780
	0.05	445	–	–	–	–
	0.01	485	625	685	750	850
Propylene glycol diacetate	0.025	465	995	1605	2220	2325
	0.05	395	1430	5185	–	–

<sup>a</sup> 0, 4, 8, 12, and 24 are the measurement times (in hour).

**TABLE III**  
**Pot Life of Modified PF Resin Depending on the Type of Acids and Alcohols**  
**Forming Analyzed Esters**

Kind of modifier	Amount (mole/100 g d.m. resin)	Dynamic viscosity (mPa s)							
		0 <sup>a</sup>	4	8	12	24	36	48	72
PF	0	530	530	530	530	535	535	535	535
Acetic acid	0.01	640	655	675	705	850	1025	1480	1950
	0.05	850	1120	—	—	—	—	—	—
Malonic acid	0.01	655	680	710	765	975	1230	1560	2030
	0.05	920	—	—	—	—	—	—	—
Ehtanol	0.01	450	455	455	455	460	470	480	500
	0.15	375	385	385	385	390	400	410	430
Butanol	0.01	490	490	490	495	515	515	520	520
	0.15	405	405	410	415	415	430	445	465
Ethylene glycol	0.05	385	385	430	480	505	560	860	1265
	0.10	360	360	360	370	415	505	640	1120
	0.15	305	305	315	320	390	435	590	825
1,3-Propylene glycol	0.05	375	375	425	430	505	585	860	1310
	0.01	375	375	375	375	415	510	665	1140
	0.15	295	305	325	345	415	485	635	860

<sup>a</sup> 0, 4, 8, 12, and 24 are the measurement times (in hour).

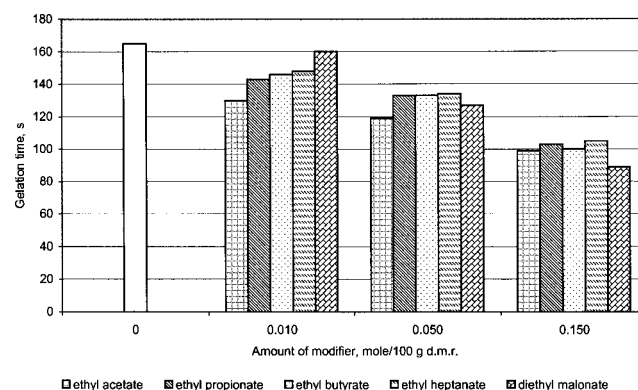
at the preservation of the stable acid radical ( $\text{CH}_3\text{COO}^-$ ) was observed for PF resin modified with ethyl acetate, while the slowest in case of modification with amyl acetate was caused by the irreversible hydrolysis to alcohol and acid, which esters undergo in the alkali medium of PF resin, with esters formed from low-molecular alcohols being most susceptible to this reaction.<sup>7,8</sup>

In turn, esters of polyols behave differently, as their addition to PF resin even in very small amounts considerably accelerates an increase in viscosity, especially in the initial testing period. Thus, when 0.025 mole ethylene and propylene glycol diacetate were introduced, after 8 h the recorded increase in viscosity in relation to unmodified resin was by 375 and 203%, respectively. It may be assumed that on the one hand it is caused by the catalytic action of acetic acid released from ester as a result of hydrolysis, while on the other hand by the possible embedding of the forming difunctional alcohol into the structure of resin, as indicated by the measurements of viscosity of PF resin modified with respective acids and alcohols (Table III). Results of these analyses showed that the presence of acids in resin intensifies its polycondensation already at room temperature to a degree preventing practical application of this modification. In turn, the introduction of difunctional alcohols to resin resulted in an almost 3-fold increase of its viscosity after 72 h. No effect was found for monohydric alcohols on viscosity of such modified PF resin, as even after 72 h, irrespective of their type and amount, viscosity of adhesive solutions increased on average by only 10%. Thus, it may be assumed that the acid formed as a result of hydrolysis catalyzes the reaction of

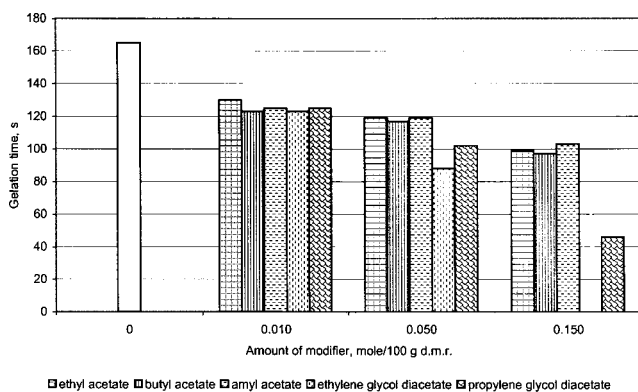
diol embedding into the resin structure, which results in such a considerable decrease of viscosity in resin modified with esters of these alcohols.

#### The effect of the type and amount of modifiers on gel time of PF resin

Testing results of the effect of PF resin modification with esters depending on the type of organic acid contained in the ester on its gel time are presented in Figure 1. It may generally be stated that all esters of monocarboxylic acids applied as additives to PF resin considerably accelerated gelation of resin, with gel time being reduced in proportion to the amount of esters added to resin. The biggest differences in gel times of modified PF resin were observed for their smallest amounts (0.01 mole/100 g d.m. resin).



**Figure 1** Gelation time of ester-modified PF resin depending on the length of carbon chain in the acid forming the ester.



**Figure 2** Gelation time of ester-modified PF resin depending on the length of carbon chain in alcohol forming the ester.

In that case, the shorter the carbon chain in the acid forming the ester, i.e. the stronger the acid, the shorter the recorded gel time. However, increasing their share in the resin to 0.15 moles considerably reduced this dependency and for that amount it was similar, irrespective of the type of acid. In turn, gel times were different when diethyl malonate, an ester of dicarboxylic acid, was applied as a modifier of PF resin. This ester, when added at 0.01 mole/100 g d.m. resin, only slightly increased reactivity of resin, whereas introduced in the amount of 0.15 mole turned out to be most effective, as gel time for such modified resin was reduced by over 45%.

A slight increase of PF resin reactivity by small amounts of diethyl malonate confirms a thesis on the double role of dicarboxylic acids in the gelation of PF resin, on the one hand as a catalyst and on the other as a modifier partly embedded in its structure. It seems that it is at its small amounts that the formation of ester bonds with resin to a certain degree eliminates its catalytic action.

Also, in case of PF resin modification with esters, depending on the type of ester-forming alcohol, resin reactivity increases with an increase in their amounts added to resin (Fig. 2). However, in case of esters of monohydric alcohols, it was observed that their action does not depend on the length of the alcohol carbon chain. For all analyzed modifiers added at 0.01 mole, gel time was shortened by a little over 20%. Also comparative studies on the effect of monohydric alcohols on gel time of PF resin did not show significant differences depending on the length of their carbon chain (Fig. 3). They only confirmed a markedly inhibitory effect of this type of alcohols on the process of their gelation.

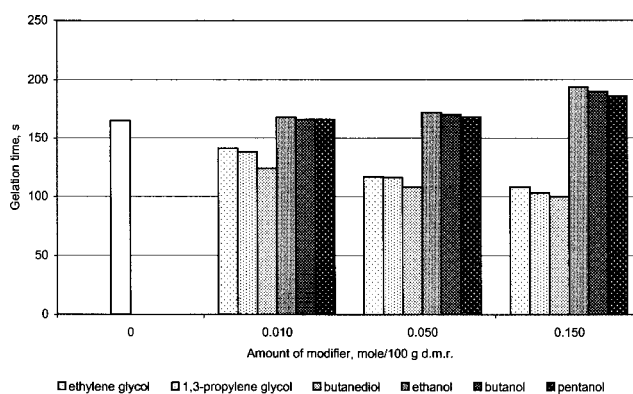
In turn, esters of diols intensively increased the reactivity of PF resin (Fig. 2). Thus, while gel times of solutions of resin modified with esters of monohydric alcohols introduced to resin at 0.15 mole/100 g d.m. resin were shortened by ~ 40%, ethylene glycol

diacetate introduced in identical amounts caused immediate gelation of resin and propylene glycol diacetate shortened its gel time by over 70%.

To determine to what extent it is caused by diols formed as a result of ester hydrolysis, the effect of alcohols alone on the reactivity of PF resin was investigated (Fig. 3). It turned out that diols accelerate resin gelation in a comparable manner to esters of monohydric alcohols (Fig. 2), at a more intensive shortening of gelation time found for alcohols with longer carbon chains. Gelation time of PF resin under the influence of butanediol introduced at 0.15 mole/100 g d.m. resin was 65 s shorter than that of unmodified resin. These observations, in combination with the fact that resin cured using only diols is considerably more elastic than resin cured with analyzed esters, suggest that in this case reactivity of PF resin is increased as a result of polycondensation, e.g. between hydroxymethylene groups of resin and alcohols, which results in the embedding of methylene bridges  $(-\text{CH}_2-)_n$ , responsible for increased elasticity of PF resin, into its structure.

#### The effect of PF resin modification on activation energy of gelation

The effect of the type and amount of modifiers used in this study, introduced to PF resin on relative activation energy of the process of its gelation, is presented in Tables IV–VI. It results from the data presented above that esters with different lengths of the carbon chain in their acid radical, introduced at 0.01 mole/100 g d.m. resin, caused a reduction of activation energy on average by 17% (Table IV). With an increase of their share in the mixed glue, its value was further reduced; however, changes found for individual esters were not big, as—except for ethyl acetate—they did not exceed 7%. However, calculated values of activation energy indicate a stronger action of esters containing a shorter carbon chain in the acid radical, i.e. those formed from a stronger of the acids.



**Figure 3** Gelation time of modified PF resin depending on the type of alcohols forming analyzed esters.

**TABLE IV**  
Activation Energy of Gelation Process of Ester-Modified PF Resin Depending on the Length of Carbon Chain in Acids Forming the Esters

Kind of modifier	Amount (mole/100 g d.m. resin)	Activation energy (kJ/mole)	ln $k_0$
PF	0	68.1	24.95
Ethyl acetate	0.010	56.1	23.12
	0.050	55.1	22.71
	0.150	49.5	20.40
Ethyl propionate	0.010	57.2	23.57
	0.050	56.2	23.16
	0.150	53.2	21.93
Ethyl butyrate	0.010	57.3	23.62
	0.050	56.4	23.24
	0.150	53.8	22.17
Ethyl heptanate	0.010	57.6	23.73
	0.050	56.4	23.24
	0.150	54.5	22.46

Results of studies on activation energy of PF resin modified with esters with different lengths of the carbon chain in the alcohol group confirm this fact (Table V). Tests showed that in case of esters of monohydric alcohols the effect of acetic acid forming the ester, and especially its dissociation constant, was more significant than the type of alcohol group. Introduction of this type of esters resulted in only slight changes in relative activation energy. In contrast, esters of diols affected activation energy of PF resin gelation. In this respect, tests showed that the introduction of ethylene glycol diacetate, already at its smallest amount, reduced the value of activation energy from 68 to 48 kJ/moles, i.e. by almost 30%, with a further drop by as much as 62% after its maximum amount was added.

**TABLE V**  
Activation Energy of Gelation Process of Ester-Modified PF Resin Depending on the Length of Carbon Chain in Alcohols Forming the Esters

Kind of modifier	Amount (mole/100 g d.m. resin)	Activation energy (kJ/mole)	ln $k_0$
PF	0	68.1	24.95
Ethyl acetate	0.010	56.1	23.12
	0.050	55.1	22.71
	0.150	49.5	20.40
Butyl acetate	0.010	55.8	23.00
	0.050	55.1	22.71
	0.150	50.1	20.65
Amyl acetate	0.010	55.8	23.05
	0.050	55.1	22.71
	0.150	53.2	21.93
Ethylene glycol diacetate	0.010	48.0	19.52
	0.050	37.0	17.81
	0.100	25.5	15.25

**TABLE VI**  
Activation Energy of Gelation Process of PF Resin Modified with Diols

Kind of modifier	Amount (mole/100 g d.m. resin)	Activation energy (kJ/mole)	ln $k_0$
PF	0	68.1	24.95
Ethylene glycol	0.025	59.9	23.57
	0.050	55.7	22.41
	0.150	51.7	21.38
1,3-Propylene glycol	0.025	54.1	21.83
	0.050	53.8	21.79
	0.150	51.1	21.10
Butanediol	0.025	57.4	22.86
	0.050	54.6	22.12
	0.150	52.8	21.66

Such behavior of diols indicates their active participation in the process of PF resin curing, competitive in relation to reactions of chemical adhesion of resin to wood, which is also confirmed by the results of studies on the effect of diols on gelation energy of PF resin (Table VI). Tests showed that all analyzed alcohols considerably reduced its activation energy. With an increase in their amounts it was further reduced; however, irrespective of the length of the carbon chain it generally remained similar.

#### The effect of applied modifiers on pH of liquid PF resin

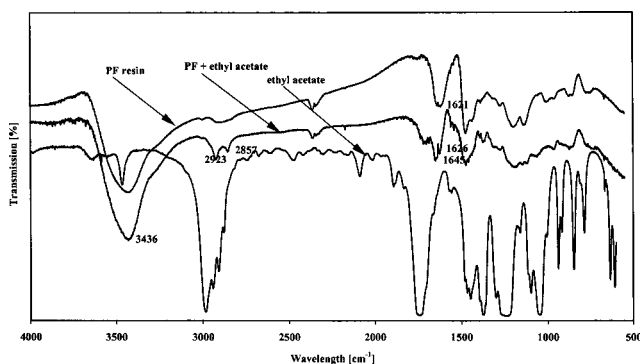
It results from the performed tests that modifiers introduced to PF resin initially do not have a significant effect on pH values of liquid resin (Table VII). In successive measurement times, a reduction was observed in pH values of solutions of resin modified with acetic acid esters, with the effect of esters of monohydric alcohols on pH being the more intensive, the shorter the chain of the ester-forming alco-

**TABLE VII**  
Values of pH of Modified Liquid PF Resin

Kind of modifier	pH			
	0 <sup>a</sup>	2	4	24
PF	11.65 <sup>b</sup>	11.65	11.65	11.65
Ethyl acetate	11.60	11.07	11.02	11.00
Butyl acetate	11.62	11.47	11.39	11.29
Amyl acetate	11.63	11.55	11.48	11.43
Ethylene glycol diacetate	11.45	10.35	10.18	10.12
Propylene glycol diacetate	11.50	11.45	10.25	10.12
Ethyl propionate	11.56	11.21	11.18	11.09
Ethyl butyrate	11.60	11.47	11.36	11.26
Ethyl heptanate	11.62	11.66	11.54	11.47
Diethyl malonate	11.51	11.30	11.24	11.01

<sup>a</sup> 0, 2, 4, and 24 are the measurement times (in hour).

<sup>b</sup> The actual value of pH of liquid resin measured before testing, stated by the manufacturer was 12.75.

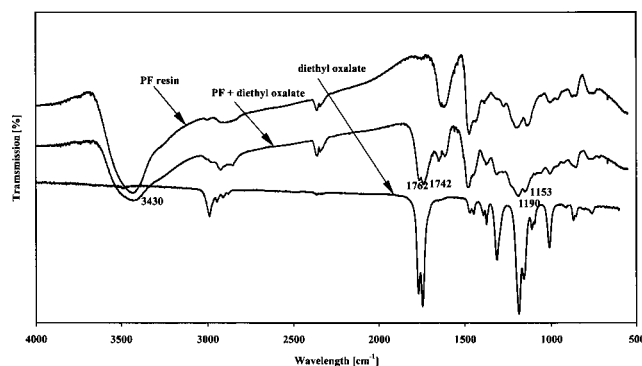


**Figure 4** IR spectra of cured PF resin modified with ethyl acetate.

hol. The lowest pH for this group after 24 h was reported for esters of dihydric alcohols. For these compounds, values of pH were reduced even to 10.12. This is probably the effect of the introduction to the system of a proportionally bigger number of  $\text{CH}_3\text{COO}^-$  ions than in case of esters of monohydric alcohols. In turn, changes in pH of PF resin solutions under the influence of esters of organic acids depending on the type of the acid radical are the bigger, the shorter the carbon chain of the ester-forming acid, i.e. the stronger the acid. However, the low value of pH for the solution of resin modified with diethyl malonate confirms its stronger action on pot life and gel time of PF resin (Table I, Fig. 2).

#### FTIR spectral analysis of cured PF resin

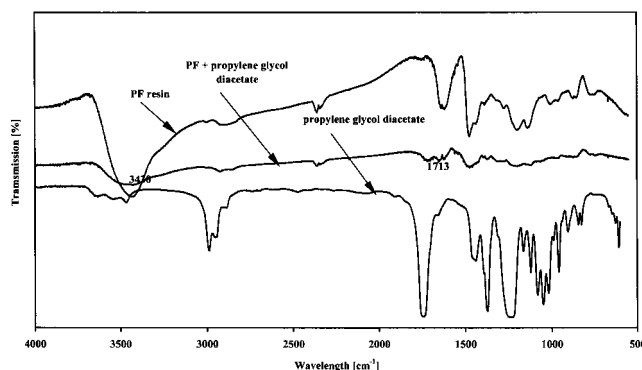
Spectral analysis of PF resin modified with ethyl acetate showed that for such modified resin the intensity of bands changed in relation to those of unmodified resin at wavelengths of 2857 and 2923  $\text{cm}^{-1}$  ascribed to the absorption of CH groups (Fig. 4). Adopting the band of vibrations of the aromatic ring at a wavelength of 1476  $\text{cm}^{-1}$  as the internal standard, the intensity of relative absorption of stretching vibrations of these bonds increased almost two-fold. It may be assumed that the increase of band intensities at these wavelengths resulted from the embedding of ester into the structure of resin, especially as it was accompanied by an increase in relative absorption (by  $\sim 40\%$ ) in the region of vibrations of the hydroxyl group at 3436  $\text{cm}^{-1}$ . Significant changes were also observed in the shape of the band at 1645–1620  $\text{cm}^{-1}$ . In this area, in the spectrum of PF resin, there was only one band at a wavelength of 1621  $\text{cm}^{-1}$ , which after modification with ester was separated into two bands at 1626 and 1645  $\text{cm}^{-1}$ . While the band at a wavelength of 1626  $\text{cm}^{-1}$  is ascribed to the shifted band of aromatic ring vibrations, the band appearing nearby at 1645  $\text{cm}^{-1}$  in modified resin should be ascribed to vibrations of compressed carbonyl  $\text{C}=\text{O}$ , introduced by the ester.



**Figure 5** IR spectra of cured PF resin modified with diethyl oxalate.

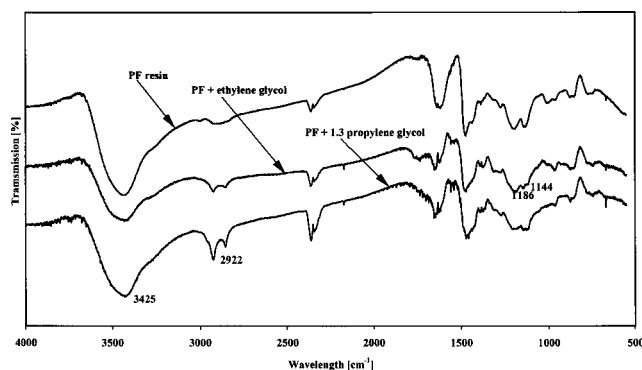
It results from spectra shown in successive figures that also esters of dicarboxylic acids and diols may become embedded into the structure of resin (Figs. 5 and 6). This is indicated by the new, very strong bands of absorption appearing in the IR spectrum of resin modified with diethyl oxalate at wavelengths of 1742 and 1762  $\text{cm}^{-1}$  (Fig. 5). They are bands, which are found in the standard and are ascribed to vibrations of the carbonyl group  $\text{C}=\text{O}$  of the ester. Significant changes were also observed in the intensity of bands at wavelengths of 1190 and 1153  $\text{cm}^{-1}$ , ascribed to vibrations of the  $\text{C}-\text{O}$  bond in the ester group. Increasing the intensity of these bands by  $\sim 40\%$  in relation to PF resin shows a reaction of reactive functional groups of PF resin with functional groups of esters. However, in contrast to resin modified with ethyl acetate, the intensity of the band ascribed to vibrations of the OH groups at 3430  $\text{cm}^{-1}$  decreased.

The trend observed for changes in case of esters of diols was similar, although the changes were less marked. In the spectrum of resin modified with propylene diacetate, presented in Figure 6, a decrease was observed in the intensity of relative absorption of OH groups at 3430  $\text{cm}^{-1}$ , by  $\sim 19\%$ , whereas for diethyl oxalate it was as much as 50% (Fig. 5). In



**Figure 6** IR spectra of cured PF resin modified with propylene glycol diacetate.





**Figure 7** IR spectra of cured PF resin modified with 1,3-propylene glycol.

turn, in the range of vibrations of the carbonyl group  $C=O$  at a wavelength of  $1713\text{ cm}^{-1}$ , the intensity of absorption increased, although it was not as big as in case of resin modified with diethyl oxalate. A detailed interpretation of the spectrum at  $1000\text{--}1300\text{ cm}^{-1}$  is connected with huge difficulties. Changes in the intensity of absorption for individual bands in this area may result both from the ester embedded or converted with resin and the overlapping of absorption bands of hydroxymethylene and ether groups, and practically prevent an objective assessment of occurring changes. In turn, the next figure (Fig. 7) presents IR spectra of phenolic resin modified with alcohols. A comparative analysis of these spectra showed that in the range of stretching vibrations of OH bonds at a wavelength of  $3425\text{ cm}^{-1}$ , in case of PF resin modified both with ethanol and 1,3-propylene glycol the relative intensity of absorption decreased, being much bigger for ethanol, as it amounted to  $\sim 30\%$ . In turn, the intensity of stretching vibrations of CH bonds at  $2922\text{ cm}^{-1}$  increased markedly, especially in the spectrum of resin modified with 1,3-propylene glycol, which indicated the conversion of both alcohols with PF resin. Certain changes were also observed in spectra of PF resin modified with alcohols at  $1375\text{--}1465\text{ cm}^{-1}$ , which may be ascribed to deformation vibrations of the CH group, the alkyl group embedded in the resin.

## CONCLUSIONS

1. The introduction of organic acid esters to liquid PF resin, with the exception of the ethyl acetate and propionate, does not have a significant effect on its pot life at  $20^\circ\text{C}$ , which is of considerable importance in case of its applications at large-scale production.
2. All types of modifiers introduced to resin caused an increase in its reactivity, manifested in a shortening of gel time and a reduction of activation energy of this process. An increase in reactivity of PF resin is inversely proportional to the length of the ester acid radical chain. In contrast, no effect was found of the type of monohydric alcohol contained in the ester on the reactivity of resin. The highest reactivity was observed for PF resin modified with esters of dihydric alcohols.
3. Results of FTIR analyses of polycondensed modified PF resin show that products of alkali hydrolysis of esters not only catalyze the cross-linking process, but also become embedded in its structure. Especially, the participation of alcohols in crosslinking of PF resin makes it possible to explain the highest effectiveness of polyol esters in reactivation of PF resin.

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