

## EFFECT OF ALKYLRESORCINOLS ON CURING BEHAVIOUR OF PHENOL-FORMALDEHYDE RESOL RESIN

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Thermal behaviour of cure-accelerated phenol-formaldehyde (PF) resins was studied using the addition of commercial mixture of water soluble oil shale alkylresorcinols (AR) to PF resin, 5-MR being as model compound. The acceleration effect of AR is based on the promotion of condensation of resin methylol groups and subsequent reaction of released formaldehyde with AR. Commercial PF resins SFŽ-3013VL and SFŽ-3014 from the Estonian factory VKG Resins have been used. The chemical structure of resins was characterised by <sup>13</sup>C NMR spectroscopy. TG-DTA analysis was carried out using labsys<sup>TM</sup> instrument Setaram. By TG-DTA measurements, the shift of exothermic and endothermic peaks and the changes of mass loss rate in the ranges of 1.5–10 g AR/100 g PF resin were studied. The effect of AR on the curing behaviour of PF resins was also followed by gel time.

Testing of the plywood when using PF resin with 5 mass% of AR shows that the press time could be reduced by about 15%.

**Keywords:** alkylresorcinols, <sup>13</sup>C NMR spectroscopy, curing, gel time, phenol-formaldehyde resins, TG-DTA analysis

### Introduction

Alkaline phenol-formaldehyde (PF) resins are currently used as exterior wood adhesives for bonded wood products such as plywood, fibreboard and oriented strand board [1, 2]. The main drawback preventing wider use of PF resins in the manufacture of wood composite panels is its relatively slow cure rate. Many attempts have been made to cure PF resins faster which would allow the wood to be bonded at higher moisture contents and at lower press temperatures. Faster curing would also result in lower emissions of volatile organic compounds during the manufacture of bonded wood composites [3]. Different catalysts, additives, or modified resin formulations have been proposed as PF resin cure accelerators [3–8]. Among a variety of investigations, special attention is paid to the accelerating effect of propylene carbonate [3–6].

Several mechanisms have been proposed to explain the accelerated cure. According to [5], average densities of crosslinking of the final resin networks are varied for different accelerating additives. Some additives used behave as a true accelerators of PF cure by the hydrogen-bonding based intermediate activated complexes. The other accelerators might well present both a similar accelerating mechanism, as well as being an active part of the process of crosslinking leading to a tighter final network [3].

As accelerator of resol phenol resin for the production of weather-resistant plywood, resorcinol or resorcinol resin has been used [1, 2, 9]. This method is based on the grafting of a reactive resorcinol into phenol resin by coreaction of resole methylol groups with free positions of resorcinol and as a result, the durable bonds in resin structure during resin curing is formed. In the commercial phenol-resorcinol-formaldehyde adhesives the mass of resorcinol in liquid resin is of the order 16 to 18% [2, 9]. The development of special applications which are used to obtain resins of 8 to 9% resorcinol content [2] have proved to be a step forward. Phenol-formaldehyde-tannin (PFT) resins have been developed with promising results in plywood manufacture [10–12]. The kinetic calculations show that polyphenol-containing resol PFT resins cure faster than the commercial PF resins [10].

Many different analytical techniques have been examined to monitor the cure of resols, such as thermomechanical analysis [5, 13], dynamic mechanical analysis (DMA) [9, 14–16], viscoelastic analysis, dielectric analysis [17]. Differential scanning calorimetry (DSC) has been extensively used to characterise the cure process of PF resins [4, 15, 17–23] both by isothermal and dynamic method [20, 22]. DSC and DMA techniques were combined to identify chemical cure and mechanical cure [9, 14, 15]. Although some authors [e. g., 24] indicate that the use of DSC for resols PF resin sometimes provides only qualitative information, this method has been effective in estab-

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lishing cure parameters for optimum cure. The DSC measurements performed in sealed pressure pans and in open pans have been compared [21] which indicated that open systems can be analysed by DSC.

In the present work, the accelerating effect of alkylresorcinols on the curing behavior of resol phenolic resin was studied. The replacement of high-cost resorcinol in phenol-resorcinol-formaldehyde resins by alternative reagent of Estonian origin looks as promising. To follow the thermal behaviour of cure-accelerated PF resins, TG-DTA method was applied which makes it possible to simultaneously follow the heat flow and mass loss of the sample during curing.

## Experimental

### Materials

Resol resins were obtained in reaction of phenol with an excess of formaldehyde in strongly alkaline water solution. Depending on the purpose of use, the resins mostly differ in viscosity, content of alkali, curing rate and shelf life. Synthesis conditions guarantee very low content of residual toxic phenol and formaldehyde.

The commercial resins SFŽ-3013VL and SFŽ-3014, labelled as PF1 and PF2 were synthesised with a formaldehyde to phenol mole ratio of 2.4 to obtain resins with viscosities suitable for veneering and flakeboard adhesives. The resin manufacturing was carried out in batches of about 5 tons, in automatically controlled reactors of capacities of about 6 cubic meters. Resins were prepared according to the following procedure: Phenol was charged into the reactor and NaOH as 49% solution and 45% formalin were added. The synthesis was performed in two stages – methylation reaction for 90 min at 44–60°C and condensation reaction for 40 to 60 min at reflux (98–100°C) to proper viscosity. After that additional amount of NaOH was added and the reaction mixture was cooled to 40°C. Resin PF1 is of a higher alkalinity than PF2, and substantially higher viscosity of PF1 was attained by evaporation of water. Batches from the same formula are close to one another in both structure and thermal behaviour. Advancement of condensation of both resins during storage is retarded because of high alkalinity.

In Table 1, the standard characteristics of the resins used in present study are presented.

Considering high amount of methylol groups in the studied resins, 2- and 4-hydroxymethyl phenol (*o*-MP and *p*-MP) were used as model compounds for studying the mechanism responsible for the acceleration. A reagent-grade *o*-MP was used after recrystallisation from benzene/ethyl-alcohol solution ( $T_m$  87°C). *p*-MP was synthesised by reduction of

**Table 1** Standard analysis of SFŽ-3013VL and SFŽ-3014

Characteristics	PF1 (SFŽ-3013VL)	PF2 (SFŽ-3014)
Dry solids, 105°C, 3 h/%	47.9	47.3
pH, 25°C	12.4	12.0
Viscosity 25°C/mPa s	404	96
Gel time, 100°C s <sup>-1</sup>	36	43
Free phenol/%	0.04	0.04
Free formaldehyde/%	traces	traces

para hydroxybenzaldehyde and recrystallised from benzene/ethyl alcohol mixture ( $T_m$  120°C).

The mixture of water soluble oil shale alkylresorcinols named as Honeyol Premium and labelled as AR, was added as an accelerating agent for PF resin curing. On the basis of chromatographic analysis, the content of the main components of the mixture is following:

5-methylresorcinol	69.8%
5-ethylresorcinol	8.3%
4,5-dimethylresorcinol	5.4%
2, 5-dimethylresorcinol	5.3%
other alkylresorcinols	11.2%

As a model component of alkylresorcinols, a reagent grade 5-methylresorcinol (Merck, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>·H<sub>2</sub>O,  $T_m$  58–61°C) labelled as 5-MR was used in this study.

### Methods

The chemical structure of resins and mixture of alkylresorcinols were characterised by high resolution <sup>13</sup>C NMR spectroscopy. A Bruker AMX500 NMR spectrometer with <sup>13</sup>C frequency at 125.77 MHz at 25°C from CD<sub>3</sub>OD solutions by 5 mm <sup>13</sup>C-<sup>1</sup>H dual probehead was used. Spectra were accumulated (22000–25000 scans) into 32 K data point and processed using exponential multiplication with 2 Hz line broadening into 128 K spectra. On the basis of peak assignments and integral intensities in <sup>13</sup>C NMR spectra, the distribution of bound F between different methylene-containing chemical groups in the region of 25–100 ppm was determined. Region of aromatic carbons (C2–C6) at 115–135 ppm shows the content of free aromatic positions and occupied aromatic positions in different substitution models. The region of carbon bearing phenolic hydroxyl (C1) at 150–160 ppm provides additional information about the content of differently substituted compounds.

TG-DTA measurements were carried out by labsys<sup>TM</sup> instrument Setaram with the heating rate of 5°C min<sup>-1</sup> and measuring sensitivity 50 μV. The temperature range scanned was from 20 to 450°C, and the measurements were recorded in nitrogen flow

(40 mL min<sup>-1</sup>), the mass of the samples being 10 to 20 mg. The TG-DTA test was carried out with an open standard platinum crucible (100 μL). Temperature calibration was performed with indium. The heat flow on DTA curves was expressed in μV s mg<sup>-1</sup>. Enthalphy of the curing reaction in these resins is not determinable, as the characteristic exoeffect in DTA curve is partly overlapped by large water evaporation endotherm. The area under endotherm characterizes water evaporation from condensation reaction as well as from the water content in the initial resin. In this study, the peak temperatures and mass loss values are the main apparent indices to characterize the curing system.

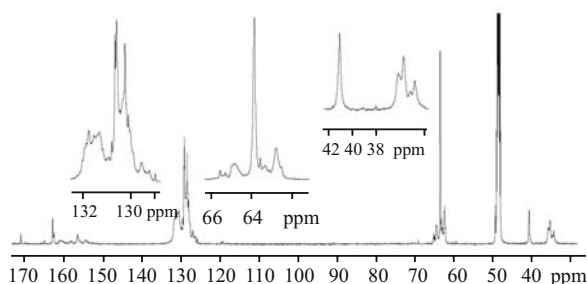
The accelerating effect of the water soluble oil shale alkylresorcinol mixture was tested on the laboratory-made plywood with glue mixture consisting of 100 part of PF1 and 5 part of AR. The 11-layer samples with dimensions of 20·20 cm from plies of thickness 1.35 mm were made at press temperature of 130°C and pressure of 1.5 MPa. The consumption of adhesive in coating was 150–160 g m<sup>-2</sup>.

## Results and discussion

The reaction between phenol and formaldehyde (F) in the alkaline range is based in two types of reactions: addition of hydroxymethyl groups to the ortho and para free positions of phenolic ring and condensation between hydroxymethyl group and free position in phenol producing methylene groups or between two hydroxymethyl groups forming dimethylene ether bonds.

In Fig. 1, the <sup>13</sup>C NMR spectrum of commercial resin PF1 is shown.

The <sup>13</sup>C NMR spectrum is a typical one for low molar mass resol resin. The signals are assigned on the basis of data in [25–30] and by means of model compounds. From the integral intensities of the peaks in the region of bound formaldehyde (30–95 ppm), it follows that approximately 65 mol% of initial formaldehyde is bonded in different methylol-containing compounds and 35 mol% in methylene groups.



**Fig. 1** <sup>13</sup>C NMR spectrum of SFZ-3013VL (PF1) in CD<sub>3</sub>OD, 20000 scans

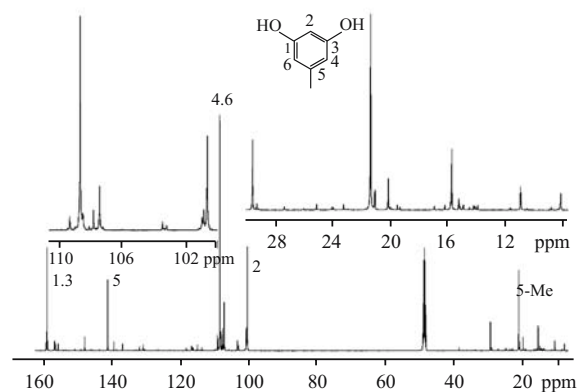
Methylol groups are present predominantly in ortho positions (62.5–65.5 ppm) due to the higher reactivity of para methylol groups (66 ppm) in the polycondensation reaction. During resin synthesis, in conditions of great excess of formaldehyde (F/P>2.1) in strongly alkaline conditions, mainly ortho-para' diphenyl-methanes by signals at 34–37 ppm were formed (~67 mol% of methylene groups), and para-para' diphenylmethanes by signal at 41–42 ppm were formed to a lesser extent (~32 mol%). Only in traces, ortho-ortho' groups at 31 ppm were detected. From the spectrum it is seen that the content of dimethylene ethers (69–71 ppm), hemiformals (83–95 ppm) and free reactive aromatic ortho and para positions (116 and 121 ppm, respectively) is very low in synthesised resin. The different signals in methylene and methylol regions are responsible for the occupation of aromatic positions of phenol in various substitution patterns (127–133 ppm).

On the basis of the <sup>13</sup>C NMR spectrum it can be concluded that the full substitution of reactive aromatic positions of phenol, especially by methylol groups, determines the mechanism of resin cure.

The synthesis of PF2 was performed to the same condensation degree as PF1 and the <sup>13</sup>C NMR spectrum of PF2 reveals the similar content of functional groups, total of methylene groups being as 36 mol% and methylol groups as 64 mol%.

The <sup>13</sup>C NMR spectrum (Fig. 2) illustrates the structure of the complicated mixture of alkylresorcinols, the chemical shifts for substituting alkyl-groups being situated in the region of 8–30 ppm.

The assignment of <sup>13</sup>C chemical shifts in spectrum of Honeyol Premium occurs in accordance with the predominant component 5-MR (CH<sub>3</sub> 21.5 ppm; C1,3 (OH) 159 ppm; C2 101 ppm; C4,6 108.5 ppm; C5 141 ppm). The resolution in CH<sub>3</sub> region depends on substitution position of CH<sub>3</sub> group in aromatic ring. By the calculated increments for OH and CH<sub>3</sub>

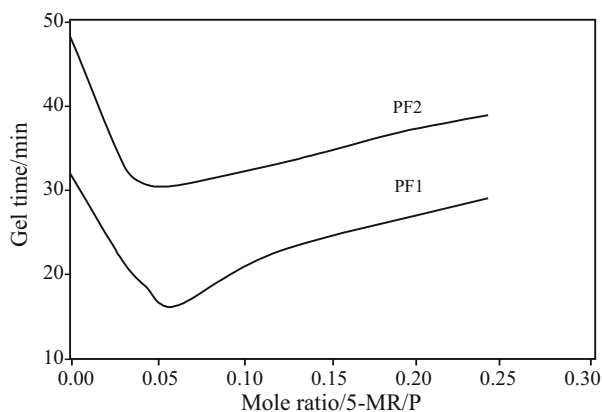


**Fig. 2** <sup>13</sup>C NMR spectrum of Honeyol Premium (AR) in CD<sub>3</sub>OD, 22000 scans

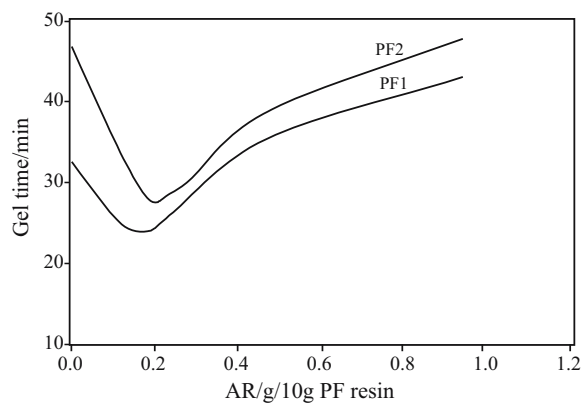
groups, the signal at 8.2 ppm belongs to 2-methyl group (mainly to 2,5-DMR) and signal at 11.0 ppm to 4-methyl group (mainly to 4,5-DMR). 5-ethylresorcinol can be interpreted by two signals ( $\text{CH}_3$  15.8 ppm;  $\text{CH}_2$  29.7 ppm).

The thermosetting curing process of PF resol resins is a continuation of the electrophilic aromatic substitution reactions that proceeded in the resin synthesis stage. The completion of curing leads to a fully methylene group-bonded phenolic polymer system with a methylene group/phenol mole ratio of 1.5 [29]. Actually the ratio is lower, due to steric restrictions. Besides that, in resol wood adhesives with  $F/P > 2.1$ , the remaining in alkali-promoted curing process formaldehyde is bound in functionalities not increasing its emission.

Chemical cure of resol PF resins as thermosetting polymers is associated with significant changes in their physical properties such as gelation and vitrification. As the condensation of resin commences, molar mass advancement occurs, leading to a gel state which is no longer soluble in water. While the water is evaporated during heating, the flexible phenolic intermediate becomes rigid and crosslinked [1].



**Fig. 3** Gel time at 100°C for PF1 and PF2 cured with 5-methylresorcinol (5-MR)

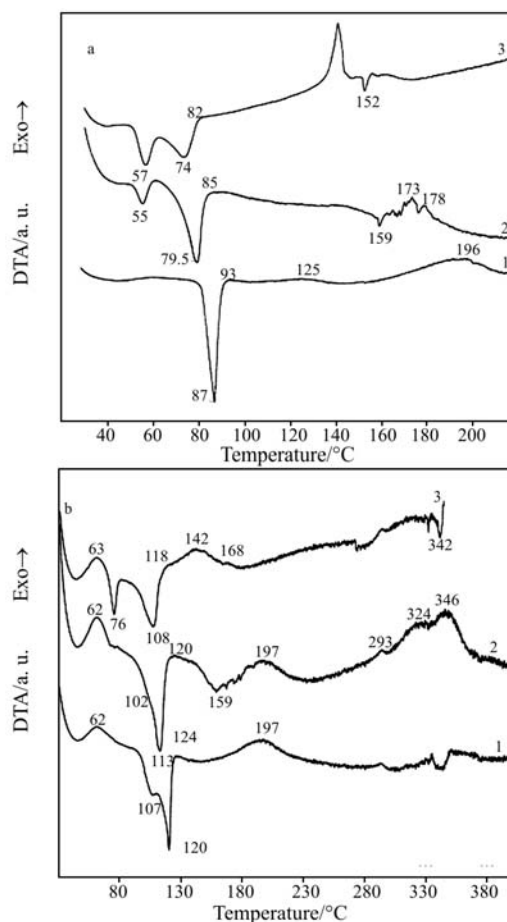


**Fig. 4** Gel time at 100°C for PF1 and PF2 cured with Honeyol Premium (AR)

Figures 3 and 4 present the gel time variation during curing at 100°C for the various PF resin formulas. The acceleration effect of two different additives – 5-methylresorcinol and mixture of alkylresorcinols on gel time values is compared.

As it can be seen from figures, the shape of gel time curves is similar in both cases for PF1 and PF2. If 5-MR was added to phenolic resin, the gel time decreased first to a minimum value at the mole ratio of 5-MR/P between 0.05 to 0.1, then increased with an increase in the content of 5-MR (Fig. 3). The addition of the commercial alkylresorcinol mixture containing about 70 mass% of 5-MR follows the same trend. In Fig. 4, the dependence of gel time on content of reagents is expressed in mass units as it is common in technological procedures. These small amounts of alkylresorcinols decreasing the gel time were taken as basis for further study.

The high content of methylol groups in PF resins gives the favourable conditions for reactions with alkylresorcinols. 5-MR and AR are very reactive towards formaldehyde accelerating the formation of *o,o*-dihydroxydibenzylethers with formaldehyde re-



**Fig. 5** DTA curves of a – *o*-MP and b – *p*-MP curing with 5-MR, 5°C min<sup>-1</sup>: 1 – methylolphenol (MP) alone; 2 – mole ratio of 5-MR/MP=0.1/1; 3 – 5-MR/MP=0.25/1

lease from dimethylene ethers which expresses in lower gel time of resins. The shape of gel time curves with the minimum is caused by the decrease of crosslinking groups of phenolic components occurring at the same time, which retards the gelling reactions.

For better understanding the results of curing behaviour of resol resin at higher temperature and an influence of accelerating compounds, the behaviour of *o*-MP and *p*-MP were examined with and without additive (Figs 5a and b). The interpretation of DTA curves is based on our earlier investigations in the field of phenol-resorcinol-formaldehyde resins [24, 30] and theoretical considerations.

The shape of the melting endotherms is different for *o*-MP and *p*-MP because of formation of some amount of *p,p'*-dimethylene ether before complete melting of *p*-MP (Fig. 5b, curve 1). In this case, the ether formation is expressed in exotherm with a peak maximum at 62°C, and the melting endotherm splits with the appearing of additional peak at 107°C. The slower formation of more stable *o,o'*-dimethylene ether occurs mainly after melting of *o*-MP ( $T_m$  87°C) in a wider temperature range (Fig. 5a, curve 1). The broad exotherm with a peak maximum at 196°C in both cases arises due to the formation of *o,p'*-methylenes because of the splitting of dimethylene ethers by free aromatic positions. As the amount of previously formed *o,o'*-ethers is higher than *p,p'*-ethers, the exoeffect is more expressed in case of *o*-MP (Fig. 5a). The quantitative formation of methylene functionalities is a final result of thermal curing of both methylolphenols. The evaporation of a small amount of water which is formed in condensation reactions occurs in a wide temperature range without the characteristic peak. The peaks from 293°C are connected with complicated rearrangements and degradation of resin.

The addition of 5-MR in mole ratios of 5-MR/methylolphenol=0.1/1 and 0.25/1 changes the shape of curing curves essentially. As it can be seen in Figs 5a and b (curves 2 and 3), when adding 5-MR to the methylolphenols the melting exotherms shift to lower temperatures. Before melting of methylol compounds, an additional endotherm due to melting of 5-MR·H<sub>2</sub>O in the ranges of 55–57°C is revealed. This does not disturb the formation of some amount of *p,p'*-dimethylene ether before the entire melting of *p*-MP (Fig. 5b, curves 2 and 3). The slow formation of *o,o'*-dimethylene ethers is not revealed in DTA curves but their accelerated transition to methylenes with increased amount of 5-MR is observed (Fig. 5a, curves 2 and 3). As in case of 5-MR/*p*-MP there are more reaction possibilities of different mechanism, the methylene formation expressed in nonresolved reaction exotherm with a peak maximum at 142°C. The rate of methylene formation in the presence of 5-MR

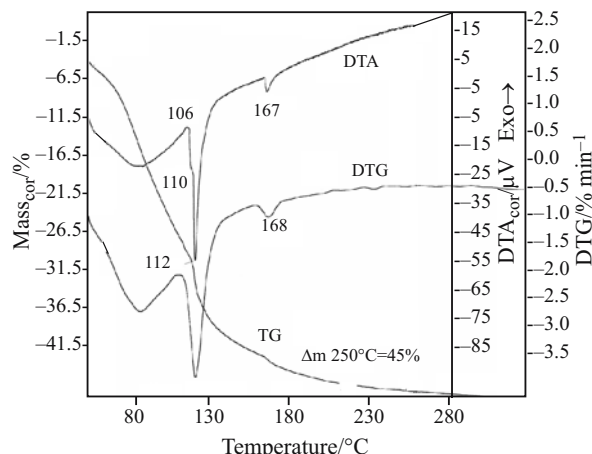


Fig. 6 TG/DTG curves of PF1 curing, 5°C min<sup>-1</sup>

is presumably quite similar for both methylolphenols whereas in phenolic mixtures the differences in component reactivities level [31].

In Fig. 6, the curing curve for PF1 in temperature ranges of 30 to 350°C is presented.

As the resin PF1 contains about 50 mass% of water depending on synthesis procedure, the DTA curve shows a sharp endothermic peak of water evaporation with peak maximum at 112°C. The left-sided shoulder at 110°C can be attributed to the evaporation of water, released in condensation reactions of methylolphenols of resin. These two peaks are better differentiated in thermal curves of PF2 (Fig. 7) in which the water content is even higher. Due to diffusional barriers arising during the first condensation reactions, the water evaporation from resins is not complete, constituting 30 mass% in case of PF1 and 32 mass% in case of PF2 at 130°C. In curing process of resin, containing about 62 mol% of F in ortho methylol groups, the first reaction is the formation of *o,o'*-dimethylene ethers. In case of lack of reactions with participation of free aromatic sites in alkali-promoted curing, the reaction of ether formation significantly accelerates and is revealed in DTA curve as exotherm with a peak maximum at 106°C. The further reactions with *o,o'*-dimethylene ethers proceed slowly and do not reveal exothermic peaks in DTA curves. As the para functionalities were exhausted in the resin synthesis, the formation of *o,o'*-methylenes can only occur by the formaldehyde splitting off. The released formaldehyde is bonded mainly in hemiformals. The complicated equilibrium between ether, methylol and hemiformal structures is formed, and in case of sufficient activation energy, *o,o'*-methylene formation occurs. The unreacted functionalities are stabilised by high content of alkali in both resins. The small water evaporation endotherm with a peak minimum at 167°C (Fig. 6) or 158°C (Fig. 7) is the result of additional polycondensation reactions.

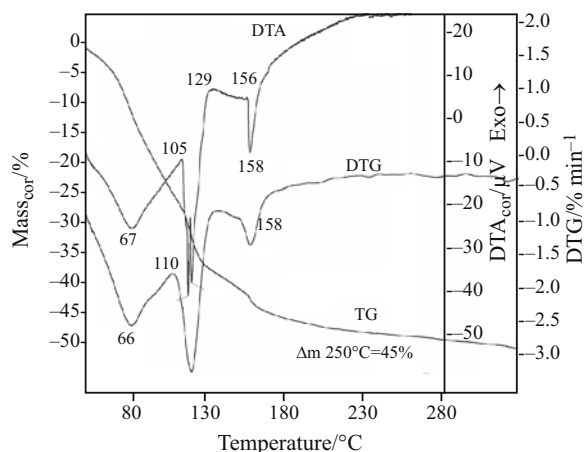


Fig. 7 TG-DTA curve of PF2 curing,  $5^{\circ}\text{C min}^{-1}$

The precise location of the exothermic effects at 106 or 105°C (Figs 6 and 7) is somewhat problematical due to immediately following overlapping large water evaporation endotherm.

Previous researches have shown that the DSC curves for phenolic resins can have a single or two exothermic peaks under certain conditions [e. g., 15, 18, 32]. Different interpretations of the nature of exothermic peaks are presented, depending on the pH and mole ratio of F/P during resin synthesis which leads to the formation of various structures. In [18], the presence of two exothermic peaks is shown. The lower exothermic peak in the temperature range of 98–129°C has been attributed to the addition reaction of free formaldehyde to phenolic ring, and the upper exothermic peak in the range of 139–151°C has been attributed to chain-building condensation reactions, involving hydroxymethyl groups attached to various phenolic species. Two distinguishable exothermic peaks at about 110 and 160°C are obtained [20] which were assigned to two independent reactions – the addition of formaldehyde to phenol to form hydroxymethyl phenols and their following condensation to methylene and methylene ether-bridged compounds. It is shown [19] that at lower F/P mole ratios exothermic signals are overlapping while at mole ratios of 2.15–2.30 two well-separated exothermic peaks are revealed. The first peak is explained by the condensation of methylol groups with phenol forming methylene groups or by the condensation of methylol groups to form dibenzyl ether groups, and the second peak as the condensation of ether groups to methylene groups. In [33] is indicated that the addition reactions were almost completed during the resin synthesis, and the DSC curve expresses the condensation reactions. Our study is consistent with this interpretation.

The addition of 5-MR or mixture of alkylresorcinols to the resol resin creates quite a new situation as there appears a component which con-

tains free aromatic sites. The influence of both these accelerators should be similar to somewhat lesser effect of alkylresorcinol mixture due to the lower functionality (of about 2.8) as compared to 5-MR (3). Independently from the amount of the added 5-MR (1.5–10 mass% of resin), the excess of ortho methylols in relation to the free aromatic sites remains great. Cocondensation reaction between phenolic methylols and resorcinols needs great excess of the latter component [25]. In this case, 5-MR promotes the formation of *o,o'*-dimethylene ether with subsequent release of formaldehyde as the resorcinolic accelerator needs formaldehyde for the formation of the homocondensate resin.

As an example of system PF with added 5-MR, the spectrum of the PF1 heated with 10 mass% of

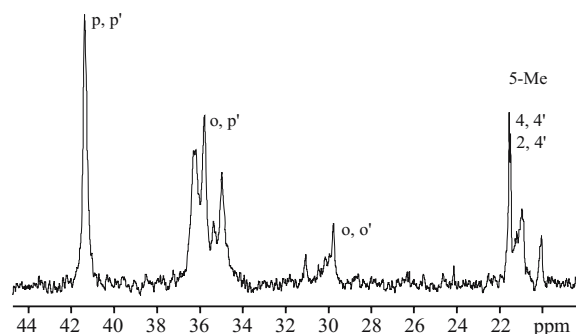


Fig. 8  $^{13}\text{C}$  NMR spectrum of PF1 cured with 10 mass% of 5-MR at  $100^{\circ}\text{C}$  in  $\text{CD}_3\text{OD}$ , 24000 scans

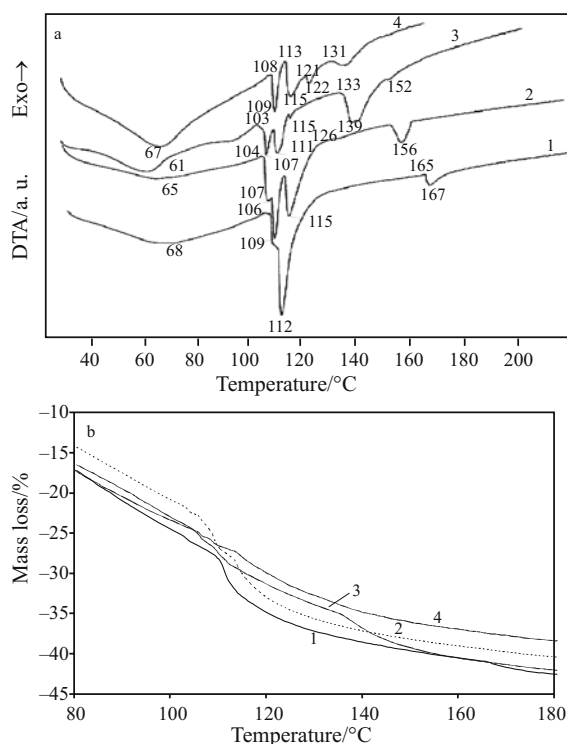
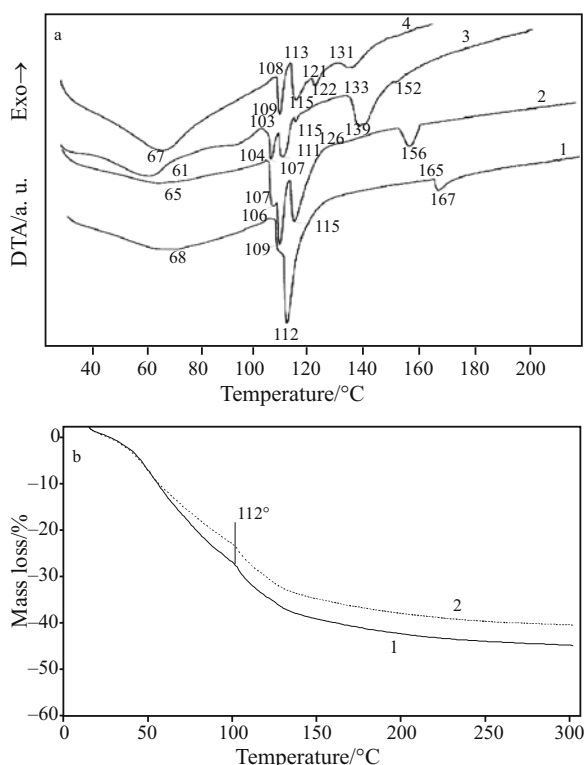


Fig. 9 a – DTA and b – TG curves of PF1 curing with 5-MR,  $5^{\circ}\text{C min}^{-1}$ : 1 – resin alone; 2 – 1.5 mass%; 3 – 3 mass%; 4 – 5 mass% of 5-MR

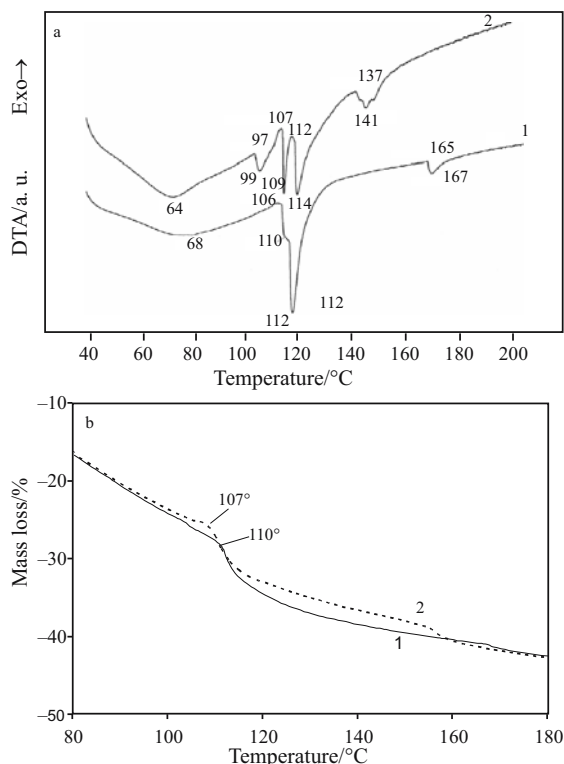
5-MR at 100°C is presented (Fig. 8). The formation of *o,o'*-methylene with the typical signal at 30–31 ppm and 4,4'- and 2,4'-methylenes of 5-MR homocondensates (signals at 20–21 ppm) were ascertained. The typical signal for more expected *o,4*-methylene of condensate at 27 ppm is not observed.

The TG-DTA curves are consistent with the proposed mechanism (Figs 9–13).

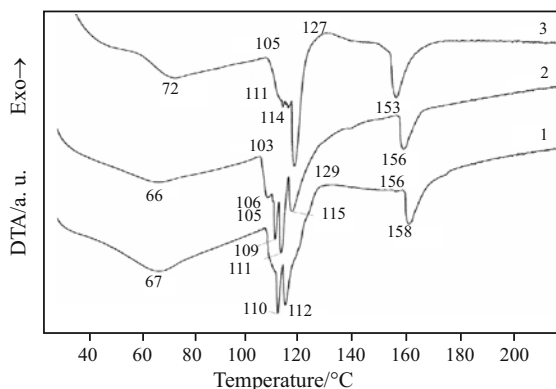
From DTA curves in Fig. 9a is revealed that if 5-MR is added in amount of 1.5–3 mass% of resin (curves 2 and 3), the exotherm with a peak maximum at 106°C (curve 1) shifts to the lower temperature while in case of greater amount of 5-MR (curve 4) is situated at higher temperature. Greater amount of water due to accelerated formation of *o,o'*-dimethylene ethers increases the role of immediately followed endotherm of water evaporation, and changes its shape by splitting to different peaks. Corresponding TG curves in Fig. 9b show that the sharp mass loss in case of PF alone (curve 1) begins at about 110°C, while with 1.5–3 mass% of 5-MR (curves 2 and 3) the beginning of sharp mass loss was shifted to 106°C which is caused by accelerated condensation reactions of methylolphenols. In case of 5 mass% 5-MR, the water evaporation seems to be more difficult due to the arising diffusional barriers. Decisive for the rate of 5-MR/F polycondensation is the rate of release



**Fig. 10** a – DTA and b – TG curves of PF1 curing with 5-MR+formaldehyde (F) in mole ratio of 5-MR/F=1/0.5, 5°C min<sup>-1</sup>: 1 – 1.5 mass%; 2 – 5 mass% of 5-MR



**Fig. 11** a – DTA and b – TG curves of PF1 curing with Honeyol Premium (AR), 5°C min<sup>-1</sup>: 1 – resin alone; 2 – 1.5 mass% of AR



**Fig. 12** DTA curves of PF2 curing with 5-MR, 5°C min<sup>-1</sup>: 1 – resin alone; 2 – 1.5 mass%; 3 – 3 mass% of 5-MR

of formaldehyde from *o,o'*-dimethylene ethers. The higher amount of 5-MR promotes this reaction and shifts the supposed exothermic effects to lower temperature with the immediately following water evaporation endotherms (from 167 to 133°C). The distinguishable exothermic peak becomes evident at 131°C in case of 5 mass% of 5-MR (curve 4). At the same time, the shift of water evaporation endotherm logically shows that the formation of 4,4'-methylene linkages in 5-MR/F reaction needs less activation energy in comparison with that needed in *o,o'*-methylene formation by complex reaction mechanism.

**Table 2** Laboratory-made plywood on the basis of cure-accelerated PF resin

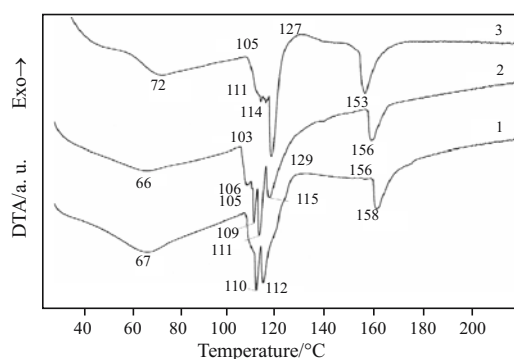
Pressing conditions				Plywood properties			
AR/PF g/100g	Temp./ °C	Pressure/ MPa	Time/ min	Thickness/ mm	Moisture/ %	Density/ kg m <sup>-3</sup>	Shear strength/ N mm <sup>-2</sup>
–	130	1.5	10.5	13.4	6.8	690	1.70
–	130	1.5	9.5	13.9	6.8	640	1.40
5.0	130	1.5	9.5	13.7	6.9	654	1.54
5.0	130	1.5	8.0	13.4	7.0	670	1.48

If 5-MR is added together with formaldehyde in mole ratio of 5-MR/F=1/0.5 (Fig. 10a), the polycondensation reactions occur at lower temperatures as compared to temperatures in Fig. 9a (curves 2 and 4). Despite the content of free aromatic sites in 5-MR is essentially lower in this case, depending on the 5-MR/F homocondensation, the effect of 5-MR as the accelerator for the *o,o'*-methylene formation strengthens due to increased reactivity of remaining free sites in 5-MR/F resin.

Figure 10b illustrates that although the more sharp water elimination starts at about the same temperature, the total mass loss at higher amount of added 5-MR is lower due to the tighter resin network in this case.

The addition of the commercial mixture of alkylresorcinols to PF1 (Fig. 11a) shows the same trend as in case of 5-MR (Fig. 9a). By the addition of even a small amount of AR (1.5 mass%), the acceleration effect in DTA curves reveals in shifting the exothermic peak of dimethylene ether formation to a lower temperature. From the strong shift of water evaporation endotherm from 167 to 141°C the acceleration of the polycondensation reactions can be supposed.

In curing PF2 resin which is used mainly in manufacturing the medium density fibreboards, in principle, the similar DTA curves have been obtained. As it was mentioned before, this resin is of lower viscosity and contains more water in initial resin than PF1. The results show that the rate of cure was increased with an increase in the water content of resins.



**Fig. 13** DTA curves of PF2 curing with Honeyol Premium (AR), 5°C min<sup>-1</sup>: 1 – resin alone; 2 – 1.5 mass%; 3 – 10 mass% of AR

In Figs 12 and 13, the DTA curves using different amounts of 5-MR or the mixture of alkylresorcinols are illustrated.

In case of a greater amount of added AR (Fig. 13, curve 4), additional exotherm reveals at 63°C which can be explained by the complicated composition of AR.

When comparing the effect of the amount of added alkylresorcinols on gelling of PF resins at 100°C (Figs 3 and 4) to the curing behaviour in temperature ranges of 30 to 300°C (Figs 9–13), it must be considered that the conditions for resin curing in determination of gel time and dynamic DTA analysis with curing rate of 5°C min<sup>-1</sup> are different. The resin gelling occurs at a determined, but quite low level of polycondensation. It means that the added 5-MR in amounts of 2–2.5 mass% is sufficient to promote the polycondensation to the gel point. Despite that the effect of 5-MR is proved by the decreased gel time, the DTA curves do not show the optimum amount of 5-MR (or AR), accelerating the resin curing in actual processing conditions. In this study, our approach in selecting the small amounts of accelerators arose rather from practical considerations.

The results of manufacturing and testing plywood if using PF1 resin with AR as curing accelerator are presented in Table 2.

The results show that the press time could be reduced by 1.5 min at the shear strength exceeding the standard for exterior-grade board (1.0 N mm<sup>-2</sup>). A reduced press time for a given temperature may have a marked influence from the industrial point of view increasing the manufacture productivity.

## Conclusions

TG-DTA analysis of phenolic resins for wood bonding shows that, in spite of the disturbing evaporation of water, open systems under ambient pressure can be used for characterisation of acceleration effect of 5-MR and alkylresorcinol mixture on curing resol resins, although the analysis sometimes provides only qualitative information.

On the basis of <sup>13</sup>C NMR spectrum, the essential structure-determining characteristics were ascer-



tained. The full substitution of reactive aromatic positions of phenol, especially by methylol groups, determines the mechanism of resin cure. The first exotherm in DTA curve corresponds to the formation of dimethylene ethers from condensation of methylol groups. The crosslinking reactions do not reveal sharp exothermic peaks in DTA curve. Water evaporation endotherm which shifts to the lower temperatures with adding alkylresorcinols to PF resin gives evidence about occurring polycondensation reactions.

The testing shows that, when using commercial phenolic resol resin SFŽ-3013VL with 5 mass% of mixture of water soluble oil shale alkylresorcinols Honeyol Premium of Estonian origin, the press time could be reduced by about 15% in making plywood. The shear strength was found to abundantly exceed the standard for exterior-grade board.

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