Reactivity and spectral comparisons of alkylresorcinol laminating resins with phenolic and resorcinolic resins

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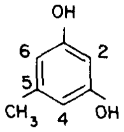
Two alkylresorcinol-based laminating resins, DFK-14R and FR-100, are compared in reactivity and structure with resorcinol- and phenol-based adhesive resins. The alkylresorcinols, derived from Estonian shale oil, replace costlier, less-reactive resorcinol in adhesives in the USSR. Differential scanning calorimetry quantitates the reactivity advantage. Infrared spectroscopy and proton nuclear magnetic resonance provide spectral patterns to distinguish the alkylresorcinol resins from the families of resorcinol- and phenol-based resins. Structural features are assigned for most of the spectral absorptions, with aid from ^{13}carbon nuclear magnetic resonance spectra of the shale oil resins.

Key words: adhesives; reactivity; resorcinols; alkylresorcinols; shale oil; infrared spectrophotometry; nuclear magnetic resonance; calorimetry.

Over the past decade, scientists in the Estonian SSR have been studying and developing structural adhesives from a dry-distillate fraction of kerogen, or shale oil, found in that region. Despite a decade of use in the USSR and five years of marketing in Japan, these unique resins have been little discussed in Western publications.

These alkylresorcinol adhesives are unique materials both in structure and reactivity. Comparison of these characteristics with resins presently being used in the West can provide information about structure-reactivity relationships, and about how such reactive materials can be controlled to make useful products. It may some day be possible to obtain chemicals like these commercially from other fuel sources, such as domestic shale oil, tar sands or direct coal liquids. Alkylphenols constitute up to 20% of the products from such direct liquefaction processes as H-coal, solvent-refined coal and a donor solvent process liquid[1]. New catalytic[2] and microorganism[3] processes may help free these feedstocks of less desirable nitrogen- and sulphur-containing compounds.

The unique composition of Estonian shale oil gives a product directly from the distillation process that is low in basic nitrogen-containing groups and paraffins and is high in oxygenated groups, especially phenols[4,5]. The first crude fraction, distilled between 276°C and 318°C[5], is termed 'summary diphenols' (SDP), or 'crude water-soluble phenols', and this is used in some of the resins. However, further distillation of the SDP provides a 'technical fraction', or 'summary alkylresorcinols' (SAR or alkyres), that is used in other resins. The crude SDP and refined SAR products are composed primarily of resorcinol substituted with methyl and higher alkyl groups at various positions and to differing extents[6,7], giving an average empirical formula equal to dimethyl resoricinol[5] but with 5-methyl resorcinol (orcinol) as the most abundant species[6,7].



5-methyl resorcinol (orcinol)

The reactivity of these SDP and SAR products was found[5] to be greater than that of more expensive resorcinol; they are used to create cold-setting, durable adhesives to replace resorcinol-formaldehyde adhesives and acid-curing phenolic adhesives.

The cohesive properties and durability of hardened alkylresorcinol adhesives approach those of resorcinol adhesives, with the strength of joints for coniferous wood species higher than the natural wood strength[8]. Various working properties of the formulated adhesives and adhesive strength evaluations have been described[5,9-11]. Applications have been for wood adhesives in agricultural construction[9], bridge girders and utility poles[4,5,11], and as binders for inorganic construction materials[11] or tyre cord[5].

The excessive reactivity of these alkylresorcinols created problems with the control of the formaldehyde addition reaction and with storage and pot lives[5]. It was found that the inclusion of acetone or other carbonyl compounds, such as caprolactam, gives hydrogen bonded complexes with the phenolic hydroxyls. These complexes slow the hydroxymethylation reaction[6]. Caprolactam slows the reaction by more than a factor of 10, though the reaction is still

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eight times faster than the rate of resorcinol hydroxymethylation[6,7].

Copolymers of the alkylresorcinols with hydroxymethyl compounds are made for various applications. Phenol or hydroxymethylated phenol is sometimes incorporated for economy. N-hydroxymethyl caprolactam and N,N'-dihydroxymethyl urea are also used.

Only a very limited number of papers on the infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy of resorcinol and phenol-resorcinol resins were found that could be used in analysis of the shale oil resins. The present work supplements these papers and presents a side-by-side comparison of spectral characteristics useful in analysing resins of these families. Evaluation of bond strength and durability of the shale oil resins will be reported elsewhere[12].

Experimental details

Methods

Infrared spectra for 12 resins were obtained with a Beckman IR 12 or a Nicolet 6000 Fourier-transform infrared spectrometer. The uncured resins were spread as-received on a KBr crystal or cast on KBr as a water- or acetone-diluted solution, and were then vacuum dried.

^{1}H-NMR spectra of the 12 resins without added hardener were obtained with a Varian T-60 NMR spectrometer at 60 MHz. The resins were vacuum dried and redissolved in DMSO-d_6 (dimethyl sulphoxide). In some cases, pyridine-d_5 was used as a shift solvent to separate overlapping peaks. Peaks due to labile hydrogens in the resin structures are identified by their disappearance upon the addition of deuterium oxide.All NMR absorptions are reported as chemical shifts (δ in parts per million, ppm) relative to tetramethylsilane (TMS) as internal standard.

^{13}C-NMR spectra were obtained with a Bruker Cryospec WM250 FT-NMR spectrometer at 62.89 MHz. The spectra were obtained at ambient temperature with broad-band decoupling, a 15 kHz sweep width, a 10 μs (75°) pulse width, 1 s pulse delay, and 8 K data points. The shifts were measured relative to internal DMSO-d_6 and converted to TMS values.

The reactivity of catalysed resin was measured with a Perkin-Elmer DSC-2 differential scanning calorimeter (DSC). The calorimeter has a Scanning AutoZero to minimize baseline curvature. The sample heating assembly and the dry box enclosing it were purged with nitrogen gas. Perkin-Elmer large volume capsules (LVC), made of stainless steel, were used to prevent interference from the water vaporization endotherm. The LVCs can withstand vapour pressures of 1.4-2.1 MPa. Instrumental heating rate effects were determined by comparing the observed onset of melting of an indium sample, at the desired heating rate, with its true melting temperature. Each reaction peak temperature was corrected to eliminate the instrumental factor. The samples were 10 to 17 mg drops of catalysed resins sealed in LVCs. They were heated from 17°C to 207°C at rates of 10, 20 or 40°C min^{-1} (and 5°C min^{-1} for one resin). Most resins were scanned once at each of three heating rates.

Materials

A total of 12 resins was used in this study: four sent by the Ministry of Building Construction, Moscow, USSR, and eight resins from the USA. Most of the latter resins are commercial, and were used for comparison purposes here.

Appropriate hardeners were supplied by the manufacturers and were mixed as specified with the respective resins, except for the already-catalysed alkaline phenolic resins, for the DSC tests.

Resins from USSR

DFK-14R is a phenol-modified alkylresorcinol-formaldehyde (ARF) resin. Phenol comprises 30-50% of the active ingredients[8] in the commercial version, DFK-14. The resin contains some alkali[6,7]. The solvent is a mixture of ethanol, water and ethylene glycol[6,7].

FR-100, an ARF resin, contains limited amounts of urea complexing agent to increase its shelf life[10].

FRF-50 is a phenol-resorcinol-formaldehyde (PRF) resin with a phenol-to-resorcinol ratio of 1 : 1, no combustible solvents and 3-6% free phenol[8].

SFKh is a low-temperature acid-curing phenol-formaldehyde (PF) resin. It contains 1% or less of either free phenol or formaldehyde[8]. It is low in alkali[8], and has ethylene glycol as a noncombustible solvent[10]. The catalysts for this resin are usually weak sulphonic acids[8], among which is Petrov's fluid – a kerosene-based catalyst[10].

Resins from USA *

Resins *1-RF* and *7-RF* are commercial resorcinol-formaldehyde (RF) cold-setting adhesives which are used for bonding applications similar to those of FR-100 and DFK-14R.

Resins *4-PRF*, *5-PRF* and *8-PRF* are commercial PRF adhesives. These and *FRF-50* are useful in providing comparisons for the partial phenolic structure of DFK-14R.

Resin *6-PF* is a commercial, highly alkaline-catalysed PF resol.

Resin *3-PF* is a resol (F/P = 2) synthesized at this laboratory according to a published procedure[13].

Resin *2-PF* is a commercial, acid-catalysed resol.

Results and discussion

Infrared spectral characterization

The uncured resins can be identified by certain characteristic absorption bands in their IR spectra (see Table 1). The most helpful region for distinguishing between these types of resins was between 810 and 1700 cm^{-1}. The IR spectra of the two resins of primary interest, the alkylresorcinol-based adhesives (see Fig. 1), can be compared with the spectra of two more common types of resorcinol-based resins, the RF resin 1-RF (see Fig. 2a) and PRF resin 4-PRF (see Fig. 2b).

Phenolic and resorcinolic resin bands

Resins containing resorcinol absorb energy moderately to strongly at 1175 cm^{-1} (see Table 1), whereas phenolic-only resins absorbed weakly at this wavelength. Yamao[14] used the 1170 cm^{-1} region as a measure of the resorcinol content in RF resins. Resorcinol-containing polymers and resorcinol itself absorb strongly at 1140-1160 cm^{-1}. Phenolic-only resins absorb moderately in this region. The absorption band near 1150 cm^{-1} in resorcinol and phenol is assigned[15] to in-plane bending of aromatic C-H bonds. This band is more intense if polar groups are bonded to the aromatic

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*The American resins are given codes so that results will not imply an endorsement of any product.

Table 1. Summary of observed infrared regions found to differ substantially among the various uncured resins

Spectral region (cm^{-1})	Assignments[a]	Phenolic				Both phenolic and resorcinolic					Resorcinolic		
		Acid-cure		Alkaline-cure		PRF				ARPF	ARF	RF	
		SFKh	2-PF	3-PF	6-PF	FRF-50	5-PRF	4-PRF	8-PRF	DFK-14R	FR-100	1-RF	7-RF
2930-90	Aliphatic C-H	M	M	M	M-w	M	w	w-M	w	M	M	w	M-w
2850-80	Aliphatic C-H	M	M-S	M-S	M-w	w	w	w	w	w	w	—	w
1660-70	Amide C=0	—	—	—	—	—	—	—	—	—	M	—	—
1610-25	Aromatic C=C	M	M_d	S-M_d	S	S	S	S	S	S	S	S	S
1480-1520	Aromatic C=C (weaker for penta substitution)	S_d	M-S_d	S_m	S	S_m	M-S_m	S_m	S_m	w-M	w-M	S_m	S_m
1360-90	Ar-OH; C-CH_3	w-M	S-M	S	—	M	M-w	S-M	M-S	M-S	M-S	S-M	S
1280-1300	Ar-OH; Ar-O-R	w	—	—	S-M	M-w	w	S	w-M	M-S	M-S	S	S
1175	Aromatic C-H; Ar-OH	—	w	w-M	—	M-S	M-S	S	M-S	M_{sh}	M	M-S	M-S
1140-60	Aromatic C-H; Ar-OH	M	M-w	M	M	S	S	S	S	S-M	S-M	S	S
1080-1100	Ethyl; R-O-R; CH-OH	—	—	w	—	M	w-M	w-M_d	M	S	S	S	S
1040-60	-CH_2OH; ethyl; R-O-R (including dibenzylether[14])	w	w	w-M_{sh}	—	w-M	M-w	M	w	M-S	M	M	S-M
1020-30	Ar-CH_2OH; R-CH_2OH; Ar-O-R	S	S	S	M-S	—	—	—	w	—	—	—	—
980-1000	Aromatic C-H (980 for 4- and 4,6-substituted derivatives of resorcinol[14])	(within peak above)	M-w_{sh}	w	M	M-w	w_{sh}	w_{sh}	M	M	M-w	M	M
960	Aromatic C-H (960 in unreacted resorcinol[14])	(within peak above)	(within peak above)	(within peak above)	(within peak above)	M	M	M	M	(within peak above)	(within peak above)	M	M
880	Aromatic C-H	M	w-M	M-w	w-M	w	—	w	w	M-w	w_{sh}	w	w
840	Aromatic C-H	—	w-M	M	w	M	M	M	M	M	M	M-S	M-S
790-810	Aromatic C-H	—	—	—	M-w	—	—	—	—	—	—	—	—
780	Aromatic C-H	M-w	w_{sh}	w_{sh}	w_{sh}	—	w_{sh}	—	—	—	—	—	w_{sh}
760	Aromatic C-H	M-w	M	M	—	M	M	M	M	w	—	M	M

[a] Based on References 14, 16, 17 and 19

S = strong band; M = medium band; w = weak band; d = two peaks or peak + shoulder; m = multiple peaks; sh = shoulder

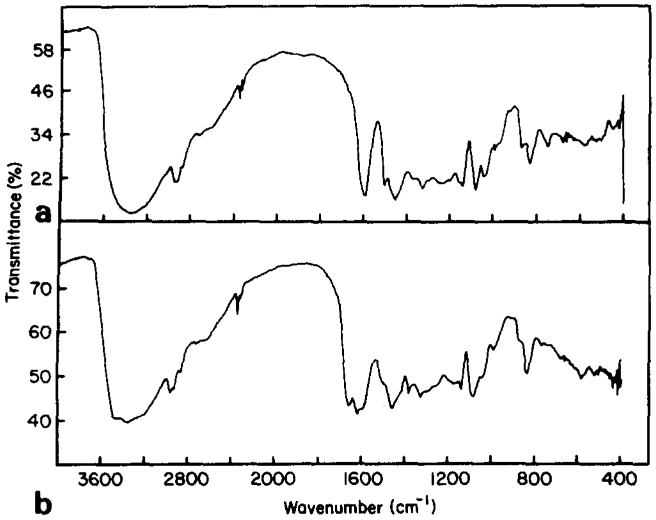


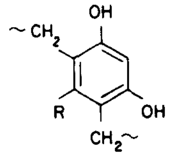
Fig. 1 Infrared spectra of two Estonian shale oil-based resins (uncured, dried): (a) DFK-14R; (b) FR-100

rings[16]. Aromatic hydroxyl groups will produce absorption peaks somewhere in the region 1100 to 1300 cm^{-1} (Ref 17).

Predominantly phenolic resins (see Table 1) have strong-to-medium absorptions at 1020–1030 cm^{-1}, where those resins containing resorcinol have, at most, weak bands. This spectral region is assigned to C-O stretching of primary alcohols (such as hydroxymethyl groups), secondary alcohols or aromatic ethers[16,17]. Since the phenolic resins are resols, this absorption is attributed to their hydroxymethyl groups, which are rarely stable in resorcinolic resins[18].

Alkylresorcinol resin bands

The infrared spectra of the two alkylresorcinol-based adhesives, DFK-14R and FR-100, have some features which distinguish them from the others (see Table 1). At 1480-1520 cm^{-1},where all the other uncured resins have strong absorptions, the two alkylresorcinol resins have much weaker absorptions. The absorptions in this region caused by aromatic C=C stretching are affected by substitutions on the ring[19,20]. The absorption peak appears to be weak only in penta-substituted rings, like 2,3,5,6-tetramethyl phenol[21]. Predominantly uncrosslinked or unbranched phenolic and resorcinolic resins would have only 3 and 4 ring positions, respectively, substituted. A 5-alkylresorcinol resin would have five positions substituted:



The alkylresorcinol resins are the only two of the resorcinolic types that show no significant absorbance at 960 cm^{-1}, an absorption caused by C-H bending vibrations of resorcinol[16,22]. They do, however, have a medium intensity peak at 980 cm^{-1} (seen as a shoulder to the peak at 1000 cm^{-1} in Figs 1(a) and 1(b)). This peak is attributed to the unreacted hydrogen at the 2-position for resorcinols substituted at the 4-position[14]; this situation might be expected with a 5-alkylresorcinol that has been condensed with formaldehyde through the 4- and 6-positions.

A peak observed only in the FR-100 resin (see Table 1) is that near 1660-1670 cm^{-1}. This peak is attributable to the amide structure of urea, which is often added to FR-100 to improve the stability of this resin[7]. A spectrum of urea showed its strongest absorption to be in the 1560-1670 cm^{-1} region with secondary absorption around 3330 and 3450 cm^{-1}. This pattern is also present in the FR-100 spectrum.

Other absorption bands

The bands in the 1040-1060 cm^{-1} and 1090 cm^{-1} regions could be due to a number of vibrations, including those from solvents. Absorptions in these two spectral regions are stronger in the resorcinolic resins. The Russian resins DFK-14 and SFKh were noted earlier to contain alcoholic solvents, and resorcinolic resins also contain alcoholic solvents[18].

As will be seen in the NMR section, there is evidence indicating the presence of ethanol in all the resorcinolic-type resins, except FRF-50, though all were vacuum dried before spectra were determined.

Nuclear magnetic resonance spectral characterization

^{1}H-NMR spectra provide another tool for distinguishing between the alkylresorcinol resins (see Fig. 3) and other phenolic-type resins (see Table 2). For the resins of particular interest here, DFK-14R and FR-100, ^{13}C-NMR spectra (see Fig. 4) help clarify some ^{1}H-NMR assignments. Peaks and broad adsorption regions caused by labile hydrogen regions are, with one exception, assigned to hydroxyl groups and are not considered.

Resin aromatic ring atoms

1) Hydrogen spectrum. All the resins have peaks in the 5.8-7.4 ppm region (see Table 2). This region is characteristic of aromatic ring hydrogens. Resins containing resorcinol-type structures are distinguished from those having only phenolic-type structures by resonance peaks in the 5.4-5.8 ppm region. FR-100, alone among the resins studied, has almost no peaks for aromatic ring hydrogens in the 6.4-7.4 ppm region. This is understandable because the main component of FR-100, orcinol or 5-methylresorcinol, has this same gap in its spectrum[23].

2) Carbon spectrum. Aromatic carbon assignments for shale oil resin FR-100 (see Fig. 4b) were made by reference to Lippmaa *et al*[24] on straight orcinol-formaldehyde resins

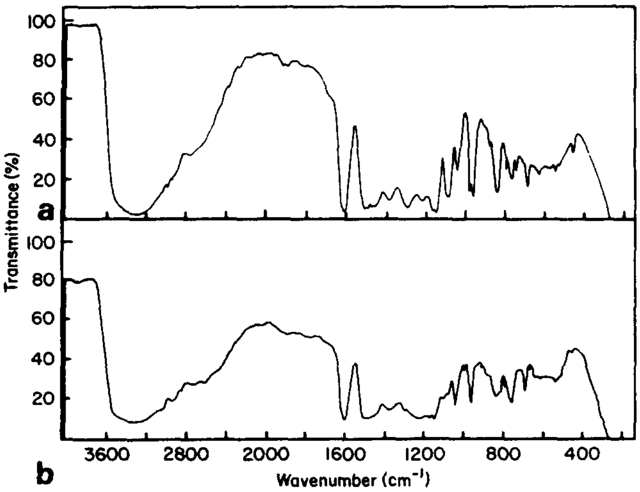


Fig. 2 Infrared spectra of two resins used for comparison (uncured, dried): (a) 1-RF, a resorcinol-formaldehyde resin; (b) 4-PRF, a phenol-resorcinol-formaldehyde resin

Table 2. Summary of ^{1}H-NMR peak positions and characteristics of the various uncured resins

δ^a (ppm)	Assignments	Peak characteristics	Phenolic				Phenolic and resorcinolic					Resorcinolic		
			Acid-cure		Alkaline-cure		PRF				ARPF	ARF	RF	
			SFKh	2-PF	3-PF	6-PF	FRF-50	5-PRF	4-PRF	8-PRF	DFK-14R	FR-100	1-RF	7-RF
1.06 (J = 7 Hz)	$C\underline{H}_3$-CH_2-	Triplet	–	–	–	–	–	Small	Small	√^{b}	√^{c}	√^{c}	√^{c}	√^{c}
1.6-2.8	Alkyl groups	Peaks and hump	–	–	–	–	–	–	–	–	√	√	–	–
1.9-2.1	$C\underline{H}_3$-Ar		–	–	–	–	–	–	–	–	Strong	Very strong	–	–
2.2-2.4	Probably $C\underline{H}_3$-Ar or CH_3-$C\underline{H}_2$-Ar		–	–	–	–	–	–	–	–	Very small	Medium intensity		
3.2	Solvent related; probably R-O-$C\underline{H}_3$	Singlet	–	–	–	Very small sharp peak^c	Small^c	Sharp peak	Small	Small	–	–	Small	Small^c
3.2-4.1	Ar-$C\underline{H}_2$-Ar; could include solvent related -CH_2-$C\underline{H}_2$-O- or R-O-$C\underline{H}_3$	Hump	√	√	√	√	√	√	√	√	√	√	√	Small
3.4	O-$C\underline{H}_2$-$C\underline{H}_2$-O in solvent, probably ethylene glycol	Singlet	–	–	–	–	Very intense	–	Very intense	–	Very intense	Very intense	–	Very intense
3.46 (J = 7 Hz)	CH_3-$C\underline{H}_2$-O-(H)	Quartet	–	–	–	–	–	Small	Small	√	√^{c,d}	√^{c}	√^{c}	√^{c}
4.4-4.8	4.4 p HO-Ar-$C\underline{H}_2$OH 4.5-4.6 o HO-Ar-$C\underline{H}_2$OH 4.7-4.8 Ar($C\underline{H}_2$O)$_2$H (benzyl hemiformal) 4.3-4.55 (Ar-$C\underline{H}_2$)$_2$-O (benzyl ether links)	–	Large sharp peak	3 peaks (1 large)	3 peaks (1 large)	Large sharp peak	2 fairly small peaks	–	Very small hump	2 very small peaks	2 fairly small peaks	–	–	–
5.2-5.7	$\underline{H}_2$NCON$\underline{H}_2$	Singlet (labile)	–	–	–	–	–	–	–	–	–	Medium intensity	–	–
5.8-6.4	Resorcinolic aromatic hydrogens	Peaks and hump	–	–	–	–	√	√	√	√	√	√	√	√
6.4-7.4	Aromatic hydrogens generally (but not 5-alkylresorcinols)	Peaks and hump	√	√	√	√	√	√	√	√	√	–	√	√

[a] Peak position (usually ± 0.02 ppm), or center of split peaks, or range for absorptions in d_6-DMSO

[b] Check mark (√) indicates this feature appears as a prominent, regular feature

[c] Intensity varied in different preparations, relative to aromatic H region

[d] Quartet buried in other signals when in DMSO-d_6 solution; discernible in pyridine-d_5 solution spectrum

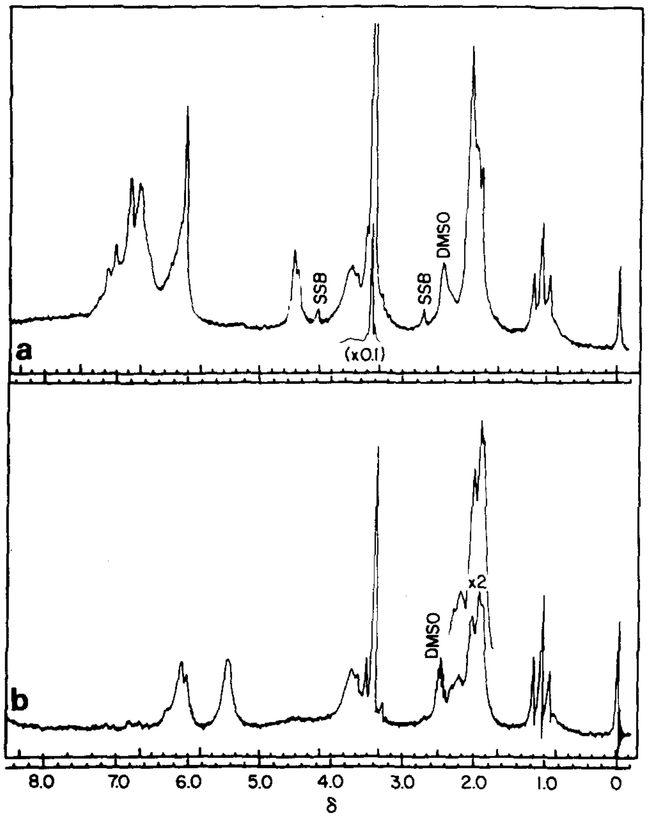


Fig. 3 ^{1}H-NMR spectra of two Estonian shale oil-based resins (uncured, vacuum dried, dissolved in DMSO-d_6): (a) DFK-14R; (b) FR-100. The peak labelled DMSO results from solvent molecules not fully deuterated, and the small extraneous peaks labelled SSB are spinning side bands of the intense peak midway between them

and to other work[25,26] on resorcinolic resins. Ring carbons C1 and C3 bound to hydroxyls are assignable to the 150-159 ppm region. The alkyl substituted C5 is indicated by signals from 138 to 141 ppm. Various C2, C4, C6 and unsubstituted C5 carbons produce signals in the region from 100 to 137 ppm.

Resin oxymethylene groups

1) Hydrogen spectrum. Only the straight phenolic resins have large peaks in the 4.4-4.8 ppm region (see Table 2). These peaks for phenolic resins are assigned to various oxymethylene groups, predominantly hydroxymethylene groups, attached to the rings[22,27,28]. The three American phenolic resins (2-PF, 3-PF and 5-PF) are resols and should contain many $-CH_2OH$ groups. The small peaks seen in the 4.4-4.6 ppm region for four resins of mixed phenolic and resorcinolic character indicate the presence of oxymethylene structures perhaps from the phenolic component. The assignments of Table 2 (for DMSO-d_6 solutions) are made by analogy to the spectra of Woodbrey *et al*[22].

2) Carbon spectrum. Neither spectrum (Fig. 4) of the shale oil resins shows peaks in the 68-73 ppm region where Kim *et al*[29] found signals for benzyl ether structures linking phenolic rings. Resin DFK-14R did produce signals at 59 and 60 ppm, which probably arise from ortho hydroxymethylene groups on phenol. FR-100 shows no signals at 59-60 ppm.

Resin alkyl groups

1) Hydrogen spectrum. The spectra of the two shale oil resins are distinguished from the RF- and PRF-type resins by absorbances below 3.0 ppm due to alkyl groups (see Table 2). There is a cluster of absorbance peaks for the shale oil resins in the region from 1.6 to 2.8 ppm. This cluster has the appearance of a broad, low hump with other peaks superimposed on it. One group of strong peaks stretches from 1.9 to 2.1 ppm. Experimentally, the methyl signal for 5-methylresorcinol in DMSO-d_6 is at 2.1 ppm, and the chemical shift for 2-methylresorcinol is smaller than that for 5-methylresorcinol[23]. There is a second group of fairly strong peaks from 2.1 to about 2.4 ppm. This range is common for methyl groups attached to aromatic rings and for aliphatic methyl and methylene groups adjacent to carbonyl groups. The latter explanation is an unlikely one for the present case, since the ^{13}C-NMR spectra show no signal in the 162-220 ppm region typical of most carbonyl groups (see Fig. 4). At least part of the 2.1-2.4 ppm cluster may be caused by methylenes attached to aromatic rings, since 4-ethylresorcinol shows a quartet at 2.5 ± 0.2 ppm[23]. Signals may be shifted somewhat out of their general range by: (a) the presence of two hydroxyl groups meta to each other, (b) heavy substitution of the rings, and (c) the steric hindrance resulting from condensation of several rings. The methyl groups of 5-ethyl side chains contribute to the triplet at 1.06 ppm. A better separation of the peaks and humps in the various regions is shown by Fig. 5 for FR-100 in pyridine-d_5, a shift solvent.

All the samples appear to have a broad, sometimes pointed, hump-shaped signal between 3.2 and 4.1 ppm.

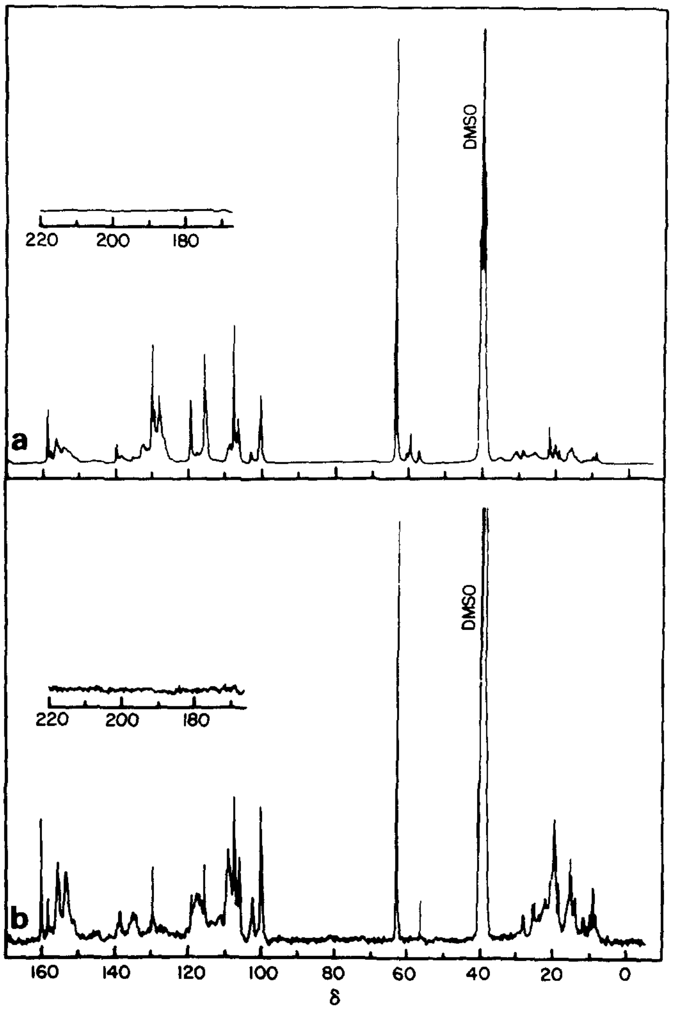


Fig. 4 ^{13}C-NMR spectra of two Estonian shale oil-based resins (uncured, vacuum dried, dissolved in DMSO-d_6): (a) DFK-14R; (b) FR-100. Peaks labelled DMSO are from the solvent

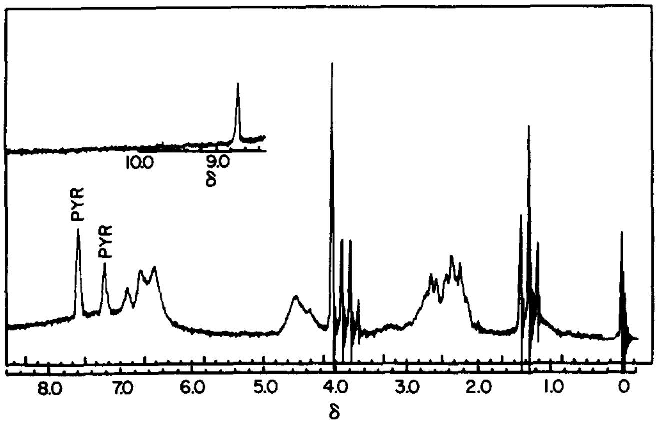


Fig. 5 ^{1}H-NMR spectrum of resin FR-100 (uncured, vacuum dried) showing the separation of signals achieved by using pyridine-d_5 as solvents. Peaks labelled PYR result from solvent molecules not fully deuterated

This is probably due to an aggregation of weak-to-moderate absorption peaks. Resonance peaks for methylene bridges between phenolic rings have been assigned[22,30] to the upper end of the region from 3.6 to 4.1 ppm ($\delta_{o,o'} > \delta_{o,p'} > \delta_{p,p'}$). Signals from retained solvent are also often seen in the 3.2–4.1 ppm region.

2) Carbon spectrum. The alkyl region in the ^{13}C-NMR spectrum (see Fig. 4) ranges from about 8 to 31 ppm. Lippmaa *et al*[24] found signals for methyls attached to resorcinolic rings at various positions: 7.7 ppm for C2, 14.2 ppm for C4 and 20.5 ppm for C5. They also found signals for methylene links in an orcinol-formaldehyde condensate: 15.4 ppm for a 2,4′-link and 19.6 ppm for a 4,4′-link. For a resorcinol-formaldehyde condensate they found the methylene links at slightly different chemical shifts: 23.3 ppm for the 2,4′-link and 28.8 ppm for the 4,4′-link. These signals contain most of the prominent signals that are found in the alkyl region of the shale oil resins. The peak for DFK-14R at 30 ppm, not seen for FR-100, is attributed to a 2,2′-methylene link between two phenol rings, and a very small signal at 35 ppm to a 2,4′-link between phenolic rings[31,32].

Urea

1) Hydrogen spectrum. As previously noted, urea is added to FR-100 to improve its stability. The ^{1}H-NMR spectrum for FR-100 (see Fig. 3(b)) contains a moderately strong peak for a labile-type hydrogen atom at 5.5 ppm. Urea (neat) in DMSO-d_6 gives a signal at 5.7 ppm. Such signals are attributable to nonsubstituted amide groups[33]. There is no peak for a labile hydrogen between 6.4 and 7.0 ppm, which is the range associated with mono-substituted amide groups. Kjeldahl analysis indicates FR-100 has 2.2 weight % nitrogen. If all the nitrogen is present as urea, then urea is 4.7 weight % of the FR-100 resin solution. There are no peaks to indicate the presence of other complexing agents commonly used for shale oil resins.

2) Carbon spectrum. The spectrum for FR-100 (see Fig. 4(b)) contains a signal at 160.2 ppm. The carbonyl carbon of urea (neat) in DMSO-d_6 produces a signal at 161.8 ppm.

Other groups

Solvent entrained with the resins contributes to several ^{1}H-NMR signals. Extensive vacuum drying (up to 20 h at 400 Pa vacuum at room temperature) does not eliminate the signals.

The triplet centered at 1.06 ppm ($J = 7$ Hz) and the less intense quartet centered at 3.46 ppm ($J = 7$ Hz) vary considerably in size compared with the aromatic hydrogen signals (see Table 2), depending on drying conditions. This variability indicates the signals are due to a volatile component. These signals are primarily due to ethanol, which is a common solvent for resorcinolic-type resins. Resins DFK-14, 8-PRF, 1-RF and 7-RF are known to contain ethanol. ^{13}C-NMR spectra for the two shale oil resins (see Fig. 4) show peaks at 18.6–18.7 and 56.3–56.5 ppm, very close to previous assignments for ethanol[34].

Five of the resins with resorcinolic-type groups have a very intense singlet in their ^{1}H-NMR spectra at 3.4 ppm (see Table 2). Different sample preparations did not significantly affect this signal, so the source compound has low volatility. The signal did not fit the spectral pattern of any of the following neat solvents run in DMSO-d_6: ethylene glycol or its monomethyl or dimethyl ethers, glycerol or diethylene glycol monoethyl ether. All these solvents have strong peak in the 3.3-3.6 ppm region produced by $O\text{-}\underline{CH_2}\text{-}CH_2$ groups. However, DFK-14 is known[6,7] to contain ethylene glycol, which is the suspected source of the 3.4 ppm signal. In support of this contention, the ^{13}C-NMR spectra of both shale oil resins show a strong signal at 63 ppm, where ethylene glycol in DMSO-d_6 has its only signal.

The ^{1}H-NMR spectra of several resins contain a peak at 3.2 ppm, and the intensity of this signal varies considerably with sample preparation. This signal has the same chemical shift as the methoxyl group signal for several of the previously mentioned solvents. The 3.2 ppm signal is attributed to the methoxy component of an undetermined solvent molecule.

Analyses of integrated peak areas to provide an empirical formula or average structure were attempted for the ^{1}H-NMR spectra of the shale oil resins, but they are too complex to yield an accurate analysis. The difficulty is due to overlapping absorption regions and the wide variety of molecular species.

Calorimetric evaluations

The reactivity of the catalysed resins can be determined by DSC. For example, the scan of a PRF resin, Fig. 6, shows two reaction exotherms – one each for the resorcinolic (lower temperature) and phenolic (higher temperature) components. The temperatures corresponding to the peaks of the broad exotherms are selected as the characteristic cure reaction temperatures. A more reactive resin has a lower peak temperature, if resins are compared at the same heating rate. The heating rate $\beta = 10^\circ\text{C min}^{-1}$ was used for the following comparisons.

Lower-temperature peak reactivities

The resins all contain a resorcinolic component, which produces a peak temperature between 76 and 96°C upon curing (see Table 3). A ranking of the activities of these resins, based on which have the lowest peak temperatures, gives:

$$\text{FR-100} > \text{8-PRF} \cong \text{DFK-14R} > \text{5-PRF} > \text{4-PRF}$$
$$> \text{7-RF} > \text{FRF-50} \cong \text{1-RF}$$

This lower-temperature exothermic peak was previously found for resorcinol with formaldehyde-type hardeners[35,36], for an RF polymer with paraformaldehyde[34] and for a PRF polymer with paraformaldehyde[20].

Higher-temperature peak reactivities

Those resins containing a phenolic component have a peak temperature between 123 and 174°C (see Table 4). Based strictly on peak temperatures, the reactivity ranking is:

5-PRF > 6-PF ⩾ 4-PRF ⩾ FRF-50 ⩾ DFK-14R

The lower-temperature reaction solidifies the resin before the higher-temperature reaction becomes significant. The higher-temperature reaction may, however, play a part in determining long-term strength. Chow[20] measured a softening temperature to get an indication of the extent of cross-linking that took place during cure of a PRF resin. The softening temperature increased in two stages depending on the temperatures used for curing. Softening temperatures increased as curing temperatures rose to 100°C. This was followed by little change in softening temperature when the curing temperature was between 100 and 130°C. Softening temperatures again increased when curing temperatures increased beyond 130°C. For phenol-formaldehyde

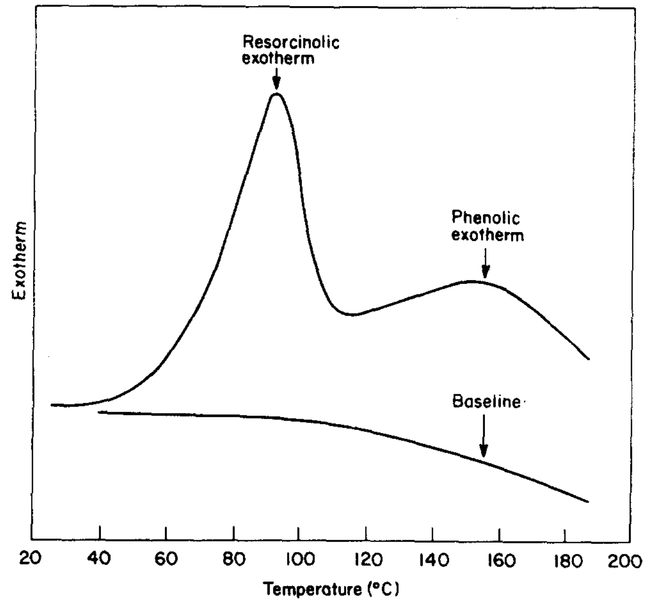


Fig. 6 Differential calorimetry scans at 10 K min^{-1} of resin 4-PRF (uncorrected temperatures)

Table 3. Calorimetric data for the lower-temperature curing reaction

Resin	Heating rate, β (K min^{-1})	Peak temperatures[a] (°C)	Activation energy, E (kJ mol^{-1})	Coefficient of determination (r^2)	Calculated rate at 20°C (K min^{-1})
Shale oil-based resins					
DFK-14R	10	84	64	1.000	0.072
	20	94			
	40	107			
FR-100	10	76	68	0.987	0.103
	20	83.5			
	40	94.5			
	40	95.5			
Controls					
FRF-50	10	95	70	0.964	0.024
	20	101.5			
	40	116.5			
5-PRF	10	80	78	1.000	0.033
	20	89			
	40	99			
4-PRF	10	91.5	90	0.991	0.005
	20	101.5			
	40	108.5			
8-PRF	10	83	84	0.998	0.017
	20	91			
	40	100			
1-RF	10	96	64	0.990	0.038
	20	105.5			
	40	121			
7-RF	10	93	84	0.998	0.007
	20	101			
	40	112			

[a]Corrected for heating rate effect

condensation reactions, Šebenik *et al*[37] found exothermic peak temperatures ($\beta = 4°\text{C min}^{-1}$) ranging from 154°C at 1% NaOH catalyst to 165°C with 0.25% NaOH to 202°C without catalyst.

Effect of heating rate on reactivity ranking

Choosing a much different heating rate results in different rankings. The change of a material's characteristic temperatures with heating rate is determined by the thermal activation energy for the reactions. Scanning calorimetry data are plotted as the logarithm of heating rate *vs* the reciprocal of peak reaction temperature. A straight line is fit to this data, and the slope of the line is put into an equation[38-40] which gives the thermal activation energy:

$$E \cong -18.2 \times 10^{-3} \left[\frac{\Delta(\log\beta)}{\Delta(1/T)}\right]$$

where E is the activation energy (kJ mol^{-1}), β is the heating rate (K min^{-1}) and T is the peak temperature (K).

The activation energies for the resorcinol-related lower-temperature reaction, ranging from 64 to 90 kJ mol^{-1} (see Table 3), compare with a value of 60 kJ mol^{-1}, calculated here from Chow's data[20] on a PRF resin. The condensation reaction of products of initially monomeric resorcinol with formaldehyde has an activation energy[36] of 103-133 kJ mol^{-1}.

The activation energies for the higher-temperature phenolic reaction in the PF and PRF resins ranged from 60 to 147 kJ mol^{-1} (see Table 4). The solid structures formed by the lower-temperature reaction affect the activation energies for the higher-temperature reaction. Literature values for phenolic resins range from 75 kJ mol^{-1} [41] to 100 kJ mol^{-1} [42], and analysis here of Chow and Steiner's[43] data on resoles gave 86 and 99 kJ mol^{-1}. For initially monomeric phenolic compounds reacting with formaldehyde, the activation energies for condensation range from 65 to 75 kJ mol^{-1} [37,41]. Increasing catalyst concentration will decrease the activation energies[37].

The above equation can also be used to estimate relative reactivities at various temperatures. By choosing a peak temperature to equal the temperature of interest, one can calculate the (heating) rate necessary to provide that peak temperature. A faster heating rate corresponds to a faster reaction. Comparisons of reactivities near room temperature are made here by extrapolating heating rates to a reaction temperature of 20°C. These comparisons are more important for the low-temperature reactions (Table 3) which provide the normally observed cure in laminating resins. The estimated relative reactivity of all the resorcinol-based resins studied are in this order:

FR-100 > DFK-14R > 1-RF > 5-PRF > FRF-50
> 8-PRF > 7-RF > 4-PRF

Table 4. Calorimetric data for the higher-temperature curing reaction

Resin	Heating rate, β (K min^{-1})	Peak temperatures[a] (°C)	Activation energy, E (kJ mol^{-1})	Coefficient of determination (r^2)	Calculated rate at 20°C (K min^{-1})
Shale oil-based resin					
DFK-14R	10	174	147	0.942	3×10^{-9}
	20	183.5			
	40	188			
Controls					
FRF-50	10	161.5	60	0.996	0.022
	20	177			
	40	198.5			
5-PRF	10	123.5	108	0.987	5.2×10^{-5}
	20	133.5			
	40	139.5			
4-PRF	10	149.5	117	0.964	2.0×10^{-6}
	20	159			
	40	166			
8-PRF	10	147	72	0.987	8×10^{-4}
	20	164			
	40	176			
6-PF[b]	10	145	91	1.000	7.9×10^{-5}
	20	155.5			
	40	168.5			
	5	139.5	97	0.998	2.9×10^{-5}
	5	141			
	10	149.5			
	20	159.5			
	40	171			

[a] Corrected for heating rate effect

[b] Two lots of commercial resin, of varying freshness

Table 5. Russian data relating to resin reactivity[a]

Resin	Storage life at 20°C (months)	Working life at 20°C (h)	Assembly time at 20°C (min)	Cure time at 20°C (h)
FRF-50	6	3.5	< 150	12-16
DFK-14R	6+	2.5	40-50	12-16
FR-100	6+	1	30-40	10-12

[a] From manufacturer's literature sent with the resins

Thus the alkylresorcinol-based resins seem more reactive at room temperature than the PRF or RF resins studied here. Among the Russian resins the ranking of reactivity would be FR-100 > DFK-14R > FRF-50; this is the same order that is indicated by information on working life, assembly times and cure times published for these resins (see Table 5).

Conclusions

The adhesive resins based on Estonian shale oil are more reactive than the common PRF or RF resins used as controls, judged either by lower reaction temperatures during scans at $10^\circ C\ min^{-1}$ or by rates extrapolated to room temperature. Either one or two exothermic reactions were seen in DSC scans of the various resins: one associated with the resorcinolic components curing at lower temperature, and another associated with phenolic components which cure at higher temperature.

The shale oil resins, as with common resorcinol-containing resins, absorb infrared radiation more strongly than straight phenolic resins at $1140\text{-}1160\ cm^{-1}$ and $1175\ cm^{-1}$, but more weakly at $1020\text{-}1030\ cm^{-1}$. Because of their higher level of substitution in the liquid state, the shale oil resins lack IR absorption peaks usually seen in resorcinolic resins at $960\ cm^{-1}$ and $1480\text{-}1520\ cm^{-1}$. FR-100 shows a strong carbonyl absorption at $1660\text{-}1670\ cm^{-1}$ due to the added urea.

In ^1H-NMR spectroscopy, resins containing phenol have aromatic hydrogen signals from 5.8 to 7.4 ppm. Comparable signals in resorcinol resins range from 5.4 to 7.4 ppm. Resin FR-100 lacks substantial aromatic hydrogen signals between 6.4 and 7.4 ppm, because its major aromatic component, orcinol, also lacks these. Resin DFK-14R, with phenol as a component, gives signals throughout that range.

Oxymethylene groups show ^1H-NMR signals at 4.4-4.8 ppm in resins that are phenolic resols or are known to contain phenolic groups, including DFK-14R. The pure RF resins and FR-100 do not have signals in this region.

The most striking difference in ^1H-NMR spectra between the shale oil resins and the more common phenolic and resorcinolic resins is in the strong and varied signals observed for alkyl groups in the region between 1.6 and 2.8 ppm for the shale oil resins, while the other resins gave no signals there.

The urea in FR-100 gave characteristic signals for unsubstituted amides in the ^1H-NMR spectrum and for carbonyl in the ^{13}C-NMR spectrum.

Solvents retained in resin samples include both ethanol, whose signals vary with sample drying, and ethylene glycol, whose low volatility frustrated its evaporation under vacuum.

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