DOCTORAL THESIS

Synthesis of Modified Resins Based on Resorcinol and Oil Shale Alkylresorcinols: Structure and Properties

Ana Jurkevičiūtė

TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY
TALLINN 2024

TALLINN UNIVERSITY OF TECHNOLOGY
DOCTORAL THESIS
10/2024

Synthesis of Modified Resins Based on Resorcinol and Oil Shale Alkylresorcinols: Structure and Properties

ANA JURKEVIČIŪTĖ

TALLINN UNIVERSITY OF TECHNOLOGY
School of Engineering
Department of Materials and Environmental Technology
This dissertation was accepted for the defence of the degree 14/02/2024

Supervisor:	Dr. Kaia Tõnsuaadu School of Engineering Tallinn University of Technology
Co-supervisor:	Dr. Larisa Grigorieva Laboratory of Fuels Technology Virumaa College School of Engineering Tallinn University of Technology
Opponents:	Prof Sergejs Gaidukovs Department of Polymer Materials Technology Institute of Polymer Materials Faculty of Materials Science and Applied Chemistry Riga Technical University Prof Ričardas Makuška Department of Polymer Chemistry Institute of Chemistry Faculty of Chemistry and Geosciences Vilnius University

Defence of the thesis: 27/03/2024, Tallinn

Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Ana Jurkevičiūtė

----
signature

European Union
European Regional
Development Fund

Investing
in your future

ISSN 2585-6898 (publication)
ISBN 978-9916-80-111-6 (publication)
ISSN 2585-6901 (PDF)
ISBN 978-9916-80-112-3 (PDF)
DOI https://doi.org/10.23658/taltech.10/2024
Printed by Koopia Niini & Rauam

Jurkeviciute, A. (2024). *Synthesis of Modified Resins Based on Resorcinol and Oil Shale Alkylresorcinols: Structure and Properties*. [TalTech Press]. https://doi.org/10.23658/taltech.10/2024

TALLINNA TEHNIKAÜLIKOOL
DOKTORITÖÖ
10/2024

Modifitseeritud vaikude süntees resortsinooli ja põlevkivi alküülresortsinoolide alusel: struktuur ja omadused

ANA JURKEVIČIŪTĖ

TALTECH
KIRJASTUS

Contents

Contents 5

List of Publications 6

Author's Contribution to the Publications 7

Introduction 8

Abbreviations 10

Terms 12

Symbols 13

1 Literature Overview 14
1.1 Aldehyde resins 14
1.2 Non-aldehyde resins 19
1.3 Summary of the literature review and aim of the thesis 21

2 Experimental 22
2.1 Materials used in experiments 22
2.2 Synthesis of resins 22
2.3 Analysis methods used in experimental studies 26

3 Results and Discussion 29
3.1 Formaldehyde and acetaldehyde resins 29
3.2 Non-aldehyde resins 42

Conclusions 48

List of Figures 50

List of Tables 51

References 52

Acknowledgements 57

Abstract 58

Lühikokkuvõte 61

Appendix 65

Curriculum vitae 104

Elulookirjeldus 107

List of Publications

The list of author’s publications, on the basis of which the thesis has been prepared:

I **A. Yurkevichyute**, L. Grigorieva, V. Vassiljev. “Synthesis of Solid Resorcinol-Formaldehyde Resin Modified with Styrene with the Use of a Shale Phenol Fraction with a Boiling Temperature Higher Than 270 °C”, Solid Fuel Chemistry, 50(1), 64–68, 2016, DOI 10.3103/S0361521916010122

II **A. Jurkeviciute**, L. Grigorieva, K. Tõnsuaadu, K. Blum. “Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols”, Materials Research Express, 10(3), 035304, 2023, DOI 10.1088/2053-1591/acc0e1

III **A. Jurkeviciute**, L. Grigorieva, K. Tõnsuaadu, T. Yashicheva, D. Bondarev. “Non-aldehyde resins based on resorcinol and natural alkylresorcinols modified with styrene”, Materials Research Express, 10(10), 105301, 2023, DOI 10.1088/2053-1591/acfd12

Author’s Contribution to the Publications

Contribution to the papers in this thesis are:

I The author performed the preliminary experiments and participated in the planning of all experiments. The author was responsible for performing all resin synthesis experiments. The author performed all the analytical work and analysed and interpreted the data. The author wrote the paper and the accompanying information, with contributions from co-authors, and is the first and corresponding author.

II The author planned all experiments, supervised resin synthesis, coordinated analytical analyses (GC-MS, TG/DTG/DTA, TGA, and GC), and participated in data analysis and interpretation. The author wrote the paper and the accompanying information with contributions from co-authors and is the first as well as the corresponding author.

III The author coordinated the analytical analyses (TG/DTG/DTA, TGA, and GPC) and participated in data analysis and interpretation. The author also significantly contributed to the preparation of this paper.

Introduction

The polymer industry significantly contributes to the global economy. It continues to develop materials that are more resistant and more environmentally friendly compared with those currently in use. Polycondensation resins are an important class of synthetic polymers. Because of their high thermal stability and chemical resistance, polycondensation resins play an important role in the production of insulating materials used in the electronics, aviation, and automotive industries, as well as in composites [1,2] used in the construction and aerospace industries.

Polycondensation oligomers based on phenol (Ph) and formaldehyde (F) are the most common synthetic polymers [3,4]. However, they exhibit several disadvantages: they are hygroscopic, have a high volatile content, and limited shelf life. Depending on their synthesis conditions, commercial resins could contain unreacted Ph (5%–25%) and F. According to the World Health Organisation, Ph and F are highly toxic substances with carcinogenic and mutagenic properties [5-7]. The production and properties of phenol-formaldehyde resins, however, do not meet modern environmental requirements [8,9].

One solution to reduce the environmental impact of Ph and F is to replace them with eco-friendly compounds.

Resorcinol (R) and its derivatives, alkylresorcinols (ARs), could be considered alternatives to Ph. As a rule, synthetic R is used for synthesis of resins. This increases the cost of finished products based on it. An alternative and more promising approach for the synthesis of R is the use of ARs obtained from natural sources. The most important of these natural sources is Baltic oil shale (kuckersite) [10]. In Estonia, ARs are obtained via the thermal processing of oil shale using Kiviter technology [11]. Studies on the possibility of synthesising resins from oil shale ARs and the applications of those resins have been conducted since the 1960s [12,13]. Most of these studies have been conducted between 1971 and 1993. Oil shale ARs (ALKYREZ fraction) produced by oil shale processing companies in Kohtla-Järve and Kiviõli have been used as raw materials [15]. Viru Keemia Grupp (VKG, Kohtla-Järve, Estonia) is the only company that commercially extracts and processes oil shale ARs. The company produces individual ARs, such as 5-MR and 2.5-DMR, as well as fractions containing large amounts of 5-MR (HONEYOL 50, HONEYOL 80, and REZOL). Early research on the use of ARs as raw materials mainly focused on the production of formaldehyde resins [15].

Instead of F, lower members of the homologous series of aliphatic aldehydes can be used [16-18]. Their use in reaction with R and its derivatives (ARs) allows the synthesis of novolac resins [17].

In the polycondensation process, low-molecular-weight compounds, such as water, are produced as by-products. This water also contains some unreacted compounds. The recycling and purification of that water require additional resources. Moreover, the complete removal of residual moisture from the resin via distillation is not possible. Thus, water vapour could be formed in the molten polymer mass during moulding. Voids formed in the composite deteriorate the mechanical properties of the resin [19]. This disadvantage can be eliminated by using non-aldehyde resins. The synthesis of non-aldehyde resins is currently considered the most progressive direction taken so far regarding polymers.

Depending on the requirements of various industries, the properties of resins can be significantly improved or altered through modifications. Although R imparts good mechanical and adhesion properties to rubber composites, it evaporates during compounding at temperatures above 110°C. The introduction of a modifier, such as aromatic alkene or styrene (S) [20], into the formulation partially overcomes the problems associated with R fuming, which facilitates resin processing. The evaporation of R could be completely reduced only if it contains either no free R at all or less than 1.0 wt% of R [21]. The S-modified resin dissolves well in the butadiene-styrene rubber base of the composite. The availability of a wide range of modifiers for the synthesis of non-aldehyde resins, including those based on R, makes it possible to obtain environmentally safe polymer matrices with improved technical characteristics.

In this study, formaldehyde resins (SF), acetaldehyde resins (SAc), and non-aldehyde resins (DCPDS) based on oil shale ARs (5-MR, 2.5-DMR, REZOL, HONEYOL 50, and HONEYOL 80) and their mixtures with R pre-modified with S were synthesised for the first time. The chemical structures of the products obtained, which explain the role of additives in the process, were studied using nuclear magnetic resonance (NMR) spectroscopy, thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), and gel permeation chromatography (GPC), followed by a comprehensive characterisation study.

This thesis consists of three sections. In Section 1, the patents and literature on the polycondensation of aldehyde (F and acetaldehyde) and non-aldehyde resins are reviewed. In Section 2, the characteristics of the initial components, methods used to analyse them, synthesised resins, synthesis conditions, and preparation of the samples used in the chromatographic analysis are described. In Section 3, the results presented in Sections I-III are discussed.

Publication I presents the data used in the preliminary studies on the preparation of a qualitatively new solid (alkyl)resorcinol-formaldehyde resin modified with S. In the resin, synthetic R has been partially or completely replaced by the REZOL fraction. Publication II demonstrates that in resins based on R, 5-MR, HONEYOL 50, and REZOL, the highly toxic F could be replaced with the more environmentally friendly aliphatic aldehyde acetaldehyde (Ac). It also discusses the various styrene interactions with 5-MR and 2.5-DMR and the pathways that would lead to the formation of aldehyde oligomers. Publication III is devoted to the synthesis and analysis of solid non-aldehyde resins based on HONEYOL 80 that have improved environmental and technological characteristics, the study of their molecular weight distributions using GPC, and a discussion of the results.

In addition to the above-mentioned publications, the author has presented papers at several international conferences held in Estonia, the United States, Thailand, and Russia.

Abbreviations

Ac	Acetaldehyde
ALKYREZ	Fraction of oil shale alkylresorcinols with a boiling point of 273–305 °C
ARs	Alkylresorcinols
DCPD	Dicyclopentadiene
DCPDS	General designation of resins with dicyclopentadiene
2.5-DMR	2.5-Dimethylresorcinol
2.5-DMRSAc	2.5-Dimethyl-resorcinol-acetaldehyde resin modified with styrene
DTG	Derivative thermogravimetry
5-ER	5- Ethylresorcinol
F	Formaldehyde
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GPC	Gel permeation chromatography
HMDS	1.1.1.3.3.3-Hexamethyldisilazane
Hon80$_{100}$DS	Alkylresorcinol-styrene-dicyclopentadiene resin based on the HONEYOL 80 fraction
HONEYOL 50	Fraction of oil shale alkylresorcinols with a boiling point of 270–320 °C
HONEYOL 80	Fraction of oil shale alkylresorcinols with a boiling point of 270–320 °C
Hon50$_{100}$SAc	Resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene based on the HONEYOL 50 fraction
5-MR	5-Methylresorcinol
5-MRDS	5-Methyl-resorcinol-styrene-dicyclopentadiene resin
5-MRSAc	5-Methyl-resorcinol-acetaldehyde resin modified with styrene
5-MRSF	5-Methyl-resorcinol-formaldehyde resin modified with styrene
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
Ph	Phenol
PMMA	Poly(methyl) methacrylate
PS	Polystyrene
R	Resorcinol
REZOL	Fraction of oil shale alkylresorcinols with a boiling point >270 °C
RF	Resorcinol-formaldehyde resin
RDS	Resorcinol-styrene-dicyclopentadiene resin
Rez$_{100}$SAc	Resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene based on the REZOL fraction
Rez$_{100}$SF	Alkylresorcinol-formaldehyde resin styrene-modified based on the REZOL fraction
R$_{70}$Hon80$_{30}$DS	Resorcinol-alkylresorcinol-styrene-dicyclopentadiene resin with the HONEYOL 80 fraction replacing 30 mol% resorcinol

$R_{50}Hon80_{50}DS$	Resorcinol-alkylresorcinol-styrene-dicyclopentadiene resin with the HONEYOL 80 fraction replacing 50 mol% resorcinol
RSF	Resorcinol-formaldehyde resin modified with styrene
$R_{90}Rez_{10}SF$	Resorcinol-alkylresorcinol-formaldehyde resin modified with styrene and with the REZOL fraction replacing 10 mol% resorcinol
$R_{70}Rez_{30}SF$	Resorcinol-alkylresorcinol-formaldehyde resin modified with styrene and with the REZOL fraction replacing 30 mol% resorcinol
$R_{70}Rez_{30}SAc$	Resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene and with the REZOL fraction replacing 30 mol% resorcinol
RSAc	Resorcinol-acetaldehyde resin modified with styrene
RTM	Resin transfer moulding
S	Styrene
SAc	General designation used for resins with acetaldehyde
SF	General designation used for resins with formaldehyde
TA	Thermal analysis
TGA	Thermogravimetric analysis
TLC	Thin-layer chromatography
p-TSA	*para*-Toluenesulfonic acid

Terms

Aldehyde resins	Formaldehyde and acetaldehyde resins together
(Alkyl)resorcinols	Resorcinol and alkylresorcinols together
Aralkylation	Interaction of resorcinol and/or alkylresorcinols with the aromatic alkene (styrene)
Non-aldehyde resins	Resins obtained through the interaction of resorcinol and/or alkylresorcinols with dicyclopentadiene and styrene
Polycondensation	Interaction of resorcinol and/or alkylresorcinols with aldehydes (formaldehyde and acetaldehyde)

Symbols

$T_{\text{start of dec.}}$	Temperature at the beginning of resin decomposition
T_b	Boiling temperature
G'	Dynamic modulus of elasticity
tg Δ	Dielectric loss angle
τ_{10}, τ_{50}, τ_{90}	Loss temperature 10, 50, 90 wt%
M_n	Average molar mass
M_i	Molecular weight of the i^{th} component
N_i	Number of moles in the i^{th} component
n	Number of repeating units in an oligomer or polymer
M_w	Weighted average molecular weight
N	Nitrogen content
W	Moisture content

1 Literature Overview

1.1 Aldehyde resins

Aldehyde resins include a mixture of oligomers obtained through polycondensation of Ph, R, or their homologues with aldehydes, mainly F. Aldehyde resins based on Ph and R are widely used in fields ranging from technology to everyday life. Most of the early research have focused on formaldehyde resins, because formalin was produced in large quantities and was the cheapest raw material.

However, the traditional raw materials (Ph and F) used to produce aldehyde resins are toxic and harmful to the environment and human health. Increasing attention is being paid to alternative raw materials use, preferably of natural origin and more environmentally friendly [22,23]. Obtaining resins based on such kind of alternatives is a primary task.

1.1.1 Formaldehyde resins

The environmental safety of aldehyde resins can be increased by replacing Ph with R or ARs. Resorcinol-formaldehyde (RF) novolac resins are produced through the polycondensation of R with F under acidic catalytic conditions.

The reaction of interaction of R with F in an acidic medium has already been studied in detail [17,24]. The condensation reaction between R and F when a R deficiency is present is similar to that between R and Ph. However, the reactivities of R and F differ. The reaction rate of R is 12.2 times higher than that of Ph [17]. Therefore, different reaction products can be formed (Figure 1). Because of the high reactivity of R, its polycondensation reaction with F produces a mixture of oligomers (dimers, trimers, tetramers, etc.) with different methylene-bridged structures.

The ARs obtained from oil shale processing can be used instead of R. They are multifunctional compounds that are capable to react involving carbon atoms in the nucleus or side chain. The ARs fractions ALKIREZ, REZOL, HONEYOL are used as raw materials in alkylresorcinol resin production [15,24,25]. An alkaline catalyst had been used to obtain alkylresorcinol-formaldehyde resins based on oil shale ARs [15]. The SF281 resin, prepared using the recipe described in its patent [15], is unstable and can change its technical characteristics while in storage. This change in the technical characteristics of the SF281 resin significantly affects the performance of rubber containing the resin. The storage of SF281 near heating devices or at temperatures >25 °C leads to its caking and further polycondensation. The content of mechanical impurities in the resin increases, leading to a decrease in solubility in acetone. The patent [25] provides data on the use of 5-MR and its technical mixture ALKYRES for the preparation of m-cresol-alkylresorcinol-formaldehyde copolymer. A mixture of water and methanol was used as the solvent in this preparation. The resin had an orange colour and a rather high softening point of 110–180 °C. Its average molar mass was between 500 and 750 g/mol.

The molar ratios of the initial components used in resin preparations affect the final resin characteristics [20]. Resorcinol-(alkylresorcinol)-formaldehyde resins based on the HONEYOL 80 fraction obtained from the patent [20] contain 8 wt% to 22 wt% of unreacted resorcinol components.

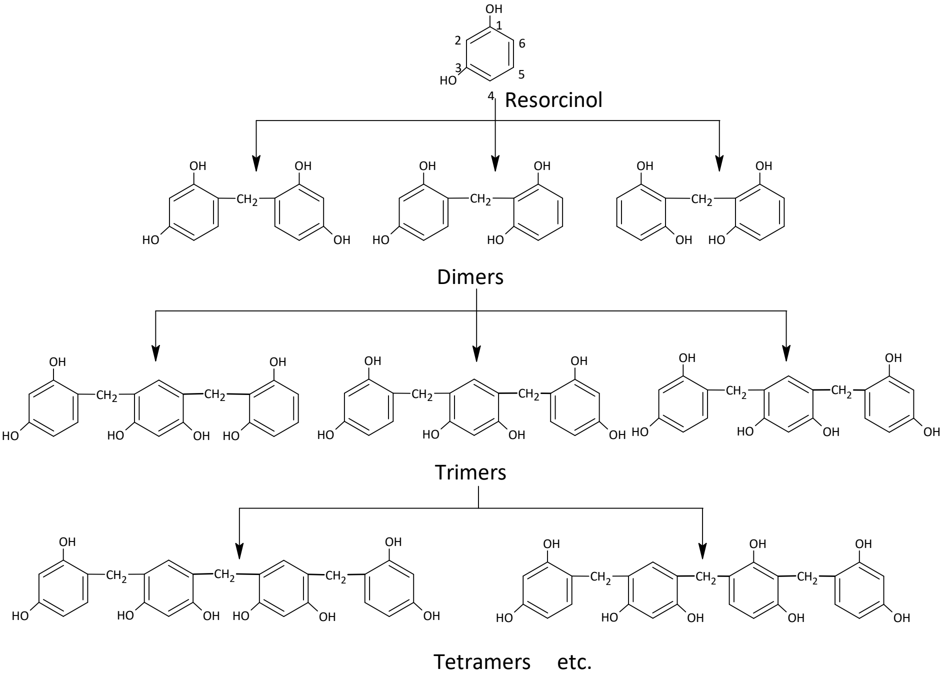


Figure 1. Structural diagrams of the linear oligomers of resorcinol and formaldehyde.

The alkyl derivative interactions of R (5-MR, 5-ER, and 2.5-DMR) were considered in [13, 24]. The direction of condensation of R and its alkyl derivatives with F is practically independent of the catalyst and reaction medium used. However, the reaction rate will significantly vary depending on the solvent used. The reaction proceeds best in water [13]. The intensity of reaction between alkylresorcinol fraction components and F is not uniform and increases in the following order: 4.5-DMR < 5-ER < 2.5 DMR < 2-MR < 5-MR [26]. According to [10], the rate of interaction between pure 5-MR and F is 80 times higher than that of the similar reaction with R. Table 1 presents the relative reaction rates of phenolic components.

Table 1. Relative reaction rates of alkylresorcinols [28].

Phenolic compound	Comparative rate
R	1
5-MR	96
Mixture of oil shale ARs	4.3

Early studies determined that the reaction centres in the 5-MR molecule are more prone to electrophilic substitution reactions. Specifically, the methyl group at the *meta*- position strongly activate the *ortho*- and *para*- positions of R [29].

The electronic charges present in the carbon atoms of R and ARs are listed in Table 2 [29]. The data presented indicate that the addition of F predominantly occurs at the *ortho*- positions.

Table 2. Charge distributions (q_C) in the R, 5-MR, 5-ER, and 2.5-DMR molecules [29].

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
R	0.207	-0.106	0.207	-0.087	0.052	-0.087	-	-
5-MR	0.214	-0.131	0.213	-0.106	0.102	-0.117	-0.099	-
5-ER	0.213	-0.119	0.213	-0.110	0.087	-0.110	-0.013	-0.008
2.5-DMR	0.184	-0.055	0.184	-0.107	0.089	-0.108	-0.077	-0.097

The behaviour of the hydrogen atoms of the aromatic nuclei or hydroxyl groups during substitution reactions as well as the properties of the resulting products enable the use of ARs as substitutes for R in the synthesis of resins [15,24,25].

In [30], a method of producing RF resins using sulphuric acid (H_2SO_4) with a low water content is presented. The softening points of the resins are in the range of 99–109 °C. However, other important technical data, such as the ash and moisture contents of the resins and the amount of unreacted R in them, are not presented.

Despite their positive properties, such as their high adhesion ability and long shelf life [31], RF resins have several disadvantages as well. One main disadvantage is the increase in resin volatility during both resin storage and operation [21].

1.1.1.1 Modified formaldehyde resins

Depending on the requirements of various industries, the properties of resins can be significantly improved or changed by modification. Aromatic [20] and aliphatic alkenes [32], as well as poly(styrene-co-divinylbenzene) [33], can be used as modifiers. The simultaneous use of several modifying agents is also possible [34]. The interactions of R with various organic compounds, producing resins with different properties based on already modified R, are presented in [17].

The introduction of a radical with a reactive allylic double bond into the aromatic core of the initial two-atomic Ph through the alkenylation of phenols and their alkyl derivatives with dienes and allyl halides increased the heat resistance of the SF281 resin [32]. The alkenylating agents used were piperylene hydrochloride and piperylene [32]. The additives increased the thermomechanical stability of the vulcanizates and retarded the release of volatile decomposition products during rubber compound processing.

The aromatic or aliphatic alkene introduced into the aromatic core of initial R improved the compatibility between the resin and butadiene-styrene rubber [21]. The preliminary aralkylation of the resorcinol resin components with aromatic alkene (S) could reduce the amount of volatile substances emitted from the RF resin during its processing, storage, and operation.

Alkylation of Ph, the phenolic fraction, R, and the alkylresorcinol fraction of HONEYOL 80 and its mixture with R using S are presented in the relevant patents [20, 35-37]. Increasing the molar amount of S in the formulation decreases its total unreacted R and ARs contents. In addition, the likelihood of the formation of polystyrene increases, and the softening point of the finished resin decreases. Moreover, ARs obtained via oil shale processing can be used in place of synthetically alkylated R. Patent [20] states that the pre-aralkylation of the alkylresorcinol fraction of HONEYOL 80 enables the production of resins with low AR contents without deteriorating the technological characteristics of the resins. The amount of S added is in the range of 0.25–1.0 mol (S) per 1.0 mol R. The quality control of the finished resin was performed based on the softening point. However, increasing S in the formulation leads to the fact that not all styrene reacts with the resorcinol component [35].

By varying the molar ratio of R, alkylresorcinol fraction, S, and F, it is possible to obtain novolac resins with different softening points and free R contents. The hydrophobic properties of the styrene groups in the novolac structure reduce the hygroscopicity of the resin [17].

1.1.2 Acetaldehyde resins

The next approach for synthesising polycondensation resins is to use Ac instead of F [38-40]. The raw materials used to produce acetaldehyde resins include Ph [38,41], alkylphenols [38,42], and a mixture of phenols obtained from the bio-oil fractions of beech wood [43] and R [17,38,44,45]. According to [20,46,47], pre-alkylated Ph and R can be used as a resorcinol component. Despite the natural origin of phenols in [43], they are more toxic than resorcinols.

Acetaldehyde resins have been synthesised using pure Ac [38,42,43] in the presence of solvents [41,48]. The solvents used were either protoactive solvents, such as water, methanol, ethanol, butanol, acetone, and dioxane, or protoinert solvents, such as benzene, carbon tetrachloride, and dichloroethane. By using benzene as the solvent, it would be possible to obtain rapidly curing thermoplastic resins with linear structures [41] and a softening point between 75 and 100 °C. When carbon tetrachloride is used as the solvent, the softening point of the resin significantly increases, reaching a value between 150 and 160 °C. Polar organic solvents can be used to facilitate smooth reactions and improve ARs solubility [44,47]. Different proportions of ethanol/water-mixed solvents can also be used. Reducing the amount of ethanol in the ethanol/water reaction medium increases its polarity. The polarity of the medium affects not only the yield and composition of the reaction products but also the reaction time.

The proposed oligomeric chain growth during the reaction between Ac and R (Figure 2) predominantly occurs via the dihydroxyalkyl derivatives of R and its dimeric products [44].

The synthesis time of resins depends on the type of solvent and catalyst used and can be in the range of 3–24 hours [43,44,49]. Acidic organic and inorganic catalysts, including sulfuric [50], hydrochloric [42-44,48], acetic and trichloroacetic [41], oxalic [49] acids, and *para*-toluene sulfonic acids (*p*TSA) [20], are mainly used to produce acetaldehyde resins. In [38,45], it was proposed to use an aqueous 50% NaOH solution as an alkaline catalyst.

R and Ac were used as a raw material and a crosslinking agent, respectively, to synthesise resorcinol-aldehyde hydrogels in a weak and basic aqueous solution via sol-gel polycondensation [45].

When organic catalysts such as trichloroacetic acid and non-polar solvents (benzene or carbon tetrachloride) were used, the synthesis time was between 3 and 5 h. With the same catalyst but with water as the solvent, the synthesis performed at 90 °C required at least 5 h [41]. In the absence of a solvent but in the presence of oxalic acid, the duration of the synthesis increased to 6 h [49]. When an inorganic catalyst (hydrochloric acid) was used in a polar solvent (ethanol), the polycondensation reaction occurred within 5–24 h [44]. The amount of catalyst used also affected oligomeric product formation. Increasing the amount of HCl to equimolar amounts can lead to an increase in the resin content of the high-molecular-weight linear oligomers.

In [38], a method of producing acetaldehyde resin using water as the solvent and without a catalyst under supercritical conditions (347 °C and 22.1 MPa) is described. By conducting polycondensation under those conditions, the degree of resin polymerisation can be increased without producing resin gelation. Gelation is an undesirable process that leads to the formation of insoluble three-dimensional polymer structures.

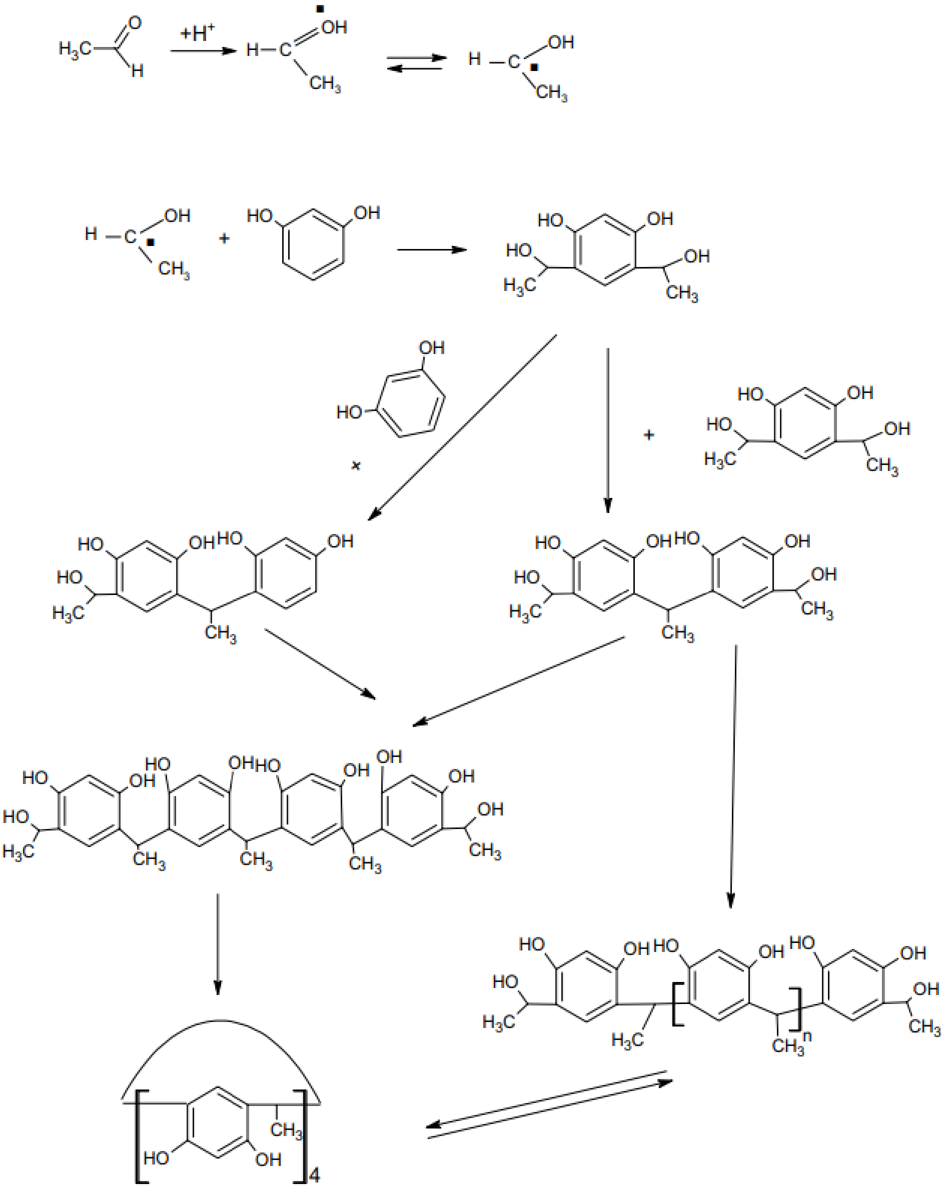


Figure 2. Proposed mechanism of polycondensation and oligocyclization [47].

The formulation of acetaldehyde resins and their method of production influence the final characteristics of the finished resin. The softening points of acetaldehyde resins based on Ph and R have a wide range of from 40 to 160 °C [20,41,44]. The dependence of softening point on the aldehyde/resorcinol ratio is shown in Figure 3 [17].

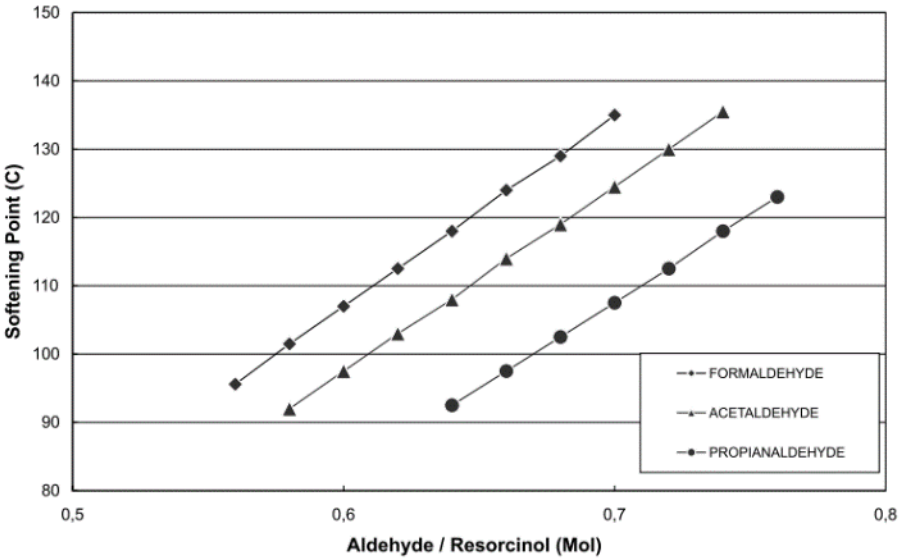


Figure 3. Softening point versus aldehyde/resorcinol ratio curve [17].

Because of its low boiling point (Tb ~20 °C), the use of Ac leads to some difficulties when introducing it into the reaction mixture. Thus, specialised equipment with additional cooling is required to synthesise resins using Ac. Due to insufficient cooling, some amount of Ac may vaporise, releasing large amounts of it into the environment.

1.2 Non-aldehyde resins

Since the focus of modern research is on the development of alternative solutions to replace phenol-formaldehyde resins, the most promising direction may be the production of formaldehyde-free resins. The synthesis of formaldehyde-free resins is presented in [20,21,51-56]. Using various variants of resin modifications [21,53,57,58], including those based on R [52,59,60], resins with improved technical and operational characteristics that meet the modern requirements for environmental safety could be obtained.

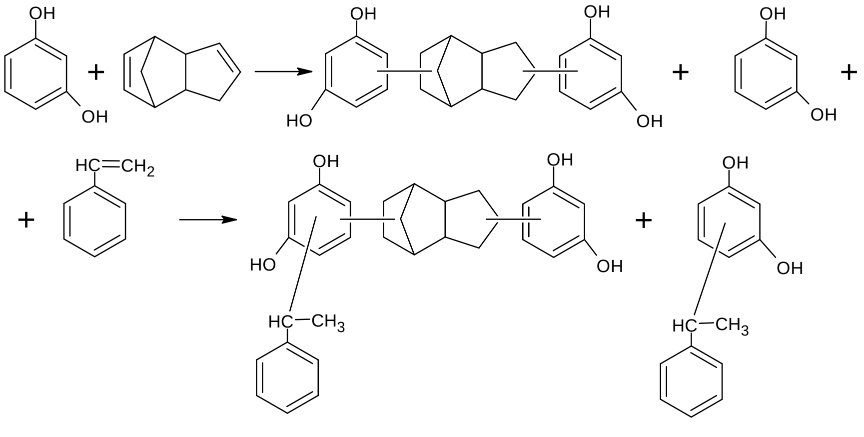


Figure 4. Non-formaldehyde resorcinolic resin synthesis [17].

R-based resins typically contain large amounts of R (up to 20 wt%). During their compounding, free R begins to smoke [21], while during their storage, unreacted R is salted out on the rubber compound surfaces owing to the high hygroscopicity of the resin. This phenomenon leads to the uneven adhesion of rubber to the reinforcing material, which adversely affects the quality of its vulcanised products. The use of modifiers comprising non-conjugated dienes (such as dicyclopentadiene (DCPD), dimethyl dicyclopentadiene, and dipentene), N-methylol-acrylamide caprolactam, and/or styrene eliminates these disadvantages [21,61,62] and produces resins with low resorcinol contents (from 0.95 to 4.5 wt%). Additionally, the mechanical properties of the resins, such as the modulus of elasticity and relative elongation, were improved.

One of the advantages of synthesising non-fuming resorcinol resins using S and DCPD, as shown in [21], is the ability to obtain a resin with a low R content of up to 1 wt%. Moreover, this method does not produce large amounts of waste and can be used at a low temperature and pressure.

At high temperatures, R readily reacts with dicyclopentadiene (DCPD) in the presence of an acid catalyst. Both inorganic acids, such as H_2SO_4 and phosphoric acid (H_3PO_4), as well as aromatic and aliphatic sulfonic acids, can be used as catalysts [21,61,62]. However, the most preferred catalyst is *para*-toluene sulfonic acid (p-TSA), which does not lead to an increase in mechanical impurities present in the resin.

Table 3. Test results pertaining to rubber compounds [21].

Methylene acceptor:	**<R**	**R/DCPD/S (1.0 : 0.4 : 1.0)**	**R/DCPD/S (1.0 : 0.3 : 1.2)**	**R/DCPD/S (1.0 : 0.25 : 1.25)**
Fuming at 120° C	Very High	None	None	None
Dynamic Properties - 0.2% Strain				
G′, MPa	18.92	23.83	23.34	21.93
tg Δ	0.089	0.079	0.085	0.086
Dynamic Properties - 2.0% Strain				
G', MPa	9.96	13.25	12.75	12.03
tg Δ	0.239	0.228	0.244	0.245
Hardness, Shore A	77	80	79	78
Tensile Properties				
100% Modulus, MPa 300% Modulus, MPa	4.23 17.15	4.43 17.23	4.24 16.35	4.18 16.34
Strength, MPa	26.57	26.83	26.65	25.89
Elongation, %	451	459	471	455
Energy to Break, N·m	23.94	24.36	25.37	23.38
Tear Strength (Die-C), KN/m	118.3	129.1	117.0	122.8

The R:DCPD molar ratio is important for obtaining a resin with the desired softening point and free R content. Figure 4 shows one of the possible reactions resulting from the interaction of R with DCPD and S.

The comparative properties of vulcanised rubbers obtained using R and resorcinol-dicyclopentadiene-styrene resin (RDS) synthesised with different molar ratios of the components [21] are shown in Table 3 to enable their comparison. The comparison demonstrated the behaviour of the rubber composite with the addition of R and RDS separately during curing, along with its physical and mechanical properties.

Table 3 shows that the incorporation of RDS into the rubber composite results in an improvement in the sub-vulcanisation time along with a slight increase in the cure time. The results of mechanical and dynamic tests also indicate the improvement of the important properties of the composites containing RDS. Particularly, the strength, hardness, and dynamic modulus of elasticity (G) of the composites are improved, while the tangent of the dielectric loss angle (tg Δ) is reduced. As a result, rubber composites in which RDS has been used have higher efficiency and better performance compared with rubber composites containing R.

1.3 Summary of the literature review and aim of the thesis

The literature review demonstrates the possibility of producing formaldehyde, acetaldehyde, and non-aldehyde resins using monoatomic phenols or R. The search for more environment-friendly raw materials that can be used in resin production has revealed the advantages that R and ARs have over phenol.

The aim of the early studies employing the alkylresorcinol fractions (ALKYREZ and HONEYOL 80) produced from oil shale at the Viru Keemia Grupp in Estonia was to produce formaldehyde resins. To improve technological conditions and elucidate the impact of S to oil shale ARs the reaction mechanism of S addition to ARs on the reaction of polycondensation; the structure and the composition of new acetaldehyde and non-aldehyde resins; as well as the thermal behaviour of formaldehyde, acetaldehyde and non-aldehyde resins in inert and oxygen environments had to be studied. Information should also be obtained on the physicochemical and technological characteristics of new resins. The full physicochemical and technical characteristics of the (alkyl)resorcinol resins obtained from oil shale raw materials are required to optimise the technological process as well as for finding their new applications.

The aim of this study was to obtain novel environmentally friendly resins (formaldehyde, acetaldehyde, and non-aldehyde resins) using local raw materials, such as oil shale ARs, both individually (5-MR, 2.5-DMR) and as a part of industrially produced fractions (REZOL, HONEYOL 50, and HONEYOL 80 fractions).

To achieve this aim, the following tasks had to be performed: replacement of Ph present in phenol-formaldehyde resins with R or ARs; reduction of the amount of volatile and unreacted compounds in resin using S modification; replacement of F in the composition with other less toxic aldehydes, such as Ac; removal of aldehydes from the resins using S or DCPD (for improved compatibility with rubber); studying the structure of the resins using NMR, TLC, GC-MS, and GPC; and studying the physicochemical and technical characteristics of the resins obtained under optimal synthesis conditions.

2 Experimental

This chapter presents the characteristics of the raw materials, analytical methods, formulations, and methods of synthesis related to aldehyde and non-aldehyde resins described in Publications I–III.

2.1 Materials used in experiments

Individual resorcinol components, such as R (99.9 wt%), 5-MR (99.97 wt%), and 2.5-DMR (99.43 wt%), were used as the raw materials. In addition, the study was conducted using the industrial fractions of water-soluble oil shale ARs, which have boiling points >270 °C for REZOL and in the range of 270–320 °C for HONEYOL 50 and HONEYOL 80. The contents of the main ARs in the fractions that were determined using GC are presented in Table 4.

Table 4. Characteristics of the fractions of water-soluble oil shale alkylresorcinols.

Component, wt%	Fraction		
	HONEYOL 50 (T_b = 270÷320 °C)	HONEYOL 80 (T_b = 270÷320 °C)	REZOL (T_b ≥ 270 °C)
Monatomic phenols	0.02	0.02	0.4
Resorcinol (R)	2.9	0.6	2.8
5-methylresorcinol (5-MR)	55.2	88.7	43.0
5-ethylresorcinol (5-ER)	9.1	5.2	12.0
2.5-dimethylresorcinol (2.5-DMR)	8.2	2.8	4.1
2-methylresorcinol (2-MR)	0.4	0.1	0.3
4-methylresorcinol (4-MR)	2.5	0.1	1.7
4.5-dimethylresorcinol (4.5-DMR)	7.6	1.2	8.3
Nitrogen (N)	0.3	0.3	0.3

The composition of HONEYOL 50 and REZOL is comparable, but HONEYOL 80 exhibits an approximately two-fold increase in 5-MR content and a reduced concentration of R, 5-MR, and 4.5-DMR.

Formaldehyde (formalin containing 37.4 wt% F) and acetaldehyde (99.5 wt%) were used as the condensing agents; dicyclopentadiene (>93 wt%) and styrene (>99 wt%) were used as the modifiers in the resin synthesis. Before the synthesis, S and DCPD were distilled and purified.

A 1M solution of H_2SO_4 and *p*-Toluenesulfonic acid was used as the catalyst. The catalyst was neutralised using a 40% NaOH solution.

Industrial fractions, individual R, ARs, and *p*-TSA were provided by the Viru Keemia Grupp. All other chemicals (e.g., toluene, acetone, and ethanol) were purchased from Sigma Aldrich, Penta and were of analytical grade.

2.2 Synthesis of resins

2.2.1 Formaldehyde resins

The synthesis recipes to be followed were selected based on the data obtained from a preliminary patent [15,20,25,30,37,39,63-65]. It is known that novolac (thermoplastic) oligomers are synthesized by reacting (alkyl)resorcinol with F in the presence of acid catalysts. As a result of the reaction, novolac formaldehyde oligomers with predominantly linear structures have been formed [17,24]. If cross-linking and/or gelation are to be prevented in novolac resins [65], the molar ratio of R to aldehyde would have to be >1. The amount of styrene present affects the completeness of the reaction with (alkyl)resorcinols. A large excess of styrene with respect to the resorcinol component can lead to a significant amount of unreacted styrene remaining in the finished resin that must be removed by distillation. Moreover, polystyrene could also form [66]. This phenomenon would negatively affect the resin properties.

The use of dibasic H_2SO_4 as the catalyst significantly reduces the amount of catalyst introduced into the reaction mass. Moreover, because dibasic H_2SO_4 inexpensive, it is often used in the manufacture of chemicals.

Table 5. Molar ratios of the initial components used in preparing formaldehyde resins.

Initial component, [mol]	Sample name						
	RF	RFS*	RSF	5-MRSF	$R_{90}Rez_{10}SF$	$R_{70}Rez_{30}SF$	$Rez_{100}SF$
	1	2	3	4	5	6	7
R	1	1	1	-	0.9	0.7	-
5-MR	-	-	-	1	-	-	-
Fraction REZOL	-	-	-	-	0.1	0.3	1
Styrene	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Formaldehyde	0.5	0.5	0.5	0.5	0.5	0.5	0.5

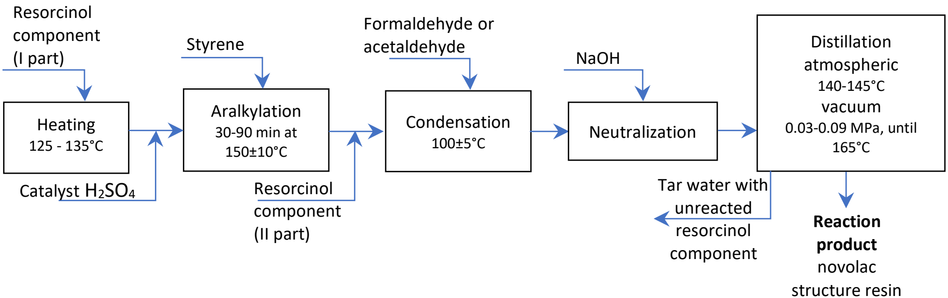
* route I

Formaldehyde resins (SF) are produced in two ways. In one method (hereinafter referred to as the route I), an aralkylating agent (styrene) is added to the entire calculated amount of (alkyl)resorcinol. In the other method (hereinafter referred to as the route II), the total amount of (alkyl)resorcinol is divided into two parts: the first part is aralkylated, and the second part of (alkyl)resorcinol is added to the reaction mass. At the end of the synthesis, atmospheric distillation followed by vacuum distillation are conducted to remove the water resulting from the polycondensation reaction as well as the water added with formaldehyde (37.4%) and the catalyst (H_2SO_4). The molar ratios of the initial materials are listed in Table 5. The same amount of catalyst (0.023 mol) was used in each synthesis. The synthesis block diagram is shown in Figure 5.

In Publications I, II, and III, the resins SF were mostly obtained using the second method, with the exception of $Rez_{100}SF$. According to Publication I, unmodified R was used to synthesise RF resins.

2.2.2 Acetaldehyde resins

Literature and patents referring to Ac resins indicate that they can be obtained either in the presence of solvents (e.g., water) or by directly introducing pure Ac into the reaction mixture [18,20,45,47,48,50,67]. However, once a reaction has been performed in a solvent, it might not be possible to completely remove the solvent from the resin.



Resorcinol component – R, 5-MR, 2.5-DMR, fractions of oil shale ARs (fractions REZOL, HONEYOL 50)

Figure 5. Block diagram of the synthesis of formaldehyde and acetaldehyde resin (route II).

The resulting resin exhibited poor technical characteristics, contained a large amount of water, and was viscous. The drying of these resins is difficult. The polycondensation reaction rate of the resin was several times lower than that obtained using pure Ac. Thus, in all subsequent experiments, pure Ac was used.

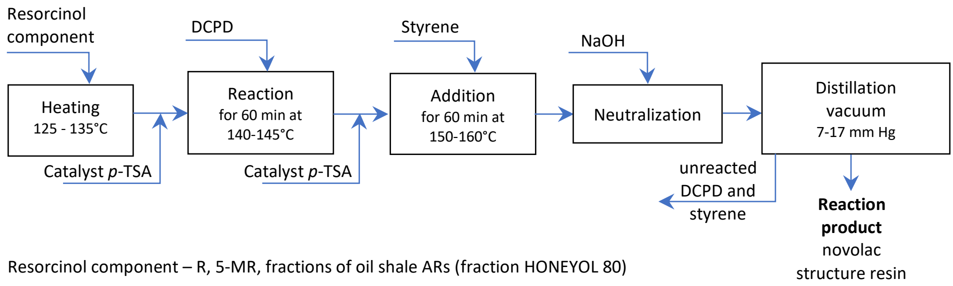
Table 6. Molar ratios of the initial components used in the synthesis of acetaldehyde resins.

Initial component, [mol]	Sample name					
	RSAc	5-MRSAc	2.5-DMRSAc	Hon50$_{100}$SAc	R$_{70}$Rez$_{30}$SAc	Rez$_{100}$SAc
	1	2	3	4	5	6
R	1	-	-	-	0.3	-
5-MR	-	1	-	-	-	-
2.5-DMR	-	-	1	-	-	-
Fraction REZOL	-	-	-	-	0.7	1
Fraction HONEYOL 50	-	-	-	1	-	-
Styrene	0.2	0.2	0.2	0.2	0.2	0.2
Acetaldehyde	0.5	1	0.75	0.75	0.75	0.75
Catalyst H_2SO_4	0.023	0.026	0.031	0.093	0.033	0.055

In Publication II, SAc was synthesised using the second method for producing SF (Figure 5). Depending on the aldehyde used, the resorcinol/aldehyde ratio affects the final softening point of resins [17]. The ratios of the initial substances and the synthesis conditions used in the experiments are listed in Table 6. The use of an appropriate reagent ratio ensured the production of thermoplastic solid resins. The amount of catalyst used varied from 0.023 to 0.093 mol, depending on the initial resorcinol content. It is known that industrial fractions (HONEYOL 50, REZOL) contained various pyridine bases [68]. Their amount converted on nitrogen in the fractions is indicated in Table 4. Pyridine bases interact with the acid catalyst. Thus, the calculated quantities of catalyst should be increased based on the values of nitrogen presented in Table 4.

2.2.3 Non-aldehyde resins

Non-aldehyde (DCPDS) resins were synthesised according to recommendations given in the literature [21,61,69]. DCPD and S were used as modifiers. A block diagram is shown in Figure 6.



Resorcinol component – R, 5-MR, fractions of oil shale ARs (fraction HONEYOL 80)

Figure 6. Block diagram showing the synthesis of non-aldehyde resins

The initial materials used in the experiments were obtained based on the molar ratios listed in Table 7. The catalyst used was *p*-TSA (0.005 mol). HONEYOL 80, containing 88.7 wt%, was selected as the raw material. 5-MR and a minimal amount of long-chain (nine or more carbon atoms) ARs [70].

Table 7. Molar ratios of the initial components used in the synthesis of non-aldehyde resins.

Sample name	Initial component, [mol]				
	R	5-MR	HONEYOL 80	DCPD	Styrene
RDS$_1$	1.0	-	-	0.4	1.0
RDS$_2$	1.0	-	-	0.4	1.0
RDS$_3$	1.0	-	-	0.4	1.0
RDS$_4$	1.0	-	-	0.5	0.7
RDS$_5$	1.0	-	-	0.5	0.3
5-MRDS	-	1.0	-	0.5	0.3
H80$_{100}$DS	-	-	1.0	0.5	0.3
R$_{70}$Hon80$_{30}$DS	0.7	-	0.3	0.5	0.3
R$_{50}$Hon80$_{50}$DS	0.5	-	0.5	0.5	0.3

The number of moles in REZOL, HONEYOL 50, HONEYOL 80 was calculated based on their average molecular weight M_n:

$$M_n = \frac{\sum_{i=1}^{\infty}(N_i \times M_i)}{\sum_{i=1}^{\infty} N_i} \qquad (1)$$

where N_i - the number of moles of the *i*-th component of the HONEYOL or REZOL fraction, M_i - the molecular weight of the *i*-th component of the HONEYOL or REZOL fraction.

2.3 Analysis methods used in experimental studies

This chapter presents data on physicochemical and analytical methods used in studying the properties of the resin samples, describing the preparation of the initial resorcinol components (R, 5-MR, 2.5-DMR, REZOL, HONEYOL 50, and HONEYOL 80) and synthesised resins required for chromatographic analyses.

2.3.1 Analytical methods

The main physicochemical resin parameters, such as the softening point [71], moisture content [72], volatile content [73,74], ash content [75,76], coke number [75], and the amount of unsaturated compounds in the distillate [77], were determined using standard methods.

The softening point was determined using a modified ring-and-ball method [73]. In this study, glycerine was used in the heating bath instead of water, considering the softening point of the resins (~100 °C).

The moisture contents in RF and SF resins (Publications I and II) were coulometrically determined using the Karl Fischer method [72].

To study the volatile content at 105 °C [73,74], ash content [75,76], coke number [27] of the resulting resins, gravimetry or TGA were used in both inert (N_2 or Ar) and oxidising environments (air). Publications I–III provide the details of the analytical parameters used.

The nitrogen contents of the initial alkylresorcinol fractions were determined using the ASTM D5291 method [78]. This indicator is important for calculating the amount of catalyst.

The thermal stability, thermal-oxidative destruction, thermal effects, and resin decomposition products were studied using TGA and TG/DTA-MS methods (Publications I–III).

The structures of the resins SF were studied using NMR ^{1}H and NMR ^{13}C, and GC-MS (Publications I–III). SF samples were analysed based on the NMR ^{1}N and NMR ^{13}C spectra obtained using a Bruker spectrometer operating at 500 MHz. The resins were first dissolved in deuteroacetone (acetone D6). The spectra were processed based on the information obtained from databases and the literature [20, 29, 68, 79-84].

TLC and GPC results (Publications I–III) were used to characterise and determine the structural parameters, such as the molecular weight distribution (MWD) and average chain length, of the oligomers.

The chromatographic parameters were calculated, and the results required for TLC were evaluated using the software Sorbfil TLC View (Publication I) and JustTLC (Publications II and III).

Most of the resin analyses were performed at the Laboratory of Fuels Technology and the Educational Laboratory of Virumaa College. The other analyses were performed at the Laboratory of Inorganic Materials, Department of Materials and Environmental Technology, Tallinn University of Technology (TG/DTA-MS), Polymer Institute in Slovakia (GPC), Saint Petersburg Institute of Technology (NMR), and St. Petersburg State University of Economics (GC-MS).

Preparation of sample required for chromatography analyses

Samples preparation for thin layer chromatography

To carry out a qualitative analysis of unreacted R and ARs using the TLC method, they were extracted from resin samples. The sample preparation technique for the analysis of aldehyde (F and Ac) resins is described in detail in Publication II, and for non-aldehyde resins in Publication III.

Samples preparation for gas chromatography

To determine their purities, individual R, 5-MR, 2.5-DMR, and oil shale alkylresorcinol fraction compositions were subjected to derivatisation. Using a mixture made of ARs and aralkylated R, 5-MR, and 2.5-DMR molecules, the nature of the interactions of styrene with R, 5-MR, 2.5-DMR, and alkylresorcinol fractions was determined (Figure 7). The silylation process is described in Publication II.

The first step in quantifying unreacted R and ARs using GC was their extraction from the resin samples, performed as in TLC (Publications II and III). The extracted unreacted R and ARs were first silylated with 1.1.1.3.3.3-hexamethyldisilazane, converting them into esters with lower boiling points than those of initial R and ARs. This technique allows the evaporation of heavy alkylresorcinols from the chromatograph injector and the determination of their compositions.

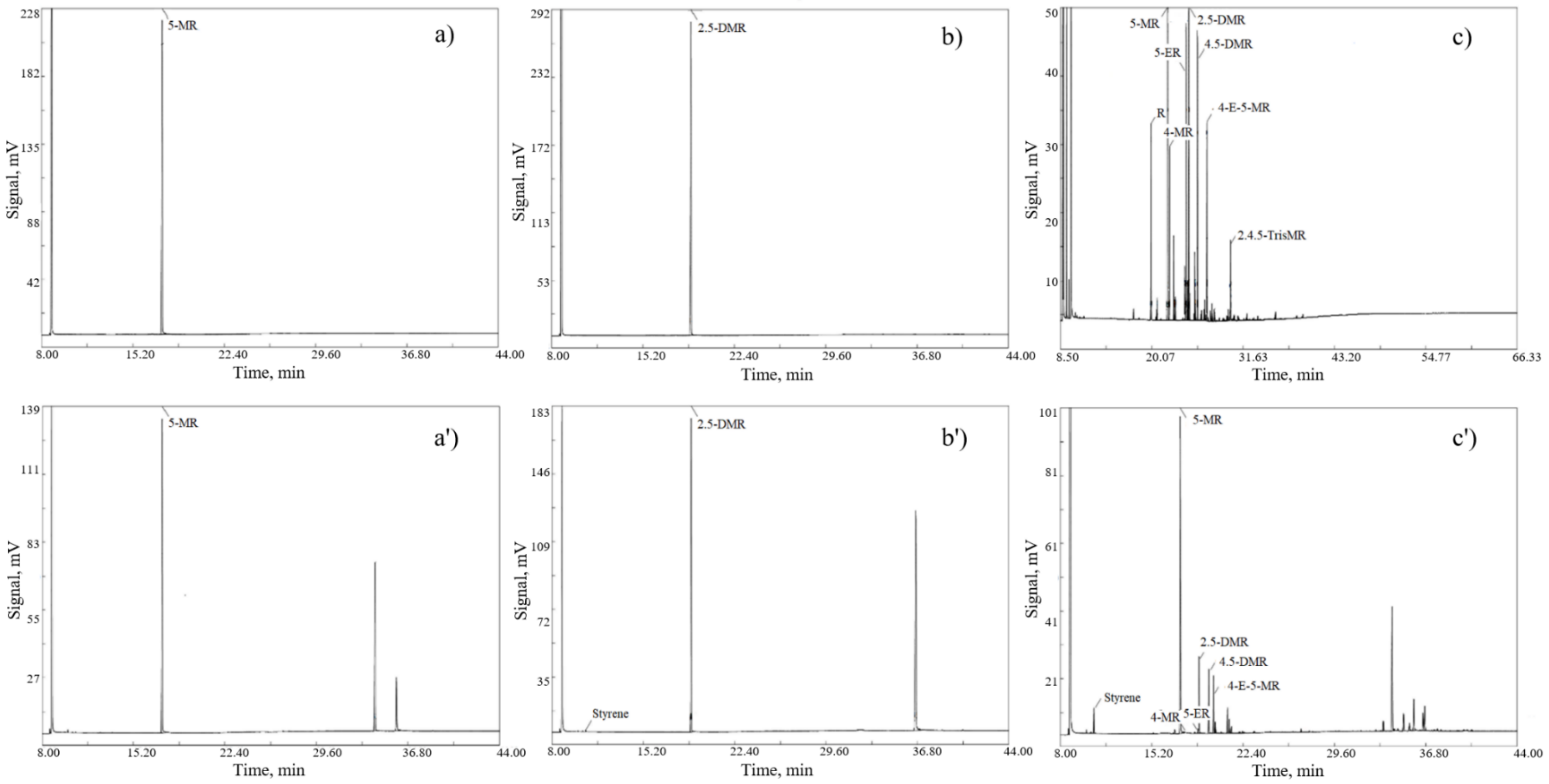


*Figure 7**.** Chromatograms of alkylresorcinols: 5-MR (a), 2.5-DMR (b), oil shale alkylresorcinol fraction HONEYOL 50 (c), and aralkylated alkylresorcinols: 5-MR (τ = 45 min) - (a'), 2.5-DMR (τ = 60 min) - (b'), fraction HONEYOL (τ = 45 min) - (c').*

3 Results and Discussion

This chapter presents and analyses the results of the studies on aldehyde and non-aldehyde resins based on the contents of R, individual oil shale ARs (5-MR and 2.5-DMR), and the commercial fractions of oil shale ARs (HONEYOL 50, HONEYOL 80, and REZOL). Options for the interactions of resorcinol components with S in the presence of an acid catalyst and the formation of polymer molecules with novolac structures were considered. Physicochemical and technical characteristics of the resins were determined using the standard methods (for example, determination of softening point and moisture content) and TGA, TLC, GPC, and NMR. The results are published in Publications I, II, and III.

3.1 Formaldehyde and acetaldehyde resins

3.1.1 Chemical reactions and structure

When the R molecule is aralkylated, three types of substituted molecules can form [17]. This finding was based on NMR and TLC studies (R and 5-MR) and literature data, which indicated that when styrene is added, it predominantly occupies the *ortho*- and *para*-positions of the (alkyl)resorcinol molecules. Moreover, as a rule, in the molecules of R, 5-MR, and 5-ER, two types of aralkylated molecules are formed (Figure 8 – 1,2,5,6) while in the molecules of 2.5-DMR, one type of aralkylated molecules is formed (Figures 8–9) depending on the electronic charges on the carbon atoms in the (alkyl)resorcinol benzene ring (Table 2). Although options for the addition of a second S molecule to the aromatic units 5-MR and 5-ER and to 2.5-DMR, are available, they are unlikely to succeed owing to the spatial structures of the aralkylated molecules and the molar ratio of the R component to S. Notably, when aralkylation occurred in an acidic environment, the amount of raw material (R) required exceeded five times the amount of S required (Tables 5 and 6). These quantities of R and S influenced the type of formation of aralkylated molecules.

Based on the NMR results, TLC analysis, and literature data, the predicted structures of the compounds present in SF and SAc are shown in Figure 8.

First of all, the R molecule will react with aldehyde (F and Ac). According to literature data [82], the reactivity of R in Positions 4 or 6 is higher than that at Position 2. This change in reactivity was facilitated by the spatial structure of the R molecule. The -OH groups in the R benzene ring can initially hinder the formation of methylene bridges at Position 2 in the presence of a two-fold excess of R. For this reason, the predominant product of the reaction will be the molecules containing 4.4'-methylene bridges. After the formation of a methylene bridge at Position 4.4′, the reactivity of the R molecule centres at Position 2 under the action of an acid catalyst increases [85-87]. The formation of methylene bridges begins at Positions 2.4 or 2.2‘. The reactivity at Position 6 simultaneously increases.

Considering the presence of unreacted R, the same compounds present in RF resin can be expected to be present in RSF, $R_{90}Rez_{10}SF$, and $R_{70}Rez_{30}SF$. It has been established that the structures of 5-MRSF and Rez100SF components correspond to those of the components of resins obtained using R. The main difference is the presence of an alkyl substituent at Position 5 (Figure 8).

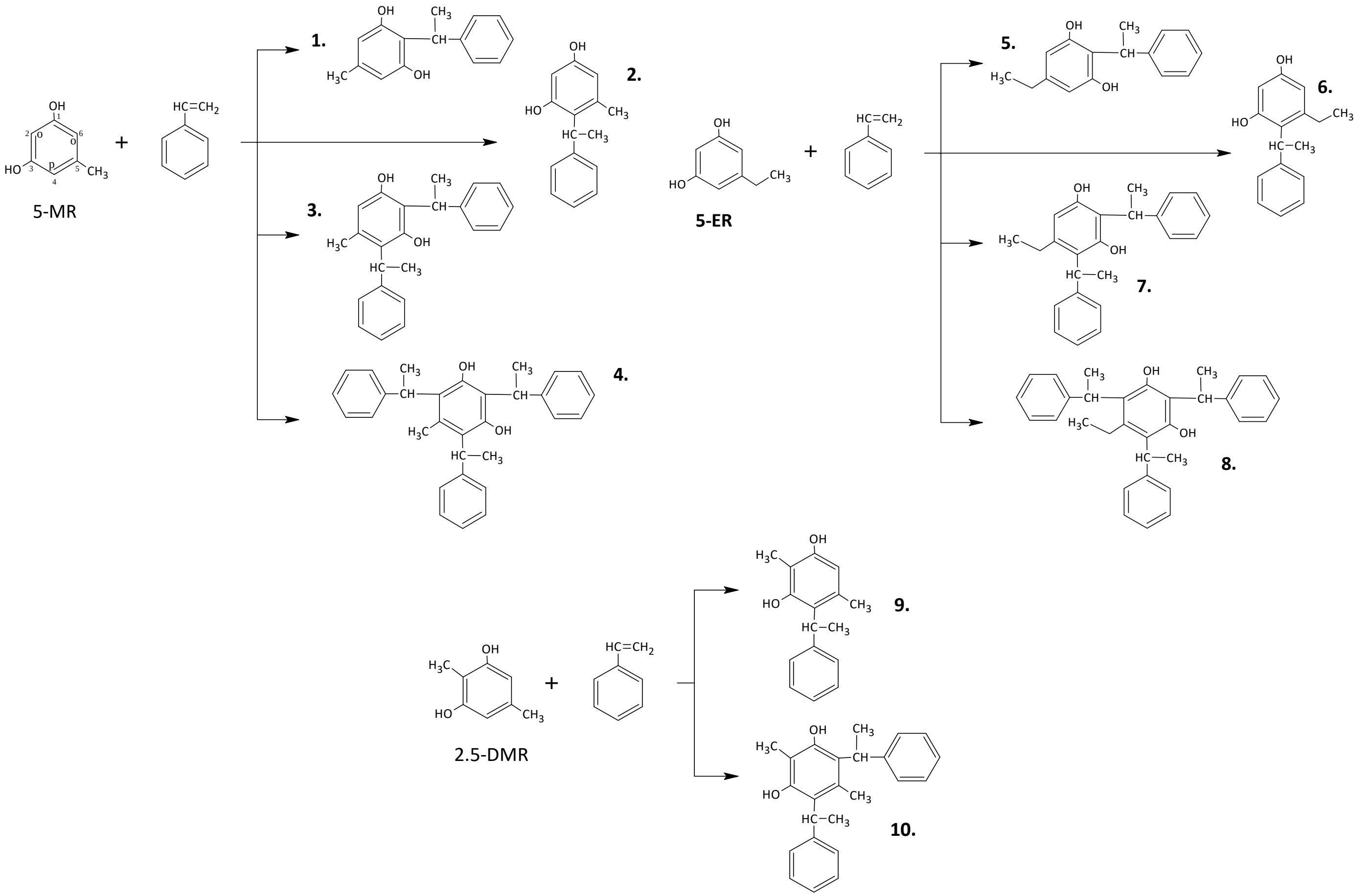


Figure 8. Reaction for producing aralkyl derivatives 5-MR, 5-ER and 2.5-DMR.

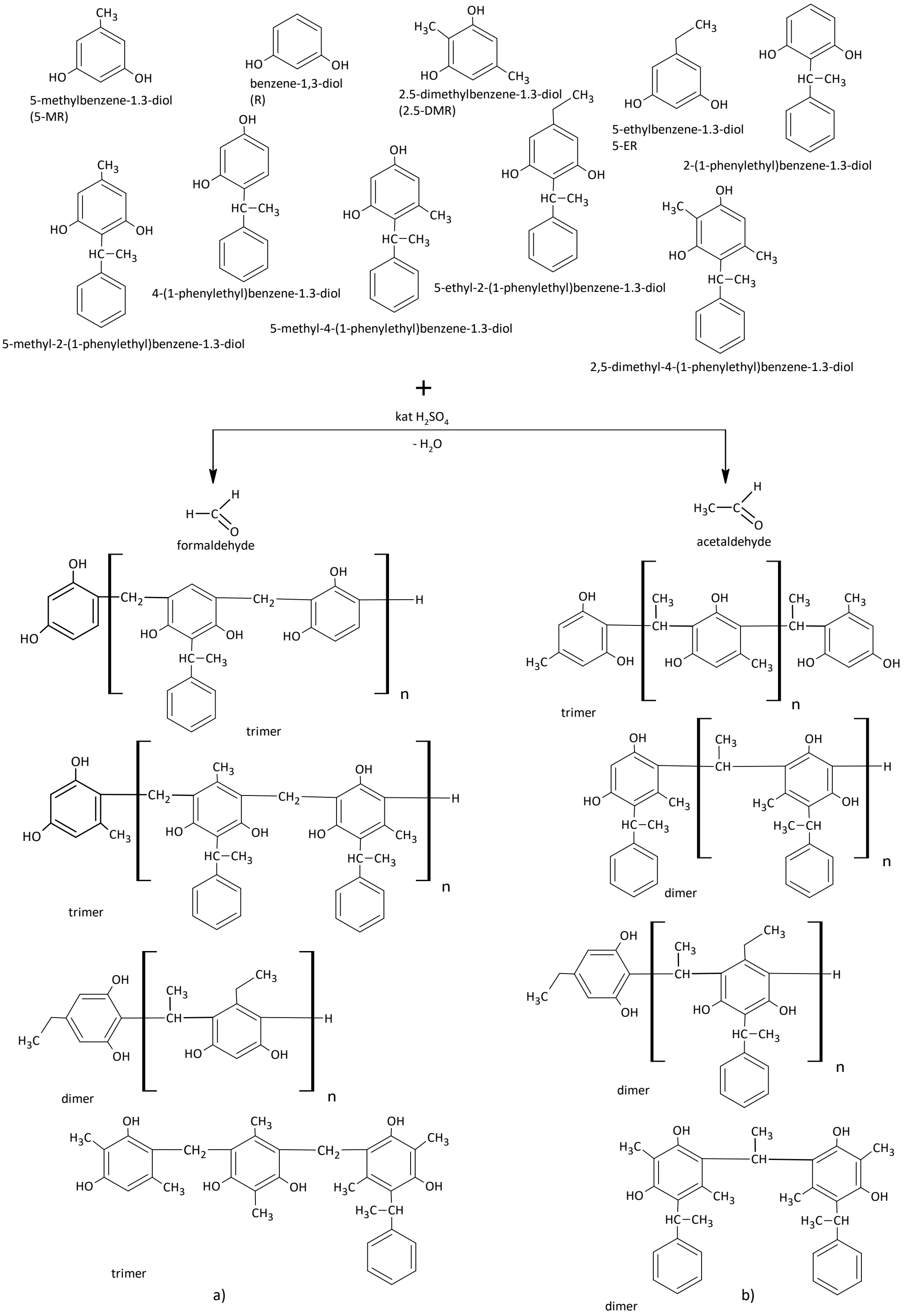


Figure 9. Possible molecular structures of (a) formaldehyde and (b) acetaldehyde novolac resins modified with styrene.

It has been established that in SF and SAc, a certain amount of unreacted initial resorcinol components as well as compounds obtained during the aralkylation process are present; that is, their interactions with F and Ac do not occur completely. Although F and Ac should have completely reacted at the molar ratio used, unreacted R and ARs were present in the resin. This presence of unreacted materials is due to the slow aralkylation between R and S and condensation with F in the first stage. According to RSF resin spectra (Figure 10 - b, b'), the aralkylation of R mainly occurs at Positions 2, 4, and 6. No products resulting from the aralkylation of R with S were detected at Position 5.

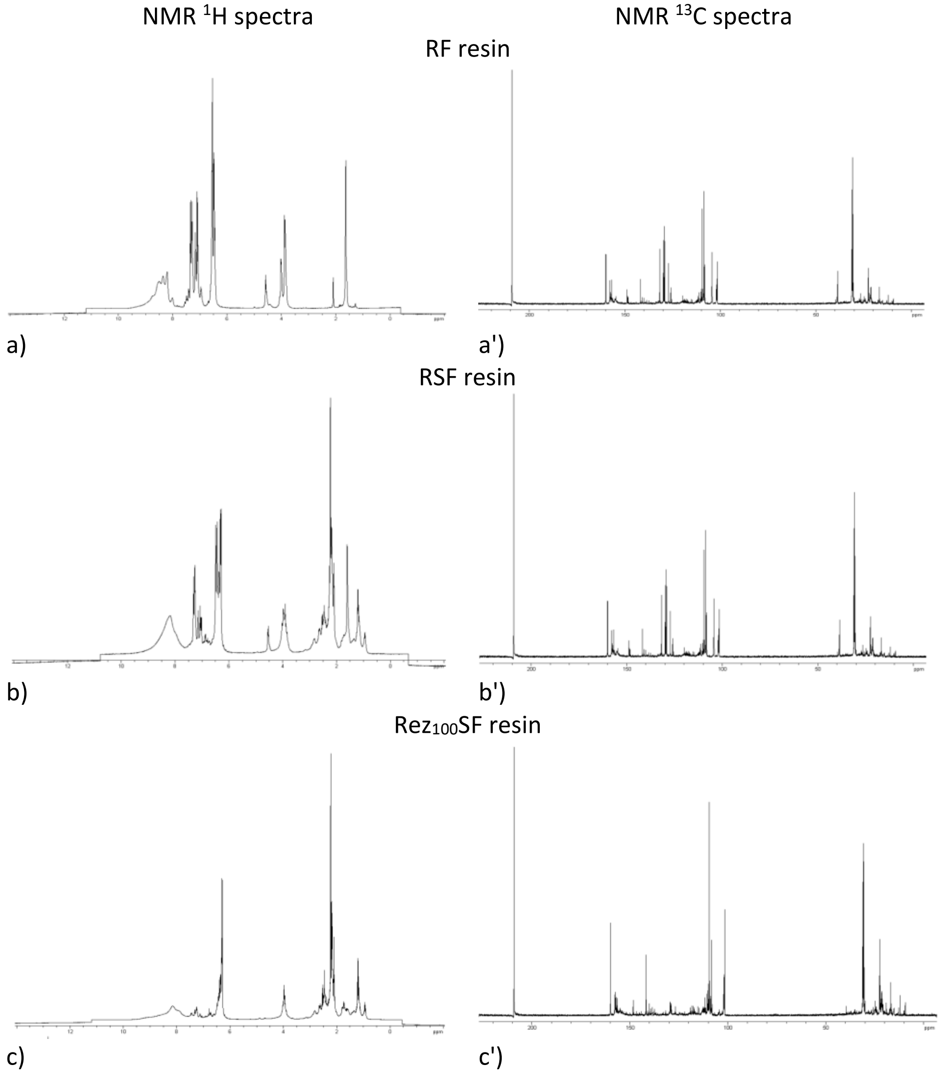


Figure 10. Nuclear magnetic resonance ^{1}H and ^{13}C spectra of the SF resins.

Based on the results of TLC (Figure 11) and NMR (Figure 10 – a, a'), and literature data [20,29,68,80-84], the structures of the main components of RF were determined. The chemical shifts of the protons and carbon atoms of the established structures fully correspond to signals similar to those in the spectra shown in Figures 10 – a and a'.

The resins RF contain significant amounts of unreacted R, slightly fewer amounts of trimers, even fewer amounts of tetramers and oligomers, and a small amount of dimers (Figure 11). This ratio of the condensation products (with a twofold molar excess of R) can be attributed to the formation of dimers, the slowest stage of the reaction. Therefore, a significant amount of R does not have time to enter the condensation reaction. Dimers are more reactive than R, and thus, they can quickly turn into trimers and then into tetramers and oligomers.

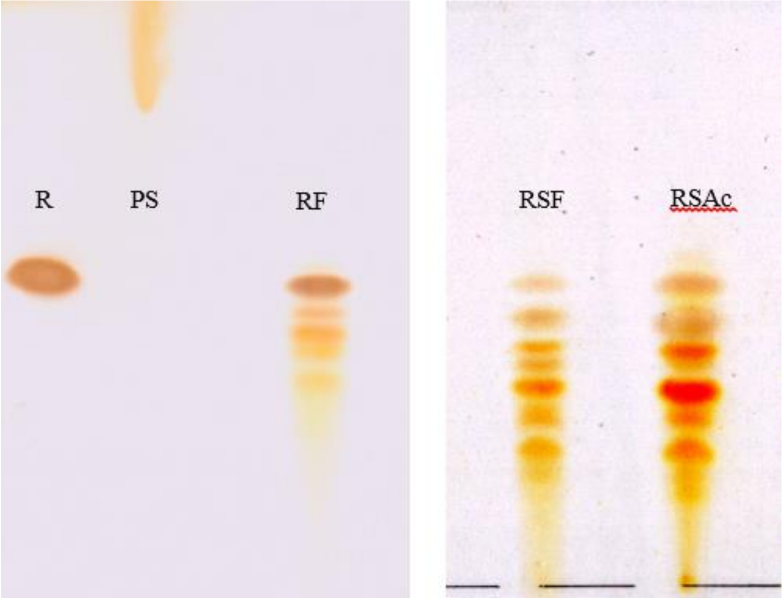


Figure 11. Thin-layer chromatography images: resorcinol (R), polystyrene (PS), resorcinol-formaldehyde resin (RF), resorcinol-formaldehyde resin modified with styrene (RSF) and resorcinol-acetaldehyde resin (RSAc) modified with styrene.

The interactions between R and F are theoretically possible at the *ortho*-, *para*-, and *meta*-positions of the aromatic ring of R. Based on the results of the NMR analysis, it was established that if the condensation of R with F proceeds to position 5, then the spectra would contain signals with carbon atoms (-CH2- group) that would chemically shift in the 22–14 ppm region. Moreover, in the presence of the methylol group -CH2-OH, the spectrum would have signals in the 49–60 ppm region. However, NMR analysis showed that condensation predominantly occurred at Positions 4 and 6, where the signals were found. The negative charge at the *ortho*-position (Table 2) of the R molecule enables the addition of F. Despite this, the spatial structure of the R molecule can hinder the formation of methylene bridges at the *ortho*-position in the initial stage of the process when a two-fold excess of R is present.

The ^{1}H and ^{13}C NMR spectra (Figure 10 b, b’) of the RSF revealed that the S added occupied the *ortho*- and *para*-positions of the aromatic ring of the R molecule. S became attached to R at the α-carbon atom to form a -CH–bridge. This phenomenon was confirmed by the presence of a quartet in the ^{1}H NMR spectrum in the 4.5–4.6 ppm region – the signal of the methine group. The split signal (doublet) in the 1.5 ppm region corresponds to the methyl group (-CH_3). Splitting of the methyl group signal into a doublet occurred because of the influence of the hydrogen atom in the tertiary carbon atom (-CH-).

The intense signals in the region of 7.2–7.9 ppm correspond to the protons of the S aromatic ring. The signals of the aromatic ring of R are in the region of 6.5–8.0 ppm. The interaction between S and R was confirmed by the data obtained using ^{13}C NMR. In the region of 31–39 ppm, the signals corresponding to the CH- and -CH_2-group-bridging structures were present in the resin. The signal in the 142–144 ppm region indicates the presence of a tertiary carbon atom linking the aromatic rings of R and S in the resin.

In the ^{1}H and ^{13}C NMR spectra of the samples of 5-MRSF, $R_{50}Rez_{50}SF$, and $Rez_{100}SF$, characteristic signals in the regions of the hydroxyl groups (8–10 ppm), protons of aromatic structures (6–8 ppm), methylene bridges (3.5–4.5 ppm), methyl groups (0.5–1.8 ppm), aromatic carbons (100–160 ppm), methylene bridges (20–40 ppm), and methyl groups (9–20 ppm) were present. The presence of these characteristic signals confirmed that the 5-MRSF, $R_{50}Rez_{50}SF$, and $Rez_{100}SF$ structures were similar to the resorcinol-derived resin structures. The only main difference is the presence of an alkyl substituent at Position 5.

In the resins obtained based on 5-MR, a mixture of the AR fractions (REZOL and HONEYOL 50) and R was prepared based on the molar ratios indicated in Tables 5 and 6, and the AR fractions (REZOL and HONEYOL 50), unreacted R, 5-MR, 5-ER, and 2.5-DMR were also present (Table 9). As with RSF, the aralkylation steps of styrene with R, 5-MR, 5-ER, and 2.5-DMR and the associated condensation of R, 5-MR, 5-ER with aldehydes were the slowest.

3.1.2 Properties of the formaldehyde and acetaldehyde resins

Chemical composition

Table 8 lists the physicochemical properties of SF and SAc. The preliminary modification of the initial components made it possible to increase the softening points and reduce the volatile contents of the (alkyl)resorcinol-formaldehyde resins. Styrene-modified RSF has been shown to have a higher softening point at ~20 °C compared with unmodified RF. The modification of initial components using styrene leads to the formation of molecules and oligomers with a higher molecular weight. The introduction of a modifier significantly reduced the hygroscopicity of the resin.

The condensation of aralkylation products with F and Ac was performed at molar ratios of 2:1 and 2:1.3, respectively. The softening point of RSAc (73.0 °C) is lower than that of RSF (84.0 °C) with an R:aldehyde ratio of 2:1. According to [17], to obtain the same softening point using Ac, the amount of aldehyde has to be increased (Figure 3).

Among synthesised SF, the best in terms of technical characteristics was the resin obtained by replacing 10% of R on the oil shale alkylresorcinol fraction REZOL ($R_{90}Rez_{10}SF$). A further increase in the alkylresorcinol fraction content led to a deterioration of resin properties. This deterioration has been attributed to the absence of a catalyst, which has been spent on neutralising the pyridine bases present in the resin. In addition, industrial fractions contain ARs coming from oil shale tar, with a boiling temperature that can reach up to 430 °C. These compounds with high boiling temperatures have alkyl chains, each with nine or more atoms, as well as cyclic side chains, such as the cores of tetralin, indane, and biphenyl. Their contents in the fraction that boils between 300 and 330 °C are significant [70]. The presence of these substituents can spatially hinder the aralkylation and polycondensation of the components.

Table 8. Resin characteristics.

Sample name	Characteristics											
	Physical and chemical characteristics						Content of the unreacted resorcinols [wt%]				Water released during the polycondensation process	
	Softening point [°C]	Volatile components at 105 °C [wt%]	Moisture [wt%]	Ash at 830 °C [wt%]		Coke number [wt%]	R	5-MR	5-ER	2.5-DMR	Iodine Number [g I$_2$/100g]	Styrene content [wt% by GC]
				Gravimetric	TGA (in air)							
RF	66.0	1.4^{TGA}	2.0	-	0.7	26.4	19.1	-	-	-	-	-
RSF*	86.3	0.9^{TGA}	0.3	-	0.3	25.6					3.2	-
RSF	84.0	0.6^{TGA}	0.2	-	0.3	24.0	7.7	-	-	-	0.0	0.0
RSAc	73.0	6.8	1.2	3.7	-	-	8.6	-	-	-	-	0.0
RDS$_4$	80.5	$<0.01^{TGA}$	-	0.2	-	-	0.9	-	-	-	-	-
RDS$_5$	97.0	$<0.01^{TGA}$	-	0.4	-	-	1.9	-	-	-	-	-
R$_{90}$Rez$_{10}$SF	89.0	0.4^{TGA}	0.3	-	0.2	23.9	5.6	8.1	2.7	-	0.0	0.0
R$_{70}$Rez$_{30}$SF	78.0	0.6^{TGA}	0.5	-	0.4	19.4	5.4	10.4	4.4	-	0.0	0.0
R$_{70}$Rez$_{30}$SAc	102.5	0.8^{TGA}	0.8	0.2	0.5	20.4	0.5	2.8	0.9	0.3	0.0	-
R$_{70}$Hon80$_{30}$DS	95.0	$<0.01^{TGA}$	-	0.2	-	-	0.5		-	-	-	-
R$_{50}$Rez$_{50}$SF	69.0	0.7^{TGA}	0.5	-	0.4	18.9	5.4	10.4	4.4	-	-	-
R$_{50}$Hon80$_{50}$DS	88.0	$<0.01^{TGA}$	-	0.04	-	-	2.1		-	-	-	-
Rez$_{100}$SF	69.3	0.9^{TGA}	0.5	-	0.1	13.8	2.1	12.1	4.5	-	67.8	-
Rez$_{100}$SAc	69.5	0.6^{TGA}	0.3	0.1	0.0	6.9	< 0.01	1.5	0.6	0.2	-	2.0
Hon50$_{100}$SAc	80.5	0.9^{TGA}	0.9	0.7	0.9	11.3	< 0.01	2.6	0.7	1.3	-	3.7
Hon80$_{100}$DS	75.0	$<0.01^{TGA}$	-	0.2	-	-	1.8		-	-	-	-
5-MRSF	81.5	1.7^{TGA}	0.9	-	0.6	17.9	-	6.4	-	-	-	-
5-MRSAc	103.0	5.05	2.6	1.1	-	-	-	2.0	-	-	-	0.1
5-MRDS	94.0	$<0.01^{TGA}$	-	0.2	-	-	0.6		-	-	-	-
2.5-DMRSAc	51.5	4.0	0.5	0.3	-	-	-	-	-	56.7	-	0.2

* I route

In the next series of syntheses, the catalyst volume was increased to calculate the content of the alkylresorcinol fraction. Owing to this, a resin in which synthetic R had been replaced by 30 mol% of the REZOL fraction ($R_{70}Rez_{30}SAc$) could be obtained. The resin $R_{70}Rez_{30}SAc$ has a softening point that is 24.5 °C higher than that of the resin $R_{70}Rez_{30}SF$, and the total contents of unreacted R and ARs in $R_{70}Rez_{30}SAc$ are less than that in $R_{70}Rez_{30}SAc$ by almost five times. The remaining physicochemical parameters of the resins were within the reproducibility limits of the methods used.

Table 9. Free resorcinol content in the resins and the degree of polycondensation.

Sample name	Components of the raw mixture	Initial content of free resorcinols [wt%]	Content of free resorcinols in the resin [wt%]	Depth of the polycondensation process [%]
RF	R	100.0	19.1	80.9
RSF*	R	100.0	11.0	89.0
RSF	R	100.0	7.7	92.3
RSAc	R	100.0	8.6	91.4
$R_{90}Rez_{10}SF$	R	87.5	5.6	93.6
	5-MR	9.7	8.1	16.5
	5-ER	2.8	2.7	3.6
$R_{70}Rez_{30}SF$	R	66.9	6.4	90.4
	5-MR	25.8	7.8	69.8
	5-ER	7.3	3.5	52.1
$R_{70}Rez_{30}SAc$	R	70.0	0.5	99.3
	5-MR	12.9	2.8	78.5
	5-ER	3.6	0.9	75.0
$R_{50}Rez_{50}SF$	R	46.5	5.4	88.4
	5-MR	41.7	10.4	74.6
	5-ER	11.8	4.4	62.7
$Rez_{100}SF$	R	2.1	2.1	0.0
	5-MR	74.3	12.1	83.7
	5-ER	25.7	4.5	82.5
$Rez_{100}SAc$	R	3.4	0.0	100.0
	5-MR	70.3	1.5	97.9
	5-ER	19.5	0.6	97.0
	2.5- DMR	6.8	0.2	96.8
$Hon50_{100}SAc$	R	2.9	0.0	100.0
	5-MR	73.2	2.6	96.5
	5-ER	12.0	0.7	93.9
	2.5- DMR	10.9	1.3	87.7
5-MRSF	5-MR	100.0	6.4	93.6
5-MRSAc	5-MR	100.0	2.00	98.0
2.5-DMRSAc	2.5-DMR	100.0	56.5	43.5

The results presented in Table 9 indicate a more complete interaction of the components using the AR fractions in Rez$_{100}$SAc than in Rez$_{100}$SF. The degree of conversion of 5-MR and 5-ER increased as the REZOL content increased. The conversion of the main components of the resin R$_{70}$Rez$_{30}$SAc resin (R, 5-MR, and 5-ER) was higher than that of the resin R$_{70}$Rez$_{30}$SF when both had the same REZOL content. 2.5-DMR exhibited the lowest conversion during polycondensation.

Thermal properties

According to TGA data (Figure 12), all of the SF behaved almost identically. In RF, a significant loss of sample weight began in an inert environment at 140 °C. Modified S resins synthesised based on individual substances (RSF*, RSF, and 5-MRSF) decompose in one stage in the temperature range of 150–400 °C (Figure 12). At ~220 °C, intensive decomposition of oligomers begins to occur. For resins with REZOL fraction additives, decomposition begins at ~190 °C.

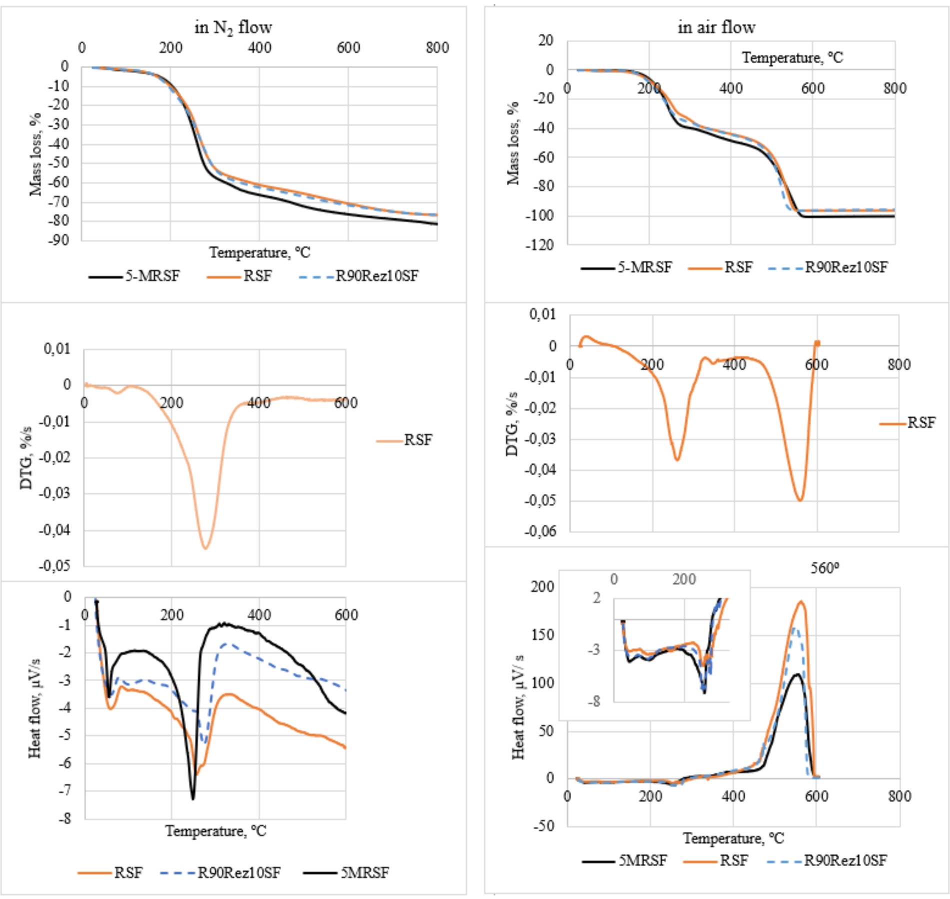


Figure 12. Thermogravimetry, derivative thermogravimetry, and differential thermal analysis curves of RSF, R$_{90}$Rez$_{10}$SF, and 5-MRSF in (a) an inert atmosphere and (b) air at a heating rate of 5 deg min^{-1}.

The maximum decomposition rate of the oligomeric structure was achieved at temperatures in the range of 220–255 °C and was characterised by the inflection point of the TGA curve. Resins RSF*, RSF and $R_{90}Rez_{10}SF$ have the highest temperatures (~255°C) at maximum decomposition rates.

In the initial stage of thermal destruction, side groups, such as -OH, $-CH_3$, and $-C_2H_5$, in the macromolecules are eliminated under the influence of heat, or bridge groups ($-CH_2$) that are part of the structure of the oligomer molecule. The aromatic groups in the macromolecules of RF increase the rigidity of the chains and the number of intermolecular interactions among them. Thus, it becomes difficult for free-radical destructive processes to occur. In addition, aromatic cyclic macromolecules prevent depolymerisation from occurring because of the high strength of the C–H bond in the benzene ring and the non-separation of hydrogen molecules from the core. The primary decomposition of the methylene bridges and the elimination of the side chains occur up to ~320 °C [88,89]. With the destruction of the macromolecules, unreacted resorcinols were removed completely and simultaneously. According to literature data, this removal occurs in the temperature range of 100 °C to 250 °C [17]. In the heat flow graphs, small endothermic effects can be seen in the temperature range of 80–120 °C, which are associated with the release of water and volatile components, as well as in the temperature range of 200–270 °C, associated with the melting and decomposition of components that have not reacted (5-MP, 5-ER, and other low molecular weight oligomers). With a further increase in temperature, thermal decomposition of the benzene ring was observed, along with the simultaneous destruction of the bridging groups connecting the phenylene rings. The intense exothermic effect above 400 °C indicates the oxidation reactions of the remaining resin components.

In RF without styrene, a 10% weight loss occurs at 158 °C within an inert environment. The addition of styrene causes the resin to lose 10% of its mass at 201 °C.

Table 10. Mass-loss temperatures of different resins in air.

Parameter	Sample name								
	RF	RSF	RSAc	RDS_5	5-MRSF	5-MRSAc	$R_{90}Rez_{10}SF$	$R_{70}Rez_{30}SAc$	$R_{70}Hon80_{30}DS$
$T_{\text{start of dec}}$, [°C]	115	155	80	170	162	182	155	105	150
τ_{10}, [°C]	174	213	194	302	214	241	205	247	289
τ_{50}, [°C]	409	467	459	440	422	421	461	397	400
τ_{90}, [°C]	527	565	543	520	561	521	554	599	480

Radical-chain oxidation reactions occur during the thermal-oxidative destruction of resins in polymer systems. The hydroxyl groups present in the macromolecules of RF first undergo oxidation, followed by methylene fragments [89]. As Figure 13 shows, the oxidation process involves the formation of water, carbon dioxide, carbon monoxide, and low-molecular-weight carbon-containing volatile products. Each bond break leads to the volatilisation of chain fragments. The destruction process occurs in two stages, which are characterised by two steps in the thermogram curve (Figure 12b). The unreacted R and ARs, as well as dimers, trimers, and alkyl groups, are first exposed to oxygen. The second stage involves the decomposition of long-chain resin molecules.

No selectivity was present during thermo-oxidative destruction. Low selectivity during the oxidation of an oxygen-containing polymer implies that both functional groups and C–H bonds are affected, along with the valence bonds of the macromolecular chain.

The maximum decomposition rates of most of the resins in the first stage were within the temperature range of 240–250 °C. In the resins RF and Rez$_{100}$SF, the maximum decomposition rate occurred at 215 °C. The resins that had the highest thermal resistance to oxidising environments were RSF, 5-MRSF, and R$_{90}$Rez$_{10}$SF.

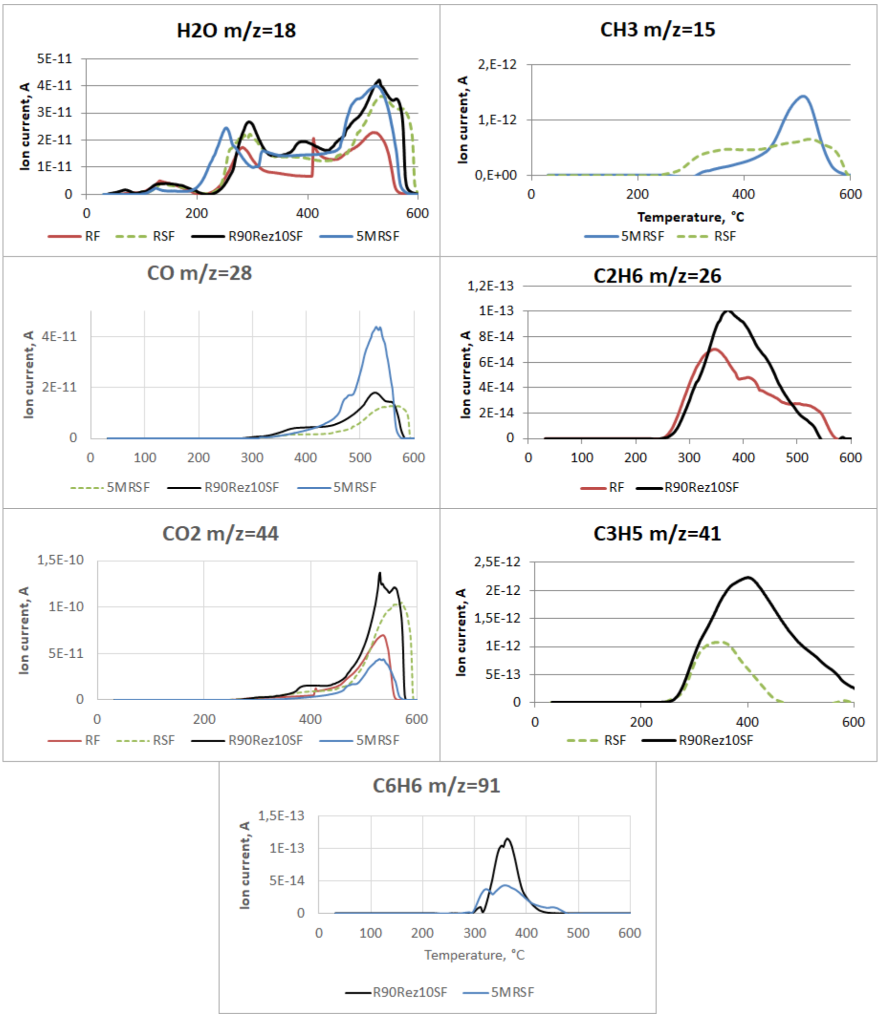


Figure 13. Gas evolution during the heating of the resins in an Ar+20%O$_2$ atmosphere at a heating rate of 5 deg min^{-1}.

The decomposition temperatures of the resins RF, RSF, 5-MRSF, and RSARF (10%) increase in an oxidising environment. This increase could be due to the presence of macromolecules with n ≥5 in the resin composition, which can branch under the influence of heat and oxygen, followed by cross-linking. Cross-linking of the macromolecular polymer structures can lead to a 50% mass loss at temperatures significantly higher than the temperature of an inert environment. This trend was not observed in resins obtained by adding more than 30% REZOL. The absence of this trend in the resins mentioned can be attributed to the presence of large amounts of unreacted ARs with long alkyl chains and cyclic groups that do not participate in the polycondensation reaction. Long-chain structures were practically absent. The resins primarily comprised dimers, trimers, and tetramers, which is consistent with the TLC, GPC, and NMR data.

The thermal decomposition of SAc that occurs when the resins are heated in an inert nitrogen environment showed that the resin $R_{70}Rez_{30}SAc$ had the highest thermal stability. The maximum decomposition rate of SAc occurs in the temperature range 210–270 °C.

A comparison of the results of the TA analysis of the resins RSAc and 5-MRSAc (Figure 14) indicates the significant influence of 5-MR on the thermal properties of Ac, despite its lower content of unreacted components (Table 8). Decomposition of SAc in an inert atmosphere also occurs in a single stage, similar to that of SF. A significant change in the mass loss of RSAc can be seen in the temperature range from 150 to 300 °C, while no noticeable thermal effects occur in 5-MRSAc at temperatures below 400 °C.

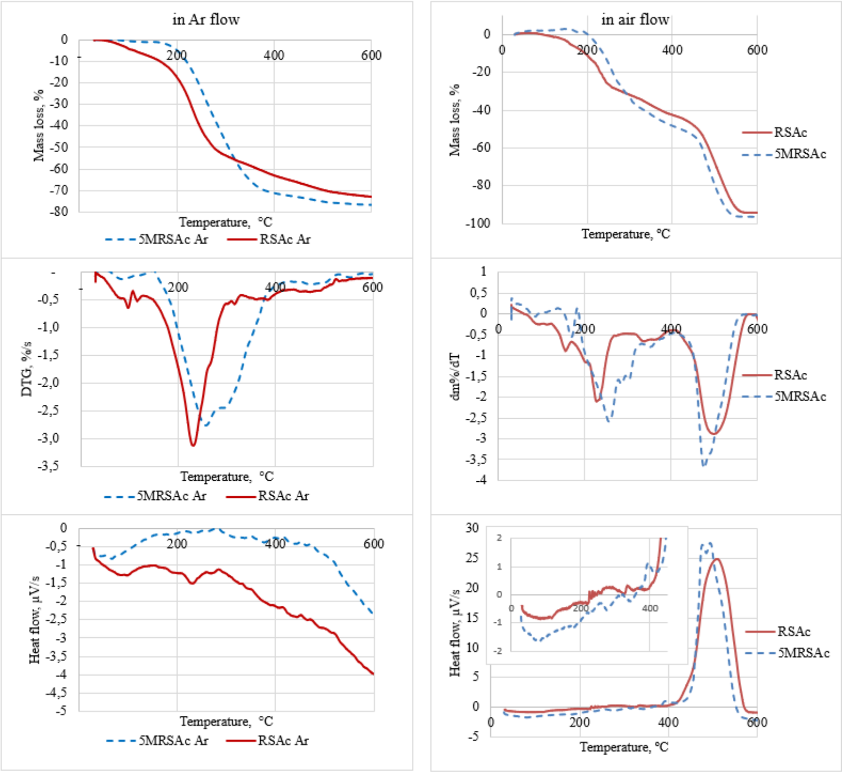


Figure 14. Thermogravimetry, derivative thermogravimetry, and differential thermal analysis curves of the resins RSAc and 5-MRSAc in (a) an inert atmosphere and (b) air at a heating rate of 5 deg min^{-1}.

As the resins decomposed in the air, the thermal analysis curves became more complex. Thus, many decomposition reactions, particularly in 5-MRSAc, would have occurred at temperatures below 400 °C. The intense decomposition reactions were particularly noticeable in 5-MRSAc at temperatures above 400 °C. The higher weight loss of RSAc within the temperature range of 80–200 °C would have occurred owing to its large moisture content (Table 8).

Physical properties/characteristics (colour, solubility)

Synthesised SF are light crimson to dark crimson in colour and have a brownish tint. SAc can be yellow, orange, or crimson. With the presence of increasing amounts of oil shale alkylresorcinol fractions (HONEYOL 50 and REZOL) in the SAc formulations, their colour became increasingly brownish. Almost all resins were transparent (Figure 15).

a) b) c)

Figure 15. Resins appearance: a) formaldehyde resin, b) acetaldehyde resins, c) non-formaldehyde resins

Table 11. Solubility of formaldehyde and acetaldehyde resins in various organic solvents.

Sample name	Solvent						
	Acetonitrile	THF	EtOH	Benzene		Acetone	Water
RF	++	++	++	--	--------	++	++
RSF	++	++	++	--	--------	++	++
RSAc	++	++	++	--	--------	++	+-
R$_{70}$Rez$_{30}$SF	++	++	++	--	--------	++	+-
R$_{70}$Rez$_{30}$SAc	++	++	++	--	--------	++	+-
Rez$_{100}$SF	++	++	++	--	--------	++	--
Rez$_{100}$SAc	++	++	++	--	--------	++	--
Hon50$_{100}$SAc	++	++	++	--	--------	++	+-
5-MRSF	++	++	++	--	--------	++	+-
5-MRSAc	++	++	++	--	--------	++	+-
2.5-DMRSAc	++	++	++	--	--------	++	+-
RDS$_4$	--------	++	++	--------	+-	++	--
RDS$_5$	--------	++	++	--------	+-	++	--
R$_{70}$Hon80$_{30}$DS	--------	++	++	--------	+-	++	--
5-MRDS	--------	++	++	--------	+-	++	--

++ - soluble, + - soluble by heating, +- - partially soluble, -- - insoluble

Table 11 shows that SF and SAc exhibit different solubilities in organic solvents. SF and SAc possess good solubility in polar (acetone and EtOH) and moderately polar (THF) organic solvents at a room temperature of 20-22 °C. RF and RSF are soluble in water. The water solubility of these resins could be due to the high content of unreacted low-molecular-weight (alkyl)resorcinols (R, 5-MR, 5-ER, etc.) with OH-groups they contain. The resins of all formulations had good water solubility in acetone.

3.2 Non-aldehyde resins

3.2.1 Chemical reactions and structure

The interaction of DCPD with R, 5-MR or other ARs can proceed according to the scheme (Figure 16).

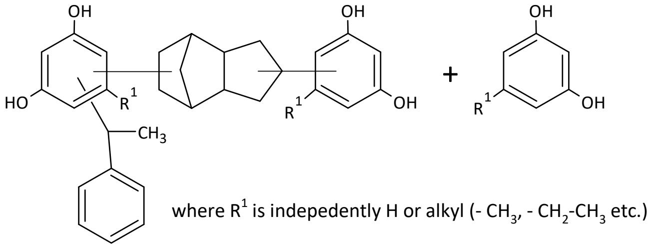


Figure 16. The structures of resin units obtained at molar ratios of resorcinol component: DCPD: S – 1: 0.5: 0.3

Based on the literature data [17] and the results of the experiments (RSD_5, 5-MRDS, $H80_{100}DS$, $R_{70}Hon80_{30}DS$), the synthesis of non-aldehyde resins based on DCPD, and S could proceed based on the scheme presented in Figure 19.

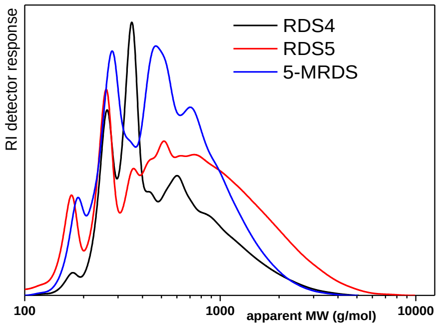


Figure 17. Gel permeation chromatography traces of the RDS_4, RDS_5, and 5-MRDS samples converted into molecular weight distribution through calculations using polystyrene calibration curve.

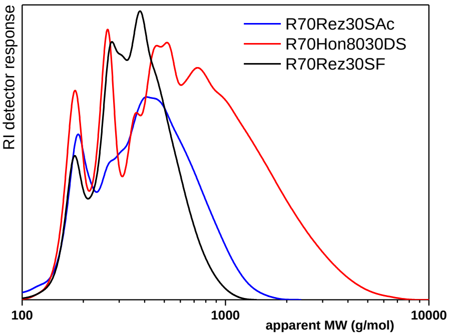


Figure 18. Gel permeation chromatography traces of the $R_{70}Rez_{30}Sac$, $R_{70}Hon80_{30}DS$, and $R_{70}Rez_{30}SF$ samples converted into molecular weight distribution through calculations using polystyrene calibration curve.

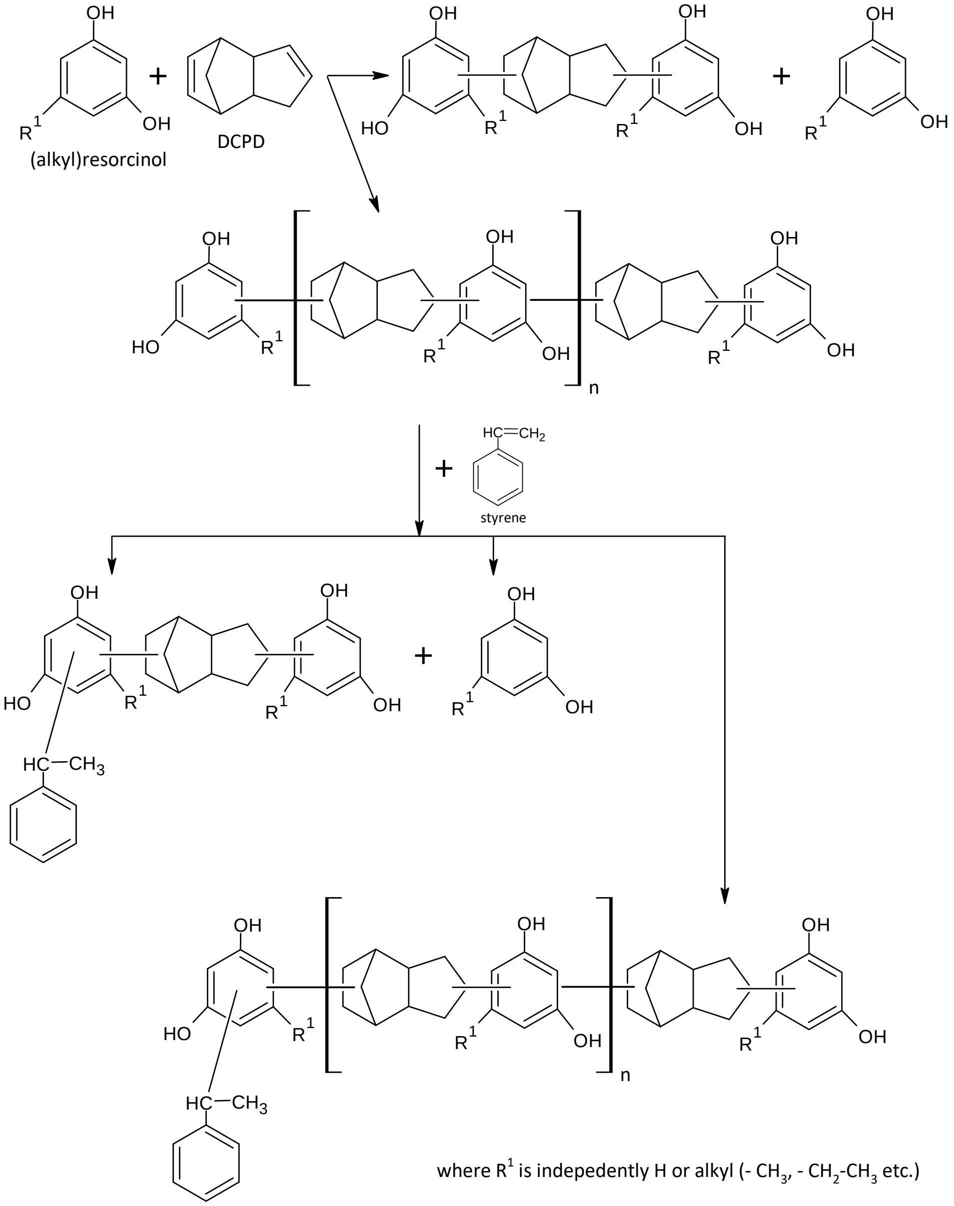
The MWD results for SF, SAc, and DCPDS are presented in the GPC elution curves (Figures 17 and 18) and TLC curves (Figure 11). In DCPDS, except in Hon80$_{100}$DS, macromolecules with predominantly linear characteristics had higher molecular weights. An increase in the molar content of the alkylresorcinol fraction decreased the number-average molar mass. This phenomenon could be due to an increase in the number of branched macromolecules of the same molecular weight in the resin. The molecular weight of the non-aldehyde resin R$_{70}$Hon80$_{30}$DS was significantly higher than that of either of the two aldehyde resin samples (R$_{70}$Rez$_{30}$SF and R$_{70}$Rez$_{30}$SAc).

The highest molecular weight achieved in the HONEYOL 80 sample was higher than that achieved in the REZOL sample by almost two times. The molecular weight characteristics of the resins are listed in Table 12. SF and SAc had lower dispersibilities than DCPDS. The dispersibility depends on the contents of the low-molecular-weight compounds. According to TLC and GPC analyses, R70Hon8030DS contained a large number of dimers, which strongly affected the molecular weight of the resins. GPC revealed that the use of F or Ac led to branching in the polymer molecules through methylene bridges.

Table 12. Molecular-weight characteristics of the samples.

Sample name	M_n	M_w	$Đ$	MW range	Low-MW content [%]
5-MRDS	420	610	1.45	120 - 3900	14
Hon80$_{100}$DS	370	520	1.41	120 - 2600	30
R$_{70}$Rez$_{30}$SF	320	380	1.20	110 - 1200	10
R$_{70}$Rez$_{30}$SAc	330	450	1.36	110 - 1900	20
R$_{70}$Hon80$_{30}$DS	450	840	1.85	120 - 7000	25
R$_{50}$Hon80$_{50}$DS	450	790	1.76	110 - 5700	22

The highest conversions of ARs were observed in the resins R$_{70}$Hon80$_{30}$DS and 5-MRDS. In SAc (except 2.5-DMRSAc), the condensation depths of R and ARs were higher than those of SF. The resin 2.5-DMRSAc exhibited the lowest polycondensation depth. Therefore, the condensation of the aralkylated 2.5-DMR molecule with aldehyde is difficult owing to its spatial structure. With an increase in the alkylresorcinol fraction in the resin formulation, the depth of conversion of R and ARs decreases. This could be attributed that the first stages of interaction between aldehyde and DCPD with R raw materials are the slowest. In the non-aldehyde resins, a high conversion of the initial components was observed.



where R^1 is indepedently H or alkyl (- CH_3, - CH_2-CH_3 etc.)

Figure 19. Synthesis reactions of (alkyl)resorcinol-dicyclopentadiene resins modified with styrene.

3.2.2 Properties of the non-aldehyde resins

Chemical composition

Among the formaldehyde-free resins, R$_{70}$Hon80$_{30}$DS and 5-MRDS exhibited optimal characteristics (Table 13). Unreacted R and 5-MR contents were less than 1.0 wt%. In addition, in contrast to polycondensed formaldehyde resins, not all formaldehyde-free resins contain volatile components. They were completely moisture-free.

Table 13. Depth of the polycondensation process.

Sample name	Components of the raw mixture	Initial content of free resorcinols [wt%]	Content of free resorcinols in the resin [wt%]	Depth of the polycondensation process [%]
RDS_4	R	100.0	0.9	98.0
RDS_5	R	100.0	1.9	96.3
$R_{70}Hon80_{30}DS$	R+5-MR	96.8	0.5	98.9
$R_{50}Hon80_{50}DS$	R+5-MR	94.5	2.1	95.6
$Hon80_{100}DS$	R+5-MR	89.3	1.8	95.8
5-MRDS	5-MR	100.0	0.6	98.8

It should be noted that the DCPDS resins obtained had a low ash content. The lowest ash content values observed for RDS and $R_{50}Hon80_{50}DS$ were 0.04 and 0.06 wt%, respectively. The TGA method (Figures 20 and 21) shows that volatile compounds in the DCPDS resins are negligible.

From the results obtained (Table 13), it follows that the highest conversion of alkylresorcinol (~ 99%) is achieved in 5-MRDS and $R_{70}Hon80_{30}DS$ resins. Increasing the amount of alkylresorcinol fraction in the formulation led to a decrease in the conversion rate of R and 5-MR. For $R_{50}Hon80_{50}DS$ and $Hon80_{100}DS$ resins, the conversion rates remained almost at the same level and were 95.6 and 95.8%, respectively.

Thermal properties

The TA results presented in Figures 19 and 20 show that in the temperature range from 70 °C to 150 °C, the release of water ($m/z = 18$) is negligible. In this temperature range, virtually no weight loss could be observed for the resin sample. The resulting DCPDS remained stable up to 200 °C. Among the samples tested, RDS_5 showed the highest stability and minimal weight loss, while $Hon_{100}DS$ was the most unstable. Starting at a temperature of 350 °C, strong boiling of the sample was observed, as evidenced by the decomposition curve shown in Figure 20.

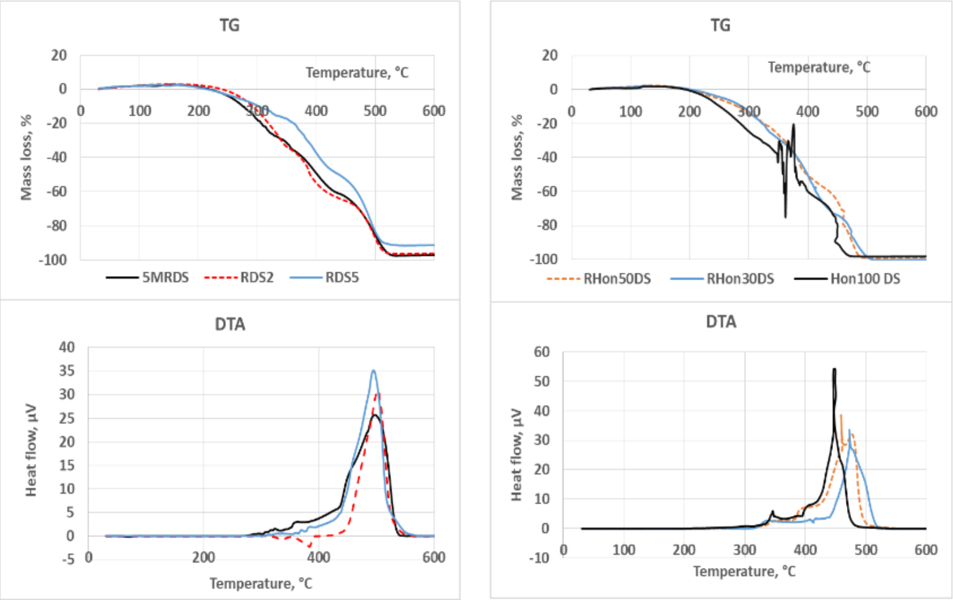


Figure 20. Thermogravimetry and differential thermal analysis curves of DCPDS in an Ar+20% O_2 atmosphere at a heating rate of 5 deg min^{-1}.

All samples exhibited mass loss, which occurred in three stages. Figure 19 shows that light hydrocarbons, including styrene, begin to release during the decomposition of resins in the temperature range 230–300 °C. The intensity of this process depends on the resin compositions. In more stable resins, such as RDS_2, RDS_5, and $R_{50}Hon80_{50}DS$, the release of components with cyclic structures (m/z = 78) occurs in the temperature range of 300–350 to 450 °C. For unstable resins, the temperature at which the release of components with cyclic structures (m/z = 78) occurred was lower by approximately 100 °C.

The oxidation (combustion) process was established by detecting the exothermic effect on the differential thermal analysis (DTA) curve and the release of CO_2 and H_2O. For DCPDS resins using R, the process became predominant at ~350 °C. For resins obtained using the alkylresorcinol fraction of HONEYOL 80, this process was evident between 400–430 °C.

Using the TGA method, the shelf life of a polymer can be preliminarily estimated [90]. This is demonstrated by the data on the behaviour of the resin when heated. Generally, the higher the decomposition temperature, the longer the polymer retains its technical and operational characteristics during storage. Table 11 shows that DCPDS begin to degrade at higher temperatures (τ%) compared with SF and SAc.

Physical properties/characteristics (colour, solubility)

The colour of DCPDS resins ranges from dark crimson to brown. The brown colour originated from the alkylresorcinol fraction of HONEYOL 80. DCPDS resins are opaque (Figure 12).

According to the data presented in Table 11, DSPDS are slightly soluble in toluene and insoluble in water. Their solubility in ethanol, acetone, and tetrahydrofuran are same as those of SF and SAc.

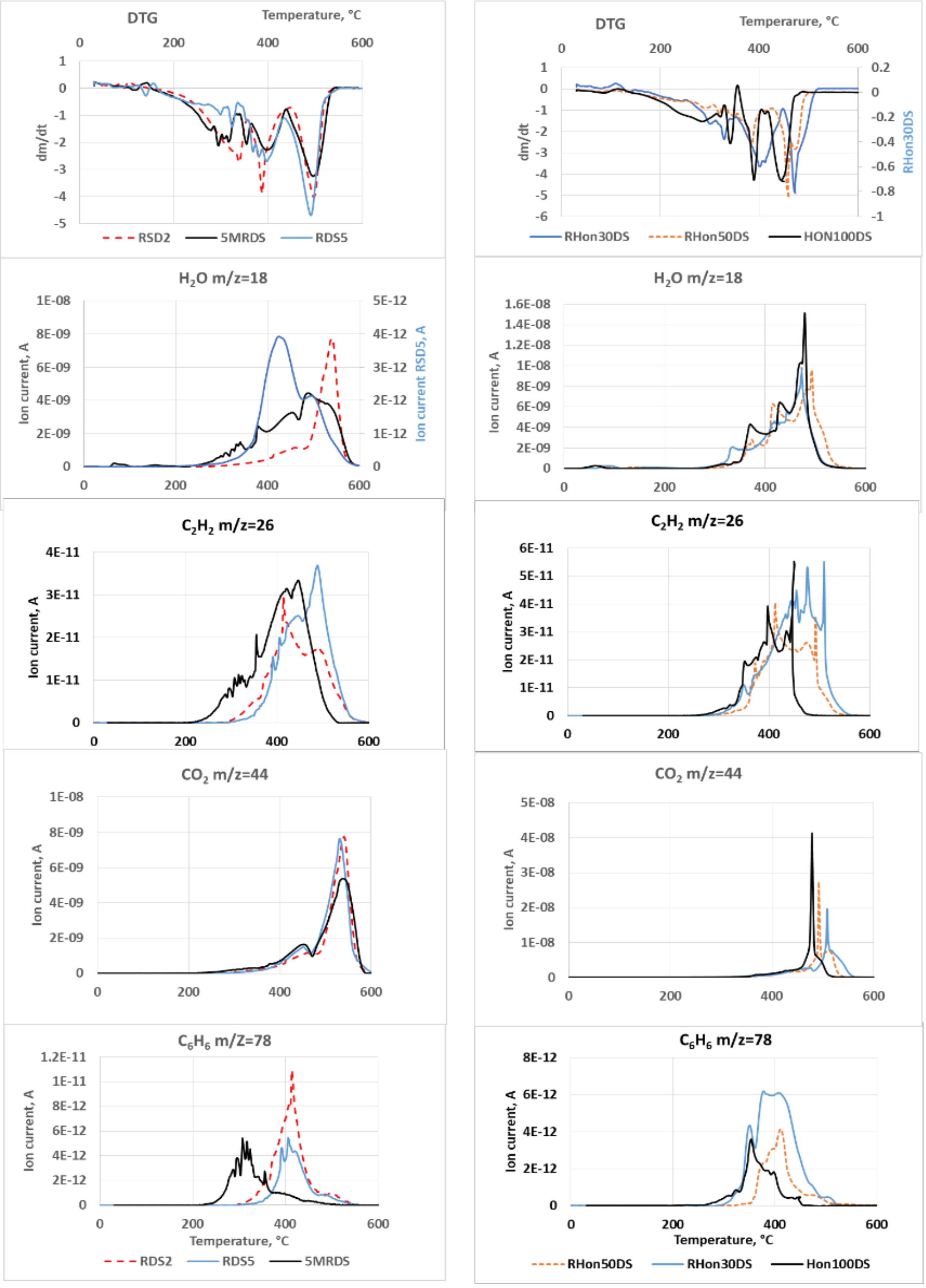


Figure 21. Evolvement of gases during resin heating in an Ar+20%O_2 atmosphere at a heating rate of 5 deg min^{-1}.

Conclusions

Novel aldehyde (formaldehyde and acetaldehyde) and non-aldehyde resins were successfully synthesized using oil shale alkylresorcinols (5-MR and 2.5-DMR) and industrial oil shale alkylresorcinol fractions (REZOL, HONEYOL 50, and HONEYOL 80), their technical characteristics, and their structures and MWDs were studied in detail. The resins SF, SAc, and DCPDS were analysed using GC, GC-MS, TLC, GPC, TGA, TG/DTG/DTA methods, and NMR spectroscopy. The following conclusions can be drawn from the studies conducted:

1. The optimal amounts of oil shale fractions in the resin synthesis were determined. The resin with 10% replacement of R to the REZOL fraction ($R_{90}Rez_{10}SF$) exhibited the best performance compared to other SFs obtained by adding more REZOL (softening point 89.0 °C, moisture content 0.3 wt%, ash content 0.2 wt%, and total contents of unreacted R 5.6 wt%, 5-MR 8.1 wt%, 5-ER 2.7 wt%, high thermal stability).
2. The possibility of synthesizing high-quality polycondensation resins without F, replacing it with Ac, has been shown. The resin synthesised with Ac ($R_{70}Rez_{30}SAc$) has a higher softening point (102.5 °C) than the resin synthesised with F ($R_{70}Rez_{30}SF$, 78 °C).
3. The use of pure Ac in the synthesis significantly decreases the volume of condensed moisture in SAc resin. This low volume of condensed moisture leads to reduction in the waste produced, requiring further purification and disposal. SAc contains 3–4 times fewer unreacted initial resorcinol components than SF.
4. The best conditions for the synthesis of non-aldehyde resins with their softening points in the range of 94–97 °C are discovered: molar ratio of R (5-MR) : DCPD: S = 1: 0.5: 0.3, temperature 135–170 °C, and synthesis time: 30 min–5 h. The resin ($R_{70}Hon80_{30}DS$) obtained using HONEYOL 80 has the best technical parameters: softening point 95 °C, ash content 0.2 wt%, total content of unreacted R and 5-MR 0.5 wt%. The synthesised non-aldehyde resins did not require any additional vacuum treatment. Insignificant amounts of water and volatile substances enable resin moulding without using additional ventilation for vapour removal.
5. The aralkylation of ARs molecules produces mainly a mixture of *ortho*- and *para*-substituted ARs that impact the oligomeric composition.
6. It has been shown that SF, SAc, and DCPDS resins are a mixture of oligomers with different chain lengths depending on the conditions of synthesis. The heterogeneity of resins was studied by TLC in the visible region of the spectrum for the first time. The TLC method provides successful separation of isomeric resin oligomers, which can subsequently be studied by NMR spectrometry.
7. Non-aldehyde resins contain many low-molecular-weight compounds (such as dimers and trimers), as determined by GPC and TLC. Their proportions can be as high as 30%.
8. All the resins (SF, SAc, and DCPDS) obtained were soluble in organic solvents such as acetone, THF, and EtOH. In addition, the RF and RSF resins were highly soluble in water, the SAc resins were only partially soluble in water, and DCPDS were generally insoluble in water.

The positive impact of the oil shale fractions to the resin properties was shown. Therefore, the production of SAc- and formaldehyde-free resins based on the industrial fractions of HONEYOL 50, HONEYOL 80, and REZOL can be considered promising, allowing the reduction of environmental damage during their synthesis and use in composites. This will open new prospects for multifunctional polymer products.

The next step will be introducing these resins to the industry, considering the modern requirements. Improving their properties leads to expanding areas of application, such as in the production of adhesive components and additives, electrical, paint and varnish, rubber products, composite materials.

List of Figures

Figure 1. Structural diagrams of the linear oligomers of resorcinol and formaldehyde. .. 15
Figure 2. Proposed mechanism of polycondensation and oligocyclization. 18
Figure 3. Softening point versus aldehyde/resorcinol ratio curve 19
Figure 4. Non-formaldehyde resorcinolic resin synthesis 19
Figure 5. Block diagram of the synthesis of formaldehyde and acetaldehyde resin (route II) 24
Figure 6. Block diagram showing the synthesis of non-aldehyde resins 25
Figure 7. Chromatograms: 28
Figure 8. Reaction for producing aralkyl derivatives 5-MR, 5-ER and 2.5-DMR. 30
Figure 9. Possible molecular structures of (a) formaldehyde and (b) acetaldehyde novolac resins modified with styrene. 31
Figure 10. Nuclear magnetic resonance ^{1}H and ^{13}C spectra of the SF resins 32
Figure 11. Thin-layer chromatography images: resorcinol (R), polystyrene (PS), resorcinol-formaldehyde resin (RF), resorcinol-formaldehyde resin modified with styrene (RSF) and resorcinol-acetaldehyde resin (RSAc) modified with styrene. 33
Figure 12. Thermogravimetry, derivative thermogravimetry, and differential thermal analysis curves of RSF, $R_{90}Rez_{10}SF$, and 5-MRSF in (a) an inert atmosphere and (b) air at a heating rate of 5 deg min^{-1}. 37
Figure 13. Gas evolution during the heating of the resins in an Ar+20%O_2 atmosphere at a heating rate of 5 deg min^{-1}. 39
Figure 14. Thermogravimetry, derivative thermogravimetry, and differential thermal analysis curves of the resins RSAc and 5-MRSAc in (a) an inert atmosphere and (b) air at a heating rate of 5 deg min^{-1}. 40
Figure 15. Resins appearance: a) formaldehyde resin, b) acetaldehyde resins, c) non-formaldehyde resins 41
Figure 16. The structures of resin units obtained at molar ratios of resorcinol component: DCPD: S – 1: 0.5: 0.3 42
Figure 17. Gel permeation chromatography traces of the RDS_4, RDS_5, and 5-MRDS samples converted into molecular weight distribution through calculations using polystyrene calibration curve 42
Figure 18. Gel permeation chromatography traces of the $R_{70}Rez_{30}SAc$, $R_{70}Hon80_{30}DS$, and $R_{70}Rez_{30}SF$ samples converted into molecular weight distribution through calculations using polystyrene calibration curve. 42
Figure 19. Synthesis reactions of (alkyl)resorcinol-dicyclopentadiene resins modified with styrene. 44
Figure 20. Thermogravimetry and differential thermal analysis curves of DCPDS in an Ar+20% O_2 atmosphere at a heating rate of 5 deg min^{-1}. 46
Figure 21. Evolvement of gases during resin heating in an Ar+20%O_2 atmosphere at a heating rate of 5 deg min^{-1}. 47

List of Tables

Table 1. Relative reaction rates of alkylresorcinols.. 15
Table 2. Charge distributions (q_C) in the R, 5-MR, 5-ER, and 2.5-DMR molecules 16
Table 3. Test results pertaining to rubber compounds 20
Table 4. Characteristics of the fractions of water-soluble oil shale alkylresorcinols. 22
Table 5. Molar ratios of the initial components used in preparing formaldehyde resins.. 23
Table 6. Molar ratios of the initial components used in the synthesis of acetaldehyde resins. 24
Table 7. Molar ratios of the initial components used in the synthesis of non-aldehyde resins. 25
Table 8. Resin characteristics. 35
Table 9. Free resorcinol content in the resins and the degree of polycondensation. 36
Table 10. Mass-loss temperatures of different resins in air. 38
Table 11. Solubility of formaldehyde and acetaldehyde resins in various organic solvents. 41
Table 12. Molecular-weight characteristics of the samples... 43
Table 13. Depth of the polycondensation process. 45

References

[1] M. Asim, N. Saba, M. Jawaid, M. Nasir, M. Pervaiz, O. Alothman. A Review on Phenolic Resin and its Composites, Current Analytical Chemistry, **2018**, 14 (3), 185–197, https://doi.org/10.2174/1573411013666171003154410

[2] P. Berdnikova, E. Zhizhina, Z. Pai. Phenol-Formaldehyde Resins: Properties, Fields of Application, and Methods of Synthesis. Catalysis in Industry, **2021**, 13, 119–124, https://doi.org/10.1134/S2070050421020033

[3] A. Alieva. Prospects for obtaining phenol-formaldehyde oligomers, Plasticheskie massy, **2021**, 9 (10), 22–26, https://doi.org/10.35164/0554-2901-2021-9-10-22-26

[4] K. Tang, A. Zhang, T. Ge, X. Liu, X. Tang, Y. Li. Research progress on modification of phenolic resin, Materials Today Communications, **2021**, 26, 101879, https://doi.org/10.1016/j.mtcomm.2020.101879

[5] R. Liteplo, R. Beauchamp, R. Chénier, M. Meek. Formaldehyde, World Health Organization, **2002**, Geneva.

[6] A. Robichaud. An overview of selected emerging outdoor airborne pollutants and air quality issues: The need to reduce uncertainty about environmental and human impacts, Journal of the Air & Waste Management Association, **2020**, 70 (4), 341–378.

[7] World Health Organization & International Programme on Chemical Safety, Phenol: health and safety guide, World Health Organization, Geneva, **1994.**

[8] Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May **2012** concerning the making available on the market and use of biocidal products, http://data.europa.eu/eli/reg/2012/528/oj (accessed: 11, 2023).

[9] European Chemical Industry Council. REACH Regulation and Formaldehyde, https://www.formacare.eu/about-formaldehyde/regulatory-status/reach-regulation-and-formaldehyde/ (accessed: 10, 2023).

[10] Yu. Lille, L. Bitter, T. Purre, A. Rätsep, K. Soo, L. Kalde, H. Nurske. Alkylresorcinols: Production methods, properties, and application, TsNIITEneftekhim, **1971**, Moscow

[11] E. Baerends, L. Grigoreva, N. Ostroukhov. Extraction of Total Water-Soluble Alkylresorcinols from the Tar Water of the Kiviter Process with Methyl Isobutyl Ketone Solid Fuel Chemistry, **2021**, 55, 177–186 https://doi.org/10.3103/S0361521921030046

[12] H. Raudsepp, V. Mihkelson, J. Ründal. Mõnede kahealuseliste fenoolide polükondensatsiooni uurimine: töö aruanne. Tallinna Polütehniline Instituut, orgaanilise keemia kateeder. Tallinna Polütehniline Instituut, **1955**, Tallinn.

[13] V. Shchipanov, H. Shumov. Study of the processes of interaction of total alkylresorcinols with aldehydes and provision of data for the development of technological processes based on them, Scientific report, **1962**, Tyumen.

[14] V. Vassiljev, K. Kiis, V. Dmitrijev, J. Izotova. Patterns of condensation of resorcinol and its alkyl derivatives with formaldehyde in an alcoholic environment, Proceedings of the academy of sciences of the Estonian SSR. Chemistry, 1987, 36 (2), 121–125, https://doi.org/10.3176/chem.1987.2.06

[15] J. Purga, K. Parve, I. Sirkel. Solid phenol formaldehyde resin, Patent EE200300522, **2003**.

[16] K. Tang, A. Zhang, T. Ge, X. Liu, X. Tang, Y. Li. Research progress on modification of phenolic resin Materials Today Communications, **2021**, 26, 101879, https://doi.org/10.1016/j.mtcomm.2020.101879

[17] R. Durairaj. Resorcinol: Chemistry, Technology and Applications, Indspec Chemical Corporation, **2005**, Pittsburgh https://doi.org/10.1007/3-540-28090-1

[18] J. Xu, N. Brodu, M. Mignot, B. Youssef, B. Taouk. Synthesis and characterization of phenolic resins based on pyrolysis bio-oil separated by fractional condensation and water extraction, Biomass and Bioenergy, **2022**, 159, 106393, https://doi.org/10.1016/j.biombioe.2022.106393

[19] Materials & Processes: Resin matrices for composites. Industry Overivew, Part I: Materials & Processes, Updated on 6/29/2022 Materials & Processes: Resin matrices for composites, Composites World (accessed: 10.2023).

[20] T. Dailey. Modified Alkylresorcinol Resins and Applications Thereof,Patent US20080090967A1, **2006.**

[21] R. Durairaj, A. Peterson. Nonformaldehyde, nonfuming resorcinolic resins and methods of making and using the same, Patent US6472457B1, **2002.**

[22] P. Sarika, P. Nancarrow, A. Khansaheb, T. Ibrahim. Bio-Based Alternatives to Phenol and Formaldehyde for the Production of Resins. Polymers, **2020**, 12(10), 2237, https://doi.org/10.3390/polym12102237

[23] J. Xu, N. Brodu, M. Mignot, B. Youssef, B. Taouk. Synthesis and characterization of phenolic resins based on pyrolysis bio-oil separated by fractional condensation and water extraction Biomass and Bioenergy, **2022**, 159, 106393, https://doi.org/10.1016/j.biombioe.2022.106393

[24] H. Lippmaa. Polycondensates of resorcinol and 5-methylresorcinol with formaldehyde, dissertation, Eesti NSV Teaduste Akadeemia, **1986**, Tallinn.

[25] Ya. Toyohiko, K. Koichi, K. Nobuo. Process for preparing resorcinol copolymers, Patent US4376854, **1983**.

[26] A. Freidin. Polymer water-based adhesives, Chemistry, **1985**, Moscow.

[27] Republican scientific conference "Synthesis of phenol-formaldehyde adhesive resins and aging of the adhesive joint." Tallinn Polytechnic Institute, **1971**, Tallinn.

[28] V. Levanovsky. Chemistry of oil shale phenols, **1976**, Leningrad

[29] Vasiliev V. V., Komarov V. Ya., Vetkova L. B., Ioniin B. I. Chemical shifts of carbon-13 mono- and diatomic phenols, Journal of Organic Chemistry, **1982**, 52(3), 524–528.

[30] Preparation method for resorcinol-formaldehyde resin, Patent CN103087282A, **2012.**

[31] J. Brydson. Plastics Materials, Seventh Edition, Publisher Elsevier, **1999**, https://doi.org/10.1016/C2009-0-30435-3

[32] B. Vladimirov, O. Kamalov, S. Bagaev. Increasing the heat resistance of tire rubber modifiers, Kirov Polytechnic Institute, Scientific report, **1985**, Kirov.

[33] J. Huang, L. Yang, P. Yunyi. Resorcinol modified hypercrosslinked poly(styrene-co-divinlybenzene) resin and its adsorption equilibriums, kinetics and dynamics towards p-hydroxylbenzaldehyde from aqueous solution, Chemical Engineering Journal, **2013**, 219 (3), 238-244, https://doi.org/10.1016/j.cej.2013.01.020

[34] Y. Bing, Y. Wenming, W. Mingyan. Resorcinol aldehyde resin formed by modification of olefin and aromatic hydrocarbon and production process thereof. Patent CN103113541, **2012**.

[35] N. Boreyko, Y. Gurvich, P, Kirpichnikov, V. Kadyrova, V. Kurbatov, A. Liakumovich, B. Matveev, S. Eppel, I. Titov, F. Miryasova, N. Okhotina, L. Sokovyh. Process for producing arylalkyl phenols, Patent SU929622A1, **1982**.

[36] L. Sogli, R. Ungarelli, L. Chapoy. Process for the alkylation of phenols, Patent US5043483, **1988**.

[37] T. Hood, M. Lamars. Rubber compounding resin, Patent US5049641A, **1988**.

[38] Ya. Horie. Synthesis of phenolic resin, Patent JP2001072731A, **2000**.

[39] Resorcinol aldehyde resin formed by modification of olefin and aromatic hydrocarbon and production process thereof, Patent CN103113541A, **2012**.

[40] Raj B. Durairaj, A. Jesionowski, A. Lawrence. Resorcinol resin-blocked isocyanates and their applications, Patent EA017875B1, **2006**.

[41] E. Yatsenko, V. Gutsalyuk, A. Safronova, L. Goncharova, L. Vasilyanova. Method of preparing phenol-acetaldehyde resin novolacs, Patent SU753855A1, **1980**.

[42] J. Xu, N. Brodu, Ch. Devougue-Boyer, B. Youssef, B.Taouk, Biobased novolac resins cured with DGEBA using water-insoluble fraction of pyrolysis bio-oil: Synthesis and characterization, Journal of the Taiwan Institute of Chemical Engineers, **2022**, 138, 104464, https://doi.org/10.1016/j.jtice.2022.104464

[43] J. Xu, N. Brodu, M. Mignot, B. Youssef, B. Taouk. Synthesis and characterization of phenolic resins based on pyrolysis bio-oil separated by fractional condensation and water extraction, Biomass and Bioenergy, **2022**, 159, 106393, https://doi.org/10.1016/j.biombioe.2022.106393

[44] D. Plachkova-Petrova, P. Petrova, St. Miloshev, Ch. Novakov. C-tetramethylcalix[4]resorcinarene, Optimization of reaction conditions for synthesis. Bulgarian Chemical Communications, **2012**, 44 (3), 208–215.

[45] Y. Kanematsu, A. Koyama, Y. Kuwabara, N. Sone, H. Oda. Control of the porous structure and the surface property of resorcinol-acetaldehyde carbon cryogels, TANSO, **2008**, 2008 (231), 13–17, https://doi.org/10.7209/tanso.2008.13

[46] F. Goodrich, J. Lawrence Dorsch, J.Smith. Internally coated reaction vessel for use in olefinic polymerization, Patent WO1982002555A1, **1982**.

[47] B. Durairaj, A. Peterson, Jr. G. Salee. Novel rubber compounding resorcinolic resins, Patent US4889891, **1989**.

[48] A. Safronova, L. Vasilyanova, V. Ivanov, V. Gabdrakipov, I. Arkhupova. Condensation of phenol with acetaldehyde in varius solvents in the presence of HCl, Vysokomolekuryarnye Soyedideneya, **1989**, A31 (9), 1904–1909.

[49] J. Rust, N. Orange. Phenolic acetaldehyde resin and process of making the same, Patent US2142076A, **1938**.

[50] J.B. Niederl, H. J. Vogel. Aldehyde-Resorcinol Condensations, Journal of the American Chemical Society, **1940**, 62 (9), 2512–2514, https://doi.org/10.1021/ja01866a067

[51] A. Despres, A. Pizzi, C. Vu, L. Delmotte. Colourless formaldehyde-free urea resin adhesives for wood panels, European Journal of Wood and Wood Products, **2010**, 68, 13–20, https://doi.org/10.1007/s00107-009-0344-y

[52] G. Foyer, B.-H. Chanfi, B. Boutevin, S. Caillol, G. David. New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors European Polymer Journal, **2016**, 74, 296–309, https://doi.org/10.1016/j.eurpolymj.2015.11.036

[53] J. Chrobak, J. Iłowska, A. Chrobok. Formaldehyde-Free Resins for the Wood-Based Panel Industry: Alternatives to Formaldehyde and Novel Hardeners, Molecules, **2022**, 27, 4862 https://doi.org/10.3390/molecules27154862

[54] A. Sinha. A novel manufacturing process of paper composite using recycled old newspaper sheets and phenol formaldehyde resin. Quarterly Journal of Indian Pulp and Paper Technical Association, **2021**, 33 (2), 13–17.

[55] Modified resorcinol resins and applications thereof, Patent CN1300206C, **2007**.

[56] M. Mohamed, L. Chia-Jung. Formaldehyde Free syntehesis of fully bio-based multifunctional bisbenzoxazine resins from natural renewable starting materials, macromolecules, Macromolecules, **2022**, 55 (8), 3106–3115, https://doi.org/10.1021/acs.macromol.2c00417

[57] D. Curvin. Modified dicyclopentadiene resins, Patent US5587007, **1996**.

[58] Ch. Xu, Y. Zhang, Z. Yuan. Formaldehyde-free phenolic resins, downstream products, their synthesis, and use, Patent US20160355631A1, **2015**.

[59] H. Dressler. Resorcinol: Its Uses and Derivatives. Publisher: Springer, **1994**, New York https://doi.org/10.1007/978-1-4899-0999-2

[60] G.-H. Hsiue, H.-F. Wei, S.-J. Shiao, W.-J. Kuo, Y.-A. Sha. Chemical modification of dicyclopentadiene-based epoxy resins to improve compatibility and thermal properties, Polymer Degradation and Stability, **2001**, 73 (2), 309–318, https://doi.org/10.1016/S0141-3910(01)00092-1

[61] Ch. Morel-Fourrier, T. Dreyfus, M. Bekhiekh, B. L. Stuck. Phenol/diene novolac resins, process of preparation and rubber-based compositions containing the said resins, Patent US6265490, **1996**.

[62] B. Durairaj, A. Lawrence. Resorcinolic derivatives and methods of making and using the same, Patent US6605670, **2001**.

[63] H. Lixin, L. Xudong, Z. Hongxing. Preparation method of alkylresorcinol formaldehyde resin, Patent CN103087284, **2013**.

[64] D. Mengcheng, H. Tao, S. Yanzhe. Production method of resorcinol formaldehyde resin, Patent CN103289036, **2013**.

[65] R. Durairaj, M. Walkup, M. Lawrence. Modified phenolic novolak resins (variants), s process for making thereof and a vulcanizable rubber composition containing thereof, Patent EA013431B1, **2010**.

[66] N. Boreyko, Ja. Gurvich, V. Kadyrova, P. Kirpichnikov, V. Kurbatov, A. Liakumovich, B. Matveev, F. Miryasova, N. Okhotina, I. Sokovykh, I. Titov, S. Eppel. Method for producing arylalkylphenols. Patent RU929622, **1982**.

[67] E. Carleton, N. Montclair. Resinous composition from phenol and acetaldehyde and process of making same, US1974605A, **1934**.

[68] V. Vasiliev. Anticorrosive, waterproofing materials based on non-traditional raw materials – shale oil and oxidized petroleum bitumen: monograph, SPbGIEU, **2007**, Sankt-Peterburg

[69] M. Cerf, S. Fouquay, I. Silberzan, B. Stuck, J.-J. Troslard. Novolac resins, process for preparing them and uses thereof, Patent 7135539, **2001**.

[70] Y. Lille, L. Bitter, H. Kundel, A. Murd, U. Peinar, L. Malko. On the composition of diatomic phenols boiling above 300 °C, Extraction and processing of oil shale, Issue 18, **1969**, Tallinn.

[71] ASTM E28. Standard Test Methods for Softening Point of Resins Derived from Pine Chemicals and Hydrocarbons, by Ring-and-Ball Apparatus.

[72] ASTM D6869. Standard Test Method for Coulometric and Volumetric Determination of Moisture in Plastics Using the Karl Fischer Reaction.

[73] ASTM E1868. Standard Test Methods for Loss-On-Drying by Thermogravimetry

[74] ISO 11358-1. Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles.

[75] ASTM E1131. Standard Test Method for Compositional Analysis by Thermogravimetry.

[76] ASTM D5630. Standard Test Method for Ash Content in Plastics.

[77] GOST 2070 Light petroleum products. Methods for determination of iodine numbers and content of unsaturated hydrocarbons.

[78] ASTM D5291. Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants.

[79] H. Liipmaa, T. Välimäe. Study of phenol-formaldehyde resin structure by spectrometric methods, Proceedings of TTU, **1990**, 719, 3–14.

[80] ChemSpider-Search and share chemistry// http://www.chemspider.com

[81] AIST: Spectral Database for Organic Compounds, SDBS, https://sdbs.db.aist.go.jp/sdbs/cgibin/direct_frame_top.cgi

[82] M. Horak, A. Pizzi, D. Ferreira, D. G. Roux. Condensates of Phenol, Resorcinol, Phloroglucinol, and Pyrogallol as Model Compounds of Flavonoid A- and B-Rings with Formaldehyde, Journal of applied polymer science, **1979**, 24, 1571 .

[83] H. Lippmaa, T. Välimäe. Study of the structure of phenol-formaldehyde resins by spectroscopic methods XI. Condensation of a mixture of resorcinol and 5-methylresorcinol with formaldehyde bound in oxymethyl groups. Proceedings of the Tallinn Polytechnic Institute, **1985**, 607, 17–26.

[84] U. Neumann. Alkylated and/or aralkylated polyhydroxy aromatic compounds and processes for their preparation and use, Patent US6277944B1, **2001**.

[85] R. Kamenev, L. Munter, Pikkov. Wastewater treatment in oil shale chemical Industry, Oil Shale, **2003**, 20, 443–457.

[86] P. Christjanson, T. Pehk, J. Paju. Structure and curing mechanism of resol phenol-formaldehyde prepolymer resins, Proceedings of the academy of sciences of the Estonian SSR, **2010**, 59, 225. https://doi.org/10.3176/proc.2010.3.05

[87] L. Pilato. Phenolic resins: 100 Years and still going strong, Reactive and Functional Polymers, 2013, 73 (2), 270–277, https://doi.org/10.1016/j.reactfunctpolym.2012.07.008

[88] Encyclopedia of polymers. Volume 1. Moscow, **1972**.

[89] Encyclopedia of polymers. Volume 3. Moscow, **1977**.

[90] N. Pavlov. Aging of plastics in natural and artificial conditions, Chemistry, 1982 Moskow.

Acknowledgements

I would like to first express my sincere and heartfelt gratitude to my supervisors: senior researcher at the Tallinn University of Technology, candidate of chemical sciences Kaia Tõnsuaadu, researcher at the Laboratory of Fuels Technology of Virumaa College, and candidate of chemical sciences Larisa Grigorieva, for their incredible support, encouragement, and motivation at all stages of my dissertation preparation. I thank you for your guidance, valuable advice, and discussion, and particularly for your patience.

I am grateful to my co-authors: Doctor of Natural Sciences Dmitry Bondarev, Senior Researcher at the Polymer Institute of the Slovak Academy of Sciences, for investigating the composition of resins using the GPC method; Doctor of Technical Sciences Valentin Vasiliev, Professor of Saint Petersburg State Mining University, for organising and analysing the NMR analysis of resins; and Tamara Yashicheva and Kristina Blum for their active participation in synthetic and analytical work.

Special thanks go to the former and current Virumaa College principals, Viktor Andrejev and Mare Roosileht, for their participation and support.

I am grateful for the financial support provided by the Kristjan Jaak National Scholarship Programme, which funded my participation in an international conference in Thailand.

I am grateful to all the people who were involved in one way or another in the preparation of my doctoral thesis.

Finally, I would like to express my heartfelt gratitude to my mother Tatjana Jurkeviciute and my sons Vadim, Daniil, Jurgis, Darius, and Adrian, who have been by my side throughout the preparation of this thesis.

Abstract

Synthesis of modified resins based on resorcinol and oil shale alkylresorcinols: structure and properties

Modern developments in the polymer industry have drawn attention to the production of polymers that are environmentally friendly and have minimal negative impacts on the environment, both during their production and use. Widely used phenol-formaldehyde resins do not meet the present technological requirements because of their high hygroscopicity, volatile substance content, including moisture content, and limited storage period. The toxicity of polycondensation resins can be reduced by replacing the phenol (Ph) and formaldehyde (F) in them with eco-friendly chemicals, such as resorcinol (R), alkylresorcinols (ARs), and other aldehydes, such as acetaldehyde (Ac). The production of non-aldehyde resins is also considered promising.

The substitution of raw materials for production of resins, including the use of oil shale ARs and various modifiers, improves the physicochemical, mechanical, ecological, and technical properties of resins. The addition of aliphatic or aromatic alkenes to the aromatic ring of (alkyl)resorcinols reduces the number of components released during resin processing and improves the interactions among polymer compound components.

The aims of this study were to (1) synthesize polycondensation formaldehyde (SF), acetaldehyde (SAc), and non-aldehyde (DCPDS) resins based on oil shale ARs [5-metylresorcinol (5-MR), 2.5-dimethylresortsinol (2.5-DMR)], industrial fractions of AR of Viru Keemia Grupp (HONEYOL 50, HONEYOL 80, and REZOL), and their blends comprising R pre-modified with styrene (S); (2) study the chemical structure of the resins obtained and the routes of their formations; and (3) determine the technical and physicochemical properties of those resins.

Aldehyde resins were synthesised in two stages. In the first stage, R was alkylated with styrene. In the second stage, F or Ac, was added to the mixture containing the alkylated molecules. The non-aldehyde resins were prepared according to the following scheme: the condensation of the resorcinol component using dicyclopentadiene (DCPD), followed by the addition of styrene to the oligomer molecules.

The catalyst mass required for the alkylation and polycondensation of the industrial fractions of ARs was calculated by considering the pyridine bases (0.3 wt% in terms of nitrogen).

The softening point, ash content, coke number, moisture content, volatile content, and the solubility of the synthesised resins in various polar and non-polar solvents were determined using standard methods. Qualitative and quantitative analyses of the resins were performed using gas chromatography (GC), thin-layer chromatography (TLC), and nuclear magnetic resonance (NMR) spectroscopy. GC and TLC were used to determine the content of unreacted (alkyl)resorcinols. The change in the styrene concentration during the aralkylation of (alkyl)resorcinols and their presence in the distillate after resins have been dried were determined using GC and iodometry. The thermal analysis and simultaneous determination of the released gases were performed to determine the thermal stability of the resins. The molecular weight distributions in the resins were determined using GPC and TLC.

It was revealed that the aralkylation of oil shale alkylresorcinol fractions under synthetic conditions occurred over a period that was two times the corresponding period of the individual ARs. It was observed that S reacted with R within 30 min. The reaction

between S and 5-MR occurred almost instantaneously. The products of the alkylation reaction were predominantly monosubstituted (alkyl)resorcinols.

The nature of interaction of individual resorcinols (R, 5-MR and 2.5-DMR) and oil shale ARs with styrene and the nature of condensation pre-modified R, 5-MR and 2.5-DMR with a cross-linking agent - F and Ac have been studied for the first time.

Aralkylation taking place in several directions has been established. Although, the addition of styrene to 5-MR, 5-ER and 2.5-DMR molecules predominantly takes place at the *ortho*- and *para*-position of the aromatic ring.

Synthesized SF resins have a deep crimson colour, SAc - from yellow to crimson, DCPDS - from crimson to brown. With increasing proportions of the ARs fractions (HONEYOL 50, HONEYOL 80, and REZOL) in the formulation, the resin acquired a brown colour. The resins obtained were hard, brittle, or plastic substances with softening points of 51.5-103 °C. The 2.5-DMRSAc resin has the lowest softening point of 51.5 °C. The use of DCPD as a cross-linking agent enabled the production of low-ash resins with softening point in the range of 75-97 °C.

The use of industrial oil shale ARs resulted in **SF resin** that had the best performance and high thermal stability when 10 mol % R was replaced by the REZOL fraction (RSARF-1/$R_{90}Rez_{10}SF$). Its characteristics were as follows: softening point: 89.0 ˚C, volatile content at 105°C: 0.4 wt. %, ash content: 0.2 wt. %, moisture content using the Karl Fischer: 0.3 wt. %, unreacted resorcinols (R and 5-MR): 13.7 wt. %, coke number: 23.8 wt. %. When the alkylresorcinol fraction (REZOL) in the formulation increased, the technical characteristics of the resin decreased.

The best technical parameters of **SAc resins** were obtained by replacing 30 mol % R with REZOL fraction: softening point: 102.5 °C, volatile content at 105 °C: 0.8 wt. %, ash content: 0.2 wt. %, moisture content: 0.8 wt. %, coke number: 20.4 wt.%, total content of unreacted resorcinols (R and 5-MR): 3.3 wt. %.

In the synthesis of **non-aldehyde resins**, it was possible to replace 30 mol % R with the HONEYOL 80 fraction. A further increase of the alkylresorcinol fraction led to a decrease of the technical characteristics. The resin $R_{70}Hon80_{30}DS$ had optimal technical parameters: softening point: 95 °C, ash content: 0.2 wt%, volatility at 105 °C: 1.2 wt%, and the amount of unreacted R and 5-MR in the resin: 0.5 wt%.

The softening point of the **acetaldehyde resins** $R_{70}Rez_{30}SAc$ and 5-MRSAc and the **formaldehyde resins** $R_{70}Rez_{30}SF$ and 5-MRSF changed from 78 to 102.5 °C and from 81.5 to 103.0 °C, respectively [Publications II and III]. The resin SAc contained ~3–10 times less unreacted resorcinol components than the resin SF.

The TLC analysis showed that the resins SF, SAc, and DCPDS comprised a set of oligomeric structures with different chain lengths. The resins **DCPDS** has a more homogeneous composition than aldehyde resins. Resins SF, SAc, and DCPDS resins were soluble in organic solvents, such as acetone, acetonitrile, THF, and EtOH. RF and RSF are highly soluble, SAc are only partially soluble, and DCPDS are insoluble in water. Thermal stability (10 % mass loss) was observed for SF up to 196-204 °C, SAc up to 194-238 °C, and DCPDS up to 250-302 °C. The oxidation of DCPDS began at temperatures above 200 °C.

Based on the study results, we could conclude that oil shale ARs could serve as an alternative to known raw materials (Ph and R). The possibility of replacing formaldehyde with acetaldehyde to obtain formaldehyde-free resins was demonstrated. The possibility of obtaining non-aldehyde resins has been demonstrated. The molar ratios of the initial components affect the characteristics of the resins and the molecular composition of the final product. It should be noted that the synthesis of SAc requires special equipment because of the low boiling point of Ac (~20 °C) [Publication II]. By pre-alkylating the resorcinol components with an aromatic alkene (S), it was possible to reduce the amount of volatiles released from the aldehyde resin during its processing and storage. The resins obtained using DCPD instead of aldehydes and modified with styrene contained less than 0.05 wt% ash and less than 1 wt% unreacted R and 5-MR. This has improved the thermal properties of the resins, and thus, during storage, they are more stable compared to aldehyde resins. The use of DCPD enables the formation of resins whose production does not require water stripping [Publication III].

Thus, the production of SAc and DCPDS resins based on individual R, 5-MR, which can partially be replaced by the industrial fractions HONEYOL 50, HONEYOL 80, and REZOL produced at the Viru Keemia Grupp, can be considered a very promising direction. The synthesis of resins based on such raw materials will allow expansion of the application area and improve their properties in comparison with traditional resins. Thus, prospects for obtaining not only the products listed in this study but also several other multifunctional polymer products have opened up. The presence of reactive functional groups and fragments in the resins allows their modification with other organic compounds. The next step of the study was to study the behaviour of these resins in various composites.

Lühikokkuvõte

Modifitseeritud vaikude süntees resortsinooli ja põlevkivi alküülresortsinoolide alusel: struktuur ja omadused

Kaasaegne polümeermaterjalide tööstuse areng on suunatud keskkonnasõbralike polümeeride loomisele, millel on minimaalne negatiivne mõju keskkonnale nii tootmisprotsessis kui ka kasutamise ajal. Laialdaselt kasutatud fenool-formaldehüüdvaigud ei vasta tänapäevastele tehnoloogilistele nõuetele suure hügroskoopilisuse, lenduvate ainete, sealhulgas niiskusesisalduse ja piiratud säilivusaja tõttu. Polükondensatsioonvaikude toksilisust saab vähendada asendades fenoolid (Ph) ja formaldehüüdid (F) keskkonnasõbralikumate komponentidega nagu resortsinool (R), alküülresortsinoolid (ARs) või teised aldehüüdid [nt atsetaldehüüd (Ac)]. Paljutõotavaks peetakse ka aldehüüdide vabade vaikude tootmist.

Praegu toodetakse põlevkivist, peale elekrienergia, peamiselt põlevkiviõli, mida kasutatakse laevakütuse lisandina, küttekatelde ja tööstuslike ahjude kütteks ja keemiatööstuse toorainena. Lisaks tootakse põlevkivist nii peenkeemia tooteid, nagu 2-metüülresortsiin, 5-metüülresortsiin-anhüdriit ja 5-metüülresortsiin-monohüdraat jne, kui ka alküülresortsinoolide tööstuslikke segusid – Honeyol™, Rezol™. Tänu segu koostisele võivad põlevkivi alküülresortsiinid asendada resortsiini, bisfenoole ja sünteetilist fenooli polümeeride sünteesis.

Tooraine asendamine, sealhulgas põlevkivi ARs kasutamine, ja erinevate modifikaatorite kasutamine võimaldab parandada vaikude füüsikalis-keemilisi, mehaanilisi, ökoloogilisi ja tehnilisi omadusi. Modifikaatorite kasutamisega alifaatsete või aromaatsete alkeenide sisseviimine (alküül)resortsinoolide aromaatsesse tsüklisse võimaldab vähendada vaigu töötlemise käigus vabanevate ühendite hulka ja parandada polümeermaterjalide komponentide vastastikmõju.

Käesolevas töös (1) uuriti formaldehüüd-, atsetaldehüüd- ja aldehüüdivabade vaikude polükondensaatsioonsünteesi kasutades toorainena põlevkivist toodetud ARs [5-metüülresortsinool (5-MR), 2,5-dimetüülresorsinol (2,5DMR)] ja Viru Keemia Grupp AS tööstuslike ARs-ide fraktsioone (REZOL, HONEYOL 50 ja HONEYOL 80) ning nende segusid R-ga. Resortsinoolide eelnevaks modifitseerimiseks kasutati stüreeni (S); (2) uuriti saadud vaikude keemilist struktuuri ja nende moodustumise kemismi; (3) määrati vaikude tehnilised ja füüsikalis-keemilised omadused.

Aldehüüdvaikude süntees viidi läbi kahes etapis. Esimeses etapis alküüliti resortsinool lähteaine S-ga. Pärast seda lisati alküülitud molekulide segule F või Ac. Aldehüüdivabad vaigud valmistati järgmise skeemi kohaselt: esmalt kondenseeriti resortsinool lähteaine ditsüklopentadieeniga, mille järel lisati oligomeeri molekulile S-i.

Alküülimis- ja polükondensatsioonprotsesside jaoks vajaliku katalüsaatori massi arvutamisel võeti arvesse ARs-de tööstuslikes fraktsioonides sisalduva püridiinaluste (~0,3 %) sisaldust.

Sünteesitud vaikude pehmenemispunkt, tuhasisaldus, koksiarv, niiskusesisaldus, lenduvate komponentide sisaldus, lahustuvus erinevates polaarsetes ja mittepolaarsetes lahustites määrati standardmeetoditega.

Vaikude kvalitatiivne ja kvantitatiivne analüüs viidi läbi gaaskromatograafia (GC) ja õhukese kihi kromatograafia (TLC) meetoditega, ^{1}H ja ^{13}C NMR spektroskoopiaga. GC- ja TLC-meetodeid kasutati ka reageerimata jääk (alküül)resortsinoolide sisalduse määramiseks. S-i kontsentratsiooni muutus (alküül)resortsinoolide alküülimise käigus ja sisaldus destillaadis pärast vaigu kuivatamist määrati GC ja jodomeetria meetoditega. Vaikude termilise stabiilsuse uurimiseks kasutati termilist analüüsi koos eraldunud gaaside samaaegse määramisega. Molekulaarmassi jaotumine vaikudes määrati geel kromatograafia (GPC) ja TLC abil.

Näidati, et põlevkivi ARs-de fraktsioonide alküülimine toimub vaikude sünteesi tingimustes kaks korda kauem kui individuaalsete ARs-idega. Leiti, et S reageerib R-dega kuni 30 minuti jooksul. S-i reaktsioon 5-MR-ga toimub peaaegu kohe. Alküülimisreaktsiooni produktid on valdavalt monoasendatud resortsinoolid. Tekivad peamiselt kahte tüüpi asendatud alküülitud molekulid, kus asendamine toimub aromaatse ringi *orto-* ja/või *para-* positsioonides.

Sünteesitud vaikude värvus varieerub: formaldehüüdvaikud (**SF**) on tume karmiinpunased, atsealdehüüdvaigud (**SAc**) kollasest karmiinpunaseni ja aldehüüdivabad vaigud (**DCPDS**) karmiinpunasest pruunini. AR fraktsioonide (HONEYOL 50, HONEYOL 80, REZOL) osakaalu suurenemisega sünteesisegus muutub vaik pruuniks. Saadud vaigud on kõvad, rabedad või plastilised ained, mille pehmenemistemperatuur on 51,5–103 °C. 2.5-DMRSAc vaigu madalaim pehmenemistemperatuur on 51,5 °C. DCPD kasutamine ristsiduva ainena võimaldab saada vähese tuhasisaldusega vaike, mille pehmenemistemperatuur on 75–97 °C.

Tööstuslike põlevkivi ARs-de kasutamine suurendas **SF vaigu** tootmise tulemuslikkust ja omadusi. 10 mol% R asendamisel REZOL fraktsiooniga (RSARF-1/$R_{90}Rez_{10}SF$) saadi kõrge termilise stabiilsusega vaik, mille pehmenemistemperatuur oli 89,0 ˚C, lenduvate komponentide sisaldus temperatuuril 105 °C – 0,4 %, tuha sisaldus 0,2 %, niiskus (Karl Fischer) 0,3 %, jääk resortsinoolide (R ja 5-MR) sisaldus 13,7 %, koksi arv 23,8 %. ARs REZOLi fraktsiooni koguse suurendamine sünteesi segus vähenedas vaigu tehnilisi omadusi.

Parimate tehniliste parameetritega **SAc vaigud** saadi R asendamisel 30 mol% REZOL fraktsiooniga: pehmenemistemperatuur 102,5 °C, lenduvate komponentide sisaldus 105°C juures – 0,8 %, tuhasisaldus 0,2 %, niiskus 0,8 %, koksi arv 20,4 %, jääk resortsinoolide (R ja 5-MR) üldsisaldus 3,3 %.

Aldehüüdivabade vaikude sünteesimisel oli võimalik 30 mol% R asendada fraktsiooniga HONEYOL 80. Parima vaigu tehnilised parameetrid: pehmenemistemperatuur 95 °C, tuhasisaldus – 0,2 %, massikadu 105 °C juures 1,2 %, jääk R või 5-MR sisaldus <0,5 % olid vaigul $R_{70}Hon80_{30}DS$. AR fraktsiooni sisalduse suurendamine alandas vaigu tehnilisi omadusi.

Atsetaldehüüdvaikude ($R_{70}Rez_{30}SAc$ ja 5-MRSAc) pehmenemistemperatuurid tõusid võrreldes formaldehüüdvaikudega ($R_{70}Rez_{30}SF$ ja 5-MRSF) vastavalt 78-lt 102.5 °C-le ja 81.5–103.0 °C-le. SAc vaigud sisaldavad ~3–10 korda vähem reageerimata resortsinoolkomponente võrreldes SF-vaikudega.

TLC analüüs näitas, et SF, SAc ja DCPDS vaigud koosnevad erineva ahela pikkusega oligomeersetest struktuuridest. **DCPDS-vaikudel** on võrreldes aldehüüdvaikudega ühtlasem struktuur. SF, SAc, DCPDS vaigud lahustuvad orgaanilistes lahustites nagu atsetoon, atsetonitriil, tetrahüdrofuraan ja etüülalkohol. RSF vaigud lahustuvad hästi, SAc lahustuvad ainult osaliselt ja DCPDS on vees lahustumatud. SF, SAc ja DCPDS vaigud on termiliselt stabiilsed (10% kaalukadu) vastavalt temperatuurini 196–204 °C, 194–238 °C ja 250–302 °C. DCPDS-vaikude oksüdeerumine algab temperatuuril üle 200 °C.

Töö tulemused lubavad järeldada, et põlevkivi ARs kasutamist võib käsitleda alternatiivina teadaolevatele toorainetele (Ph ja R). Näidati võimalusi formaldehüüdi asendamiseks atseetaldehüüdiga formaldehüüdivabade vaikude saamiseks.

Lähtekomponentide molaarsuhe mõjutab vaikude omadusi ja produkti molekulaarset struktuuri. Tuleb märkida, et SAc-vaikude süntees nõuab Ac madala keemistemperatuuri (umbes 20 °C) tõttu spetsiaalset varustust [Publikatsioon II]. Resortsinooli komponentide eelnev alküülimine aromaatse alkeeniga (S) võib vähendada töötlemise ja ladustamise käigus aldehüüdvaigust eralduvate ainete hulka. See võimaldab sünteesida madala ARs sisaldusega vaiku ilma nende tehnoloogilisi omadusi alandamata. Aldehüüdide asemel DCPD-d kasutamisel saadud ja S-ga modifitseeritud vaigud ei sisalda tuhka rohkem kui 0,05 %, reageerimata R ja 5-MR vähem kui 1 % ning neil on aldehüüdvaikudega võrreldes paremad termilised omadused ja on ladustamisel stabiilsemad. DCPD kasutamine võimaldab tootmist läbi viia ilma vee eraldamiseta destilleerimisega.

Seega võib väga perspektiivikaks suunaks pidada R ja 5-MR baasil valmistatud SAc ja DCPDS vaikude tootmist, asendades R ja 5-MR osaliselt Viru Keemia Grupp AS toodetud tööstuslike fraktsioonidega HONEYOL 50, HONEYOL 80 ja REZOL. Sellistel toorainetel põhinevate vaikude süntees laiendab nende kasutusala ja parandab omadusi võrreldes traditsiooniliste vaikudega. See avab väljavaated mitte ainult töös loetletud toodete, vaid ka paljude muude multifunktsionaalsete polümeertoodete valmistamiseks. Reaktiivsete funktsionaalrühmade ja fragmentide olemasolu vaikudes võimaldab neid modifitseerida teiste orgaaniliste ühenditega. Järgmised sammud on selliste vaikude käitumise uurimine erinevates komposiitides.

Appendix

Publication I

A. Yurkevichyute, L. Grigorieva, V. Vassiljev. “Synthesis of Solid Resorcinol-Formaldehyde Resin Modified with Styrene with the Use of a Shale Phenol Fraction with a Boiling Temperature Higher Than 270 °C”, Solid Fuel Chemistry, 50(1), 64–68, 2016, DOI 10.3103/S0361521916010122

ISSN 0361-5219, Solid Fuel Chemistry, 2016, Vol. 50, No. 1, pp. 64–68. © Allerton Press, Inc., 2016.
Original Russian Text © A.S. Yurkevichyute, L.S. Grigor'eva, V.V. Vasil'ev, 2016, published in Khimiya Tverdogo Topliva, 2016, No. 1, pp. 66–70.

Synthesis of Solid Resorcinol–Formaldehyde Resin Modified with Styrene with the Use of a Shale Phenol Fraction with a Boiling Temperature Higher Than 270°C

A. S. Yurkevichyute[a], L. S. Grigor'eva[a], and V. V. Vasil'ev[b]
[a] *Virumaa College, Tallinn University of Technology, Kohtla-Järve, 30322 Estonia*
e-mail: ana.jurkeviciute@ttu.ee; larisa.grigorieva@ttu.ee
[b] *St. Petersburg State University of Economics, St. Petersburg, 191023 Russia*
e-mail: vasvalvs@mail.ru

Received February 25, 2015

Abstract—The synthesis of modified solid resorcinol–formaldehyde resins based on resorcinol and a fraction of water-soluble shale alkylresorcinols ($T_b > 270°C$) was studied. Styrene was used as a modifier. Data on the quality of the target products depending on a molar ratio between the initial components were acquired.

DOI: 10.3103/S0361521916010122

Resorcinol–formaldehyde resins are widely used in many branches of industry, such as woodworking, tire, and mechanical rubber industries. The high cost of resorcinol–formaldehyde resins leads to the rise in price of the products on their basis. A possible version decreasing the cost is the replacement of an initial component (resorcinol) by shale alkylresorcinols, which are formed as a by-product during the thermal processing of shale. This leads to the expansion of the areas of their application and the reduction in the price of resin with the retention of high consumer indices.

It is well known that the resorcinol–formaldehyde resins are obtained by the polycondensation of resorcinols and aldehydes. The polycondensation of resorcinol and formaldehyde is a complex set of sequential and simultaneous reactions. Depending on the chemical structure of source materials, the molar ratio between components (resorcinol/alkylresorcinol : formaldehyde), and the nature of a catalyst (alkaline or acid), the following two types of resins are formed: thermoplastic (novolak) and thermosetting (resol) resins [1].

The novolak resins (thermoplastic oligomers) are obtained on the heating of a resorcinol compound with a substoichiometric amount of aldehyde, usually, in the presence of an acid catalyst. The molar ratio of the resorcinol compound to the aldehyde should be higher than unity. This is necessary in order to avoid crosslinking and/or gel formation during the synthesis of resins.

An aromatic or aliphatic alkene is introduced into the aromatic nucleus of the initial resorcinol in the synthesis of resin in order to decrease the amount of the volatile products of resorcinol–formaldehyde resin degradation in the processing of rubber mixtures and to increase intermolecular interaction between the components of rubber mixtures based on butadiene–styrene rubbers.

Aralkylresorcinols are the derivatives of resorcinol. Usually, they are obtained by interaction of resorcinol with aromatic olefins or allyl compounds. A vinyl compound such as styrene is widely used as a modifier for the production of resins with improved characteristics [2, 3]. The resorcinol : styrene molar ratio plays an important role because it leads to the formation of three types of compounds with different softening temperatures [4]. As is well known, the softening temperature is an important technological characteristic of resins.

In this work, we present the results of preliminary studies on the production of qualitatively new solid alkylresorcinol–formaldehyde resin modified with styrene, in which expensive resorcinol is partially replaced by a fraction of water-soluble shale phenols with a boiling point higher than 270°C from VKG Oil AS.

EXPERIMENTAL

Source materials for the production of resins were resorcinol (99.9 wt %), 5-methylresorcinol (99.9 wt %), a fraction of water-soluble shale phenols, which boiled away at a temperature of >270°C (Table 1), formalin (37.4 wt %), and styrene (99.99 wt %). A 2*N* solution of sulfuric acid was used as a catalyst. A 2*N* solution of sodium hydroxide was used for its neutralization.

The synthesis of resorcinol–formaldehyde resins was carried out in a round-bottom three-neck flask supplied with an Allihn reflux condenser, a separatory funnel, and a temperature control device. The temperature and stirring rate of a mixture during the synthesis were maintained with the aid of a magnetic stirrer with adjustable heating and rotation rate (IKA RCT basic). A calculated quantity of resorcinol, 5-methylresorcinol, or a mixture of resorcinol and the phenol fraction was loaded in the flask. The contents of the flask were melted. 0.2 wt % of an acid catalyst was added to the melt. Then, freshly distilled styrene was added drop by drop. The reaction was carried out for 30 min at 150°C. At the end of the aralkylation reaction, a solution of formaldehyde (37.4 wt %) was added drop by drop to the mixture. After the introduction of the entire quantity of the solution of formaldehyde, the mixture was kept for 1 h at a temperature of 100 ± 2°C. After the completion of the reaction, the catalyst was neutralized by an equivalent quantity of NaOH. Water and unreacted components were distilled from the reaction mass initially at atmospheric pressure and then in a vacuum (~0.08 MPa). The rate of stirring was maintained at a level of 150 rpm. The resulting hot resin was poured out into a metallic vessel and cooled. The resin was crushed before the determination of physicochemical characteristics.

In the synthesis of resorcinol–formaldehyde resins with the partial replacement of resorcinol by the phenol fraction, this latter was preliminarily heated and added into the reaction flask after the aralkylation of resorcinol with styrene.

In the synthesis of resin based on 100% phenol fraction (ARSF), styrene was added directly to this fraction.

The molar ratios between the initial components for conducting the experiments and the temperature and time parameters were chosen in accordance with the results obtained in a patent search [3–10]. Table 2 summarizes the experimental data.

In this work, we synthesized polycondensation resorcinol–formaldehyde resins modified by styrene based on resorcinol (RSF) and 5-methylresorcinol (5-MRSF) and with different resorcinol : phenol fraction ratios (RSARF-1, RSARF-3, RSARF-5, and ARSF) and resorcinol-formaldehyde resin without styrene modification (RF). Numbers in the designations of resins (1, 3, and 5) indicate the phenol fraction content of the formula of resin instead of resorcinol (10, 30, and 50%, respectively).

For the final product, we determined the softening temperature (°C) according to a ring-and-ball method [11], the concentration of volatile components at 105°C according to [12], the ash content at 830°C according to [13], and the coke values by thermogravimetric analysis (TGA). According to published data [14], it is possible to make a preliminary conclusion on the heat resistance of the polymer. The integral TGA curves were measured in a temperature range from 25 to 830°C at a heating rate of 5 K/min on a TGA instrument from Mettler Toledo. The moisture content of the resin samples was determined by coulometer titration on a C30 Compact Karl Fischer Coulometer from Mettler Toledo. The titration cell was filled with a solution of the reagent Hydranal Coulomat AD from Sigma-Aldrich. Thin-layer chromatography (TLC) was used for the qualitative determination of unreacted resorcinols and alkylresorcinols and semiquantitative ratios between of dimers, trimers, and other oligomers in the resins. The 1 wt % solutions of resins in acetone were prepared for TLC. The spots obtained on TLC plates (Silica gel/TLC-cards, Fluka) were processed by densitometry with the aid of the Sorbfil software. The quantitative composition of the phenol fraction and the unreacted alkylresorcinols of resin (Table 2) was determined by gas–liquid chromatography (GLC). The 1 wt % solutions of the phenol fraction and the ether extracts of the end products were chromatographed. Analysis was carried out on a Thermo Finnigan TRACE GC chromatograph with a flame-ionization detector. The analytes were separated with the use of an RTX-5 capillary column in a temperature range of 100–270°C with a heating rate of 5 K/min.

Table 1. Characteristic of the fraction of water-soluble shale phenols ($T_b > 270°C$)

Composition	Concentration, wt %
Moisture	0.3
Monohydric phenols	10.2
Resorcinol (*R*)	2.1
5-Methylresorcinol (5-*MR*)	41.0
5-Ethylresorcinol (5-*ER*)	11.4
Pyridine bases	0.3

* On a pyridine basis.

The degree of styrene interaction with resorcinol, 5-methylresorcinol, and the phenol fraction in an aralkylation reaction was determined based on the iodine number of distillate after the synthesis of resins in accordance with a published procedure [15]. The nitrogen content was determined by the combustion of the phenol fraction in a flow of oxygen with the subsequent detection of the released gases by a katharometer [16]. The values obtained were converted to the

Table 2. Effect of a molar ratio between raw material components on the physicochemical properties of resins and the concentrations of unreacted substances in them

Initial component/characteristic	Resin						
	RF	*RSF*	5-*MRSF*	*RSARF*-1	*RSARF*-3	*RSARF*-5	*ARSF*
	1	2	3	4	5	6	7
Molar ratios between the initial components used in the synthesis of resins							
R	1.5	1.5	–	1.35	1.05	0.75	–
5-*MR*	–	–	1.5	–	–	–	–
Fraction of water-soluble shale phenols (T_b > 270 °C)	–	–	–	0.15	0.45	0.75	1.5
Styrene	–	0.3	0.3	0.3	0.3	0.3	0.3
Formaldehyde	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Physicochemical indices of resorcinol–formaldehyde resins							
Softening temperature, °C	66.0	84.0	81.5	89.0	78.0	69.0	69.3
Volatile components at 105 °C, wt %	1.4	0.6	1.7	0.4	0.6	0.7	0.9
Ash content, wt %	0.7	0.3	0.6	0.2	0.4	0.4	0.1
Moisture content, wt %	2.0	0.2	0.9	0.4	0.3	0.5	0.5
Coke number, wt %	26.4	24.0	17.9	23.9	19.4	18.9	13.8
Concentration of unreacted components in resins, wt %							
R	19.1	7.7	–	5.6	6.4	5.4	2.1
5-*MR*	–	–	6.4	8.1	7.8	10.4	12.1
5-*ER*	–	–	–	2.7	3.5	4.4	4.5

quantity of pyridine bases present in the phenol fraction [17].

RESULTS AND DISCUSSION

The introduction of styrene into the formula makes it possible to increase the softening temperature of resin by a factor of 1.3 and also to sharply decrease the moisture content by a factor of 2–10. At the same time, the amount of unreacted resorcinol in RF and RSF resins decreases by a factor of 2.5.

Thus, the RF resin obtained without modification by styrene is characterized by a low softening temperature and increased concentrations of moisture, volatile components, and unreacted resorcinol. It should be noted that the RF resin is most hygroscopic among all of the obtained resins. According the data given in Table 2, the moisture content of this resin exceeds the content of volatile substances to confirm its hygroscopicity.

The amount of the phenol fraction introduced into the formula instead of resorcinol influences not only the softening temperature of resin but also other characteristics. As shown above, the phenol fraction contains pyridine bases. In the versions of the synthesis with the use of a small additive of the phenol fraction (to 10%), the influence of pyridine bases was almost absent because the reaction of polycondensation was performed in an acidic medium. A further increase in the phenol fraction in the formula affects the quality of resins to worsen them. Thus, an increase in the quantity of this fraction in the formula by 20% leads to a decrease in the softening temperature of resin by 10°C. Simultaneously, the concentrations of volatile components and low-molecular-weight oligomers (dimers and trimers) increases. In the course of the polycondensation reaction, the amount of a macromolecular structure polymer in the resin decreases as the phenol fraction : resorcinol molar ratio is increased from 0.0 : 0.15 to 1.5 : 0.0 mol : mol. An increase in the concentration of the low-molecular-weight oligomers in the resin was found with the use of TLC.

This phenomenon can be explained, on the one hand, by an insufficient amount of an acid catalyst for the polycondensation reaction. A portion of this catalyst is neutralized by pyridine bases, which occur in the fraction of water-soluble shale phenols (Table 1). On the other hand, the amount of alkylresorcinols with long-chain linear and cyclic groups increases simultaneously with the amount of this fraction in the formula [18]. They are spatially hindered and have screened active centers. This prevents the formation of macromolecules on their interaction with formaldehyde.

Table 3. Degree of conversion in the process of polycondensation

Resin	Resorcinol components of the initial mixtur	Initial concentration of free resorcinols, wt %	Amount of free resorcinols in resin, wt %	Conversion level of polycondensation, %
RF	*R*	100.0	19.1	80.9
RSF	*R*	100.0	7.7	92.3
5-*MRSF*	5-*MR*	100.0	6.4	93.6
RSARF-1	*R*	87.5	5.6	93.6
	5-*MR*	9.7	8.1	16.5
	5-*ER*	2.8	2.7	3.6
RSARF-3	*R*	66.9	6.4	90.4
	5-*MR*	25.8	7.8	69.8
	5-*ER*	7.3	3.5	52.1
RSARF-5	*R*	46.5	5.4	88.4
	5-*MR*	41.7	10.4	74.6
	5-*ER*	11.8	4.4	62.7
ARSF	*R*	2.1	2.1	0.0
	5-*MR*	74.3	12.1	83.7
	5-*ER*	25.7	4.5	82.5

Upon the addition of 30–50% phenol fraction, resin with a lower softening temperature was obtained; this fact is indicative of an insufficient degree of the reaction. In this case, both of the factors could affect the softening temperature of resin: the presence of alkylresorcinols with long-chain linear and cyclic groups in the phenol fraction [18] and an increased concentration of pyridine bases.

Upon conducting the synthesis based on 100% phenol fraction without the addition of resorcinol, resin with a low softening temperature (69°C) was obtained. The distillate contained a large amount of unreacted styrene. In this case, the influence of pyridine bases could play a decisive role. The amount of pyridine bases was almost entirely consumed the neutralization of the reaction catalyst (H_2SO_4); therefore, the aralkylation and polycondensation reactions occurred in a neutral medium, but this is undesirable in this case.

Deficiency in a catalyst and the presence of pyridine bases and long-chain alkylresorcinols in the composition of the phenol fraction affect the degree of conversion of styrene in the synthesis of resins, which is responsible for their softening temperature. In the synthesis of ARSF resin, the conversion of styrene was as high as 42%, whereas it was 100% in the synthesis of resins 2–5. In RSARF-5 resin, the degree of styrene conversion was 96%.

The ratio and type of initial components influence the concentration of coke residue in resins. The RF, RSF, and RSARF-1 resins are characterized by an increased carbon content. They are more inclined to carbonization than 5-MRSF, RSARF-3, RSARF-5, and ARSF. This was confirmed by the obtained values of coke numbers for the synthesized resins. According to Kalinina [14], the most thermally stable resins are RF, RSF, and RSARF-1.

The highest conversion of alkylresorcinols was observed in 5-MRSF resin; this can be explain by an increased reactivity of 5-MR, from which it was obtained. The lowest degree of conversion in the process of polycondensation was noted in the course of experiments with RF and ARSF resins.

From the data given in Table 3, it follows that the greatest degree of *R* conversion was reached in the synthesis of resin with the replacement of a 10 wt % amount by the phenol fraction. In this case, the minimum degrees of conversion were observed in 5-MR and 5-ER. With increasing the amount of a phenol fraction in the formula, the degree of conversion in the reaction of polycondensation decreased in resorcinol and increased in alkylresorcinols (5-MR and 5-ER).

Thus, in the course of this study, we found that solid resorcinol–formaldehyde resins modified with styrene can be synthesized based on the mixtures of resorcinol and a water-soluble shale phenol fraction ($T_b > 270°C$). This can lead to a significant reduction of the prices of resin formulas with the retention of consumer characteristics, and will extend the applicability of the fraction.

CONCLUSIONS

We carried out the preliminary syntheses of modified solid resorcinol–formaldehyde resins with the partial or complete replacement of resorcinol by the fraction of water-soluble shale phenols ($T_b > 270°C$). Styrene was used as a modifier. Data on the reactivity of raw material components in the formulas with styrene were acquired. The effect of the resorcinol : phenol fraction and styrene : phenol fraction molar ratios on the quality of the target product was studied. It was found that the pyridine bases that occur in the phenol fraction have an essential effect on the conversion of alkylresorcinols and styrene in the polycondensation performed in an acidic medium.

REFERENCES

1. Durairaj, R., *Resorcinol: Chemistry, Technology, and Applications,* US Indspec Chemical Corp., 2005.
2. Neumann, U., US Patent 6277944B1, 2001. http://www.epo.org/.
3. Harvey, T., US Patent 20080090967, 2008. http://www.epo.org/.
4. Hood, R. and Lamars, R., US Patent 5049641, 1991. http://www.epo.org/.
5. Hu, L., Lang, X., and Zong, H., CN Patent 103087284, 2013.
6. Du, M., Han,T., and Song, Y., CN Patent 103289036, 2013. http://www.epo.org/.
7. Yu, B., Yu, W., and Wang, M., CN Patent 103113541, 2013. http://www.epo.org/.
8. Durairaj, R., Walkup, M., and Lawrence, M., EA Patent 013431B1, 2007. http://www.epo.org/.
9. Hu, L., Lang, X., and Zong, H., CN Patent 103087282, 2013. http://www.epo.org/.
10. Yamaguchi, T., Kashima, K., and Kaifu, N., US Patent 4376854, 1983. http://www.epo.org/.
11. ASTM E28. http://www.astm.org.
12. ASTM E1868. http://www.astm.org.
13. ASTM E1131. http://www.astm.org.
14. Kalinina, L., *Analiz kondensatsionnykh polimerov* (Analysis of Condensation Polymers), Moscow: Khimiya, 1984, pp. 116, 228.
15. *GOST* (State Standard) *2070. Light Oil Products: Methods for the Determination of Iodine Numbers and Unsaturated Hydrocarbon Contents.*
16. ASTM D529. http://www.astm.org.
17. Vasil'ev, V.V., *Antikorrozionnye, gidroizolyatsionnye materialy na osnove netraditsionnogo syr'ya-slantsevykh smol i okislennykh neftyanykh bitumov* (Anticorrosive Waterproofing Materials Based on Nontraditional Raw Materials—Shale Oil and Oxidized Petroleum Bitumen), St. Petersburg: SPbGIEU, 2007.
18. Lille, Yu., Bitter, L., Kundel', Kh., et al., *Dobycha Pererab. Goryuch. Slantsev*, 1969, no. 18, p. 101.

Translated by V. Makhlyarchuk

Publication II

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, K. Blum. “Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols”, Materials Research Express, 10 (3), 035304, 2023, DOI 10.1088/2053-1591/acc0e1

IOP Publishing Mater. Res. Express 10 (2023) 035304 https://doi.org/10.1088/2053-1591/acc0e1

Materials Research Express

OPEN ACCESS

RECEIVED
11 November 2022

REVISED
20 February 2023

ACCEPTED FOR PUBLICATION
2 March 2023

PUBLISHED
22 March 2023

PAPER

Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols

Ana Jurkeviciute[1], **Larisa Grigorieva**[2], **Kaia Tõnsuaadu**[1] **and Kristina Blum**[3]

[1] Department of Materials and Environmental Technology, Tallinn University of Technology, Tallinn, Estonia
[2] Laboratory of Fuels Technology, Virumaa College of Tallinn University of Technology, Kohtla-Järve, Estonia
[3] Virumaa College of Tallinn University of Technology, Kohtla-Järve, Estonia

E-mail: ana.jurkeviciute@taltech.ee

Keywords: resorcinol, oil shale alkylresorcinols, acetaldehyde, formaldehyde, modification by styrene, solid polycondensation resins

Abstract

Reducing the amount of volatile compounds in alkylresorcinol-aldehyde resins, reducing the impact of their components on the environment, and improving their performance can be achieved by replacing formaldehyde with acetaldehyde and by preliminary aralkylation of the resorcinol components of the raw material. To prove this, a comparative analysis of the properties of resins synthesized based on oil shale alkylresorcinols pre-treated with styrene, formaldehyde, or acetaldehyde was carried out. The effects of the molar ratio of feedstock/aldehyde and the amount of catalyst on the yield and characteristics of the resins were considered. Both individual alkylresorcinols (R, 5-MR, 2.5-DMR) and industrial fractions (REZOL, HONEYOL) were used as the raw materials. The following indicators were used to compare the obtained resins: softening point, ash content, coke number, moisture content, volatile substances, and solubility in organic solvents. The thermal properties of the resins were studied by TG/DTG/DTA in inert and oxidative atmosphere. Qualitative and quantitative analyses of resins and distillates for the content of unreacted resorcinol, individual alkylresorcinols, and styrene were carried out using iodometry, thin-layer chromatography (TLC), and gas chromatography (GC). It has been shown that the use of acetaldehyde makes it possible to obtain resins with the stated characteristics. The formaldehyde (SF) and acetaldehyde (SAc) resins obtained consist of oligomers with different chain lengths. Synthesized SAc resins are solids with a softening point of 51 °C–103 °C. Resins are soluble in acetone, EtOH, acetonitrile, and THF, and insoluble in benzene. SAc resins contain 3–4 times less unreacted original resorcinol components compared to SF resins. The conversion of styrene in the synthesis of $\mathrm{Rez}_{100}\mathrm{SF}$ resins was 42 wt%, $\mathrm{Rez}_{100}\mathrm{SAc}$ and $\mathrm{Hon}_{100}\mathrm{SAc}$ are 98 and 97 wt%, respectively. A comparative analysis of resins synthesized using acetaldehyde instead of formaldehyde helped identify both the advantages and disadvantages of the proposed synthesis variation.

Abbreviations

HONEYOL	fraction of oil shale alkylresorcinols with a boiling point of 270–320 °C
REZOL	fraction of oil shale alkylresorcinols with a boiling point >270 °C
SF	general designation of resins with formaldehyde
SAc	general designation for resins with acetaldehyde
RF	resorcinol-formaldehyde resin
RSF	resorcinol-formaldehyde resin modified with styrene
5-MRSF	5-methyl-resorcinol-formaldehyde resin modified with styrene

$R_{90}Rez_{10}SF$	resorcinol-alkylresorcinol-formaldehyde resin modified with styrene, with replacement of 10 mol % resorcinol by REZOL fraction
$R_{70}Rez_{30}SF$	resorcinol-alkylresorcinol-formaldehyde resin modified with styrene, with replacement of 30 mol % resorcinol by REZOL fraction
$Rez_{100}SF$	alkylresorcinol-formaldehyde resin styrene-modified based on the REZOL fraction
RAc	resorcinol-acetaldehyde resin
RSAc	resorcinol-acetaldehyde resin modified with styrene
$R_{70}Rez_{30}SAc$	resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene, with replacement of 30 mol % resorcinol by REZOL fraction
$Rez_{100}SAc$	resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene based on REZOL fraction
$Hon_{100}SAc$	resorcinol-alkylresorcinol-acetaldehyde resin modified with styrene based on the HONEYOL fraction.
5-MRSAc	5-methyl-resorcinol-acetaldehyde resin modified with styrene
2.5-DMRSAc	2,5-dimethyl-resorcinol-acetaldehyde resin modified with styrene

1. Introduction

Currently, in the construction, paint, varnish, woodworking, and tire industries, both natural and synthetic polymers are used to produce aerogels, rubber, and electrical products.

The main advantages of using synthetic polycondensation resins are their high adhesion to a large spectrum of materials, water resistance, mechanical strength, and chemical and thermal stability. Among synthetic polymers, the most common are polycondensation resins based on phenol (Ph) and formaldehyde (F) [1, 2].

However, the production and use of phenol-formaldehyde resins do not meet modern environmental requirements [3, 4]. According to the World Health Organization, the resin components Ph and F are highly toxic, carcinogenic, and mutagenic [5–7]. When released into water bodies, Ph negatively impacts natural biocenoses. This causes several environmental problems. While F negatively affects the genetic apparatus of all the living organisms.

One way to reduce the impact of F and Ph on the environment is to replace them with more environmentally friendly compounds, including the lower members of the homologous series of aliphatic aldehydes, such as acetaldehyde, propionaldehyde, butyraldehyde, and resorcinol (R) or alkylresorcinols (ARs) [8, 9]. The use of aliphatic aldehydes in the reaction of R and its derivatives enables the synthesis of resinous novolac products [10]. Novolac resorcinol-formaldehyde (RF) resins are produced without F relative to R [11].

By preliminary aralkylation of the resorcinol components of the resin with an aromatic alkene (S), it is possible to reduce the amount of emitted volatile substances in the RF resin at the time of processing as well as during its storage and operation. As shown in previous research [12], RF resins without S modification are characterized by a low softening point, high moisture content, volatile components, and unreacted R. It is the most hygroscopic among SF resins modified with S. Preliminary aralkylation of the HONEYOL alkylresorcinol fraction with S makes it possible to obtain resins with a low content of ARs without compromising their technological characteristics. It should be noted that the content of the main component (5-MR) in the fraction is 84 wt% [13].

Earlier studies [10, 13–19] have shown the possibility of obtaining Ph- and R-acetaldehyde resins. However, there are no data in the literature on the synthesis of polycondensed SAc resins based on the alkyl(aralkyl) derivatives of R. The properties of resins are described in [10]. Resorcinol-acetaldehyde resins without preliminary modification of resorcinol with styrene have a softening point of 100 °C–130 °C, content of unreacted R is 9–15 wt%. An increase in the softening temperature of the resin above the melting point of resorcinol (>110 °C) leads to the release of resorcinol on the surface of the resin.

As a phenolic raw material for production, biooil fractions of beech wood are also studied [19]. They are rich in monatomic phenols (phenol, o-cresol, m-cresol, 2,6-dimethylphenol, 2,4-dimethylphenol, catechol, 3-methylcatechol, creosol ets.). Despite their natural origin, such phenols are more toxic than resorcinols.

Both R, 5-MR, and others preliminarily aralkylated with aromatic or aliphatic alkenes, as well as industrial ARs fractions obtained by processing oil shale using the Kiviter technology, can be used as raw materials for the synthesis of resins [10, 13, 20, 21]. The above sources provide data on the synthesis of resins and some physicochemical characteristics. The results of the analysis of these resins by methods: TG/DTG/DTA, TLC, GC are not available.

Table 1. Content of the main components in HONEYOL and REZOL fractions [wt%].

Component	Fraction of oil shale alkylresorcinols	
	HONEYOL ($T_b = 270 \div 320$ °C)	REZOL ($T_b \geqslant 270$ °C)
Monatomic phenols	0.02	0.4
Resorcinol (R)	2.9	2.8
5-methylresorcinol (5-MR)	55.2	43.0
5-ethylresorcinol (5-ER)	9.1	12.0
2.5-dimethylresorcinol (2.5-DMR)	8.2	4.1
2-methylresorcinol (2-MR)	0.4	0.3
4-methylresorcinol (4-MR)	2.5	1.7
4.5-methylresorcinol (4.5-DMR)	7.6	8.3

The main difficulty in the synthesis of resins based on industrial mixtures of oil shale ARs lies in the different reactivity of the components [22, 23]. Consequently, the final product (resin) may contain unreacted ARs.

The purpose of this work was to study the synthesis of SAc resins based on R and ARs preliminarily modified with S, to determine the technical and physicochemical characteristics of the resulting resins, and to compare them in all respects with SF resins [12] synthesized under different conditions.

For the first time, acetaldehyde resins were synthesized from raw materials (R, 5-MR, and 2.5-DMR) preliminarily modified with styrene and oil shale fractions of alkylresorcinols REZOL and HONEYOL, containing 5-MR ~ 43 and ~ 55 wt%, respectively.

2. Experimental

2.1. Materials used in experiments

Individual pure substances: R (99.9 wt%), 5-MR (99,97 wt%), 2.5-DMR (99,43 wt%), industrial fractions of oil shale ARs: HONEYOL ($T_b = 270$–320 °C) and REZOL ($T_b = >270$ °C), formaldehyde (Penta, 37.6 wt%), acetaldehyde (Penta, 99.5 wt%) were used as raw materials. The content of the main components of the fractions is presented in table 1.

The HONEYOL and REZOL fractions, in addition to the main components, also contain nitrogen (N) and moisture (W). Their amounts were $N_{\mathrm{HONEYOL}} = 0.3$ wt% and $N_{\mathrm{REZOL}} = 0.3$ wt%, $W_{\mathrm{REZOL}} = 0.5$ wt% and $W_{\mathrm{HONEYOL}} = 0.2$ wt%. These components influence the course of the synthesis.

Along with the listed ARs, HONEYOL and REZOL may contain other substituted ARs with an alkyl chain of various lengths (9 or more carbon atoms) in the 5-position of the ring, as well as with cyclic side chains [24]. The REZOL fraction contains more such compounds than HONEYOL. This can be explained by differences in their boiling points. Styrene (99.9 wt%) was used as the aralkylating agent. The polycondensation reaction was carried out in a slightly acidic medium using an inorganic catalyst (2N H_2SO_4 solution). An equivalent amount of NaOH was used to neutralize it.

2.2. Synthesis of resins

Polycondensation reactions for individual R, 5-MR, 2.5-DMR, HONEYL, and REZOL fractions, as well as mixtures of R: REZOL (9:1 and 7:3 mol mol^{-1}) with formaldehyde (RSF, 5-MRSF, $R_{90}Rez_{10}SF$, $R_{70}Rez_{30}SF$, $Rez_{100}SF$) and acetaldehyde (RSAc, 5-MRAc, 2.5-DMRAc, $R_{70}Rez_{30}SAc$, $Hon_{100}SAc$, $Rez_{100}SAc$) were performed.

The resins were synthesized in two stages. In the first step, a mixture of R and oil shale ARs was aralkylated with freshly distilled S in the presence of H_2SO_4 as an acid catalyst.

In the process of aralkylation of R with styrene, mono-, di-, and trimethylbenzyl-substituted derivatives of R can be obtained [10]. Figure 1 shows possible variants of the aralkylation reaction of alkylresorcinols (5-MR, 5-ER, and 2.5-DMR) with styrene. Subsequently, aldehyde, - F, or acetaldehyde (Ac) was added to the aralkylated mixture. The structures of the novolak-type resins obtained using F and Ac with R and its derivatives are shown in figure 2.

Preliminary experiments showed that the most complete interaction between S and R occurred when the latter was fractionally introduced into the reaction flask. Therefore, all further experiments on aralkylation of R

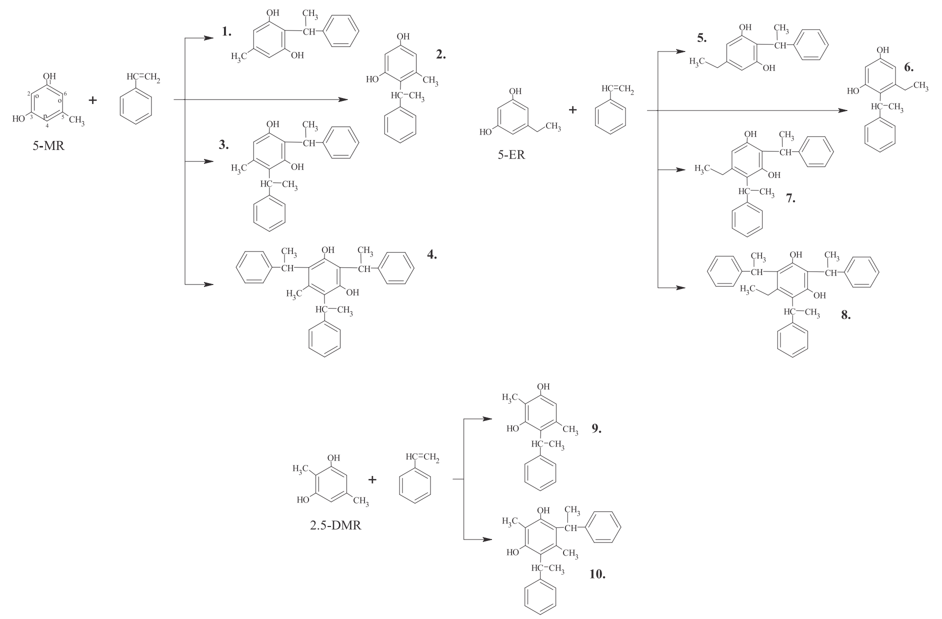


Figure 1. The reaction for obtaining aralkyl derivatives 5-MR, 5-ER and 2.5-DMR.

derivatives, individual ARs, and fractions of oil shale ARs were carried out as follows. The initial amount of the resorcinol component was divided into two parts. The first part was placed in a reaction flask and allowed to melt. Then, a calculated amount of acid catalyst was added, and S was added dropwise with constant stirring of the reaction mixture. This avoids the occurrence of side and secondary processes and prevents the polymerization of S. After introducing the entire volume of S, the second part of the initial resorcinol component was added to the reaction flask. The aralkylation reaction was performed for 30–90 min at 150 ± 10 °C. The completeness of the aralkylation reaction was controlled by both the decrease in the concentration of S in the reaction mixture by GC and the content of S in the distillate. The end of the reaction was considered as the time corresponding to the cessation of the change in S concentration.

The number of moles of the HONEYOL and REZOL fractions was calculated from their number-average molar mass M_n, which was obtained using equation (1):

$$\mathrm{M_n} = \frac{\sum_{\mathrm{i}=1}^{\infty}(\mathrm{N_i} \times \mathrm{M_i})}{\sum_{\mathrm{i}=1}^{\infty}\mathrm{N_i}} \tag{1}$$

where N_i - the number of moles of the i-th component of the HONEYOL or REZOL fraction, M_i - the molecular weight of the i-th component of the HONEYOL or REZOL fraction.

The molar ratios of the raw materials, aldehyde and catalyst are presented in table 2. The modifying agent (S) was added in an amount of 0.2 mol per mol of the resorcinol component.

The conditions for the synthesis of SF resins (RSF, 5-MRSF, $R_{90}Rez_{10}SF$, $R_{70}Rez_{30}SF$, and $Rez_{100}SF$) were described in our previous paper [12].

When carrying out the synthesis with Ac, its low boiling point of 20.2 °C was taken into consideration. Therefore, the temperature in the vessel from which Ac entered the reaction flask was maintained at approximately 10 °C. Before the introduction of Ac, the reaction flask containing the mixture was preliminarily cooled to 80 °C–90 °C, after that the calculated amount of Ac was added dropwise into it. After adding the entire amount of Ac, the reaction was conducted for 2 h at a temperature of 100 ± 5 °C. After the completion of the reaction, the catalyst was neutralized with NaOH. The pH of the medium was determined using a universal indicator paper. Next, distillation was performed to eliminate the reaction mixture of water and unreacted components. Distillation conditions: atmospheric - temperature 140 °C–145 °C, vacuum - until the temperature reached 165 °C in the flask and pressure 0.03–0.04 MPa. The mixing speed was 150 rpm. The hot resin was then poured into a metal container. The temperature and stirring rate were adjusted and controlled during synthesis using an IKA RET control-visc device (IKA®-Werke GmbH & Co. KG, Germany) with a temperature setting range of 0 °C–340 °C at a heating rate of 7 K min^{-1}.

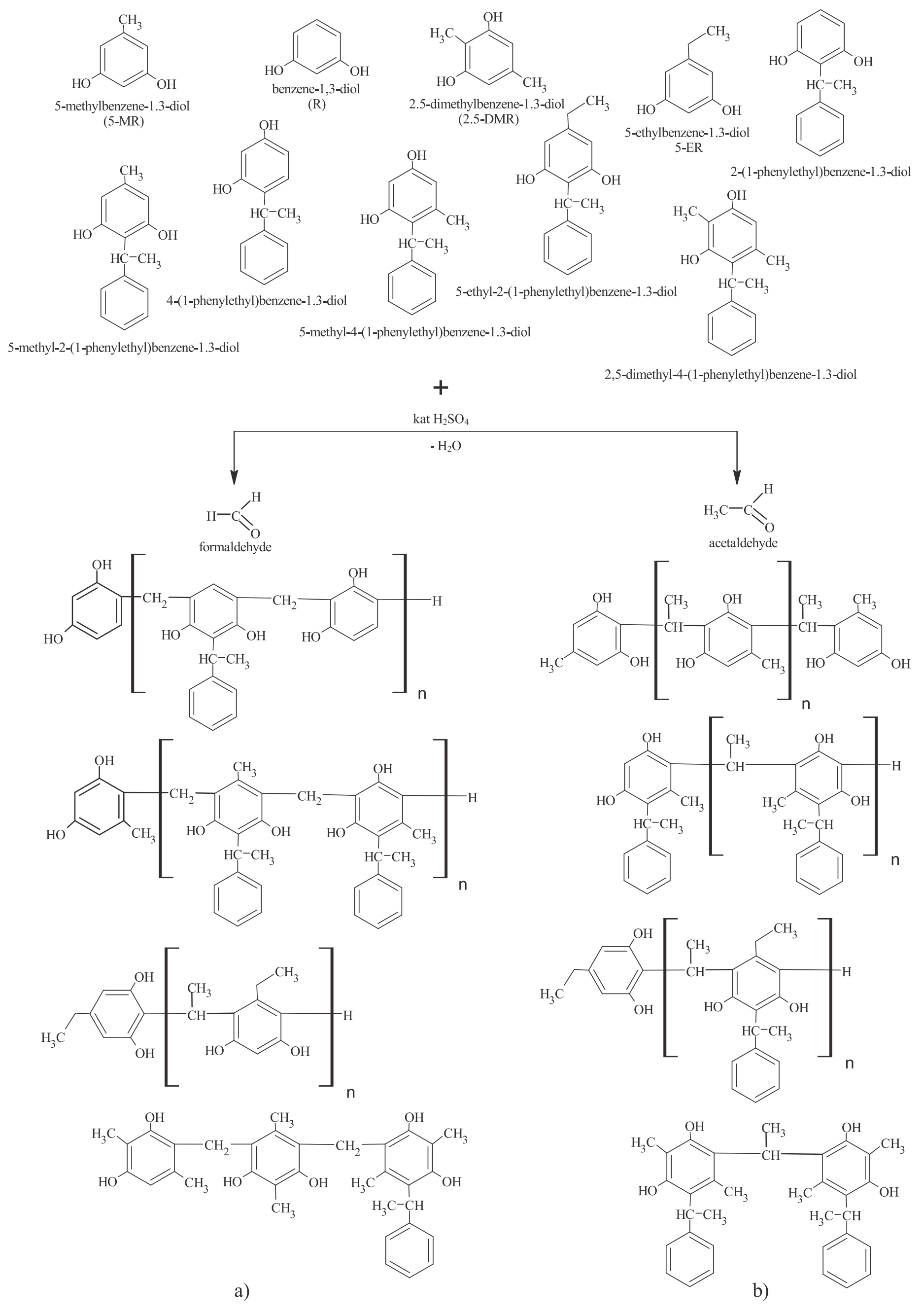


Figure 2. Possible molecular structures of formaldehyde (a) and acetaldehyde (b) novolac resins modified with styrene.

2.3. Methods used in experimental studies

2.3.1. Extraction of unreacted resorcinol and alkylresorcinols in the resins

The amounts of unreacted R and ARs in the resins were determined as follows: approximately 1 g of pre-crushed resin was dissolved in 2 ml of acetone and added to a solution of 100 ml of distilled water. The mixture was boiled for 10–15 min, filtered through a white ribbon filter and then through a blue ribbon filter using a vacuum pump. Filtration was performed until the solution became clear. 10 ml of the filtrate was transferred to a separating funnel, and an equivalent amount of diethyl ether was added, shaken, and allowed to settle until the two phases

Table 2. Formulations and characteristics of samples of resins and distillation.

Initial component/characteristic	Sample name										
	RSF 1	$R_{90}Rez_{10}SF$ 2	$R_{70}Rez_{30}SF$ 3	$Rez_{100}SF$ 4	RSAc 5	$R_{70}Rez_{30}SAc$ 6	$Rez_{100}SAc$ 7	$Hon_{100}SAc$ 8	5-MRSF 9	5-MRSAc 10	2.5-DMRSAc 11
Molar ratio of initial components											
R	1	0.9	0.7	—	1	0.7	—	—	—	—	—
5-MR	—	—	—	—	—	—	—	—	1	1	—
2.5-DMR	—	—	—	—	—	—	—	—	—	—	1
Fraction REZOL	—	0.1	0.3	1	—	0.3	1	—	—	—	—
Fraction HONEYOL	—	—	—	—	—	—	—	1	—	—	—
Formaldehyde	0.5	0.5	0.5	0.5	—	—	—	—	0.5	—	—
Acetaldehyde	—	—	—	—	0.5	0.75	0.75	0.75	—	1	0.75
Catalyst	0.023	0.023	0.023	0.023	0.023	0.033	0.055	0.093	0.023	0.026	0.031
Physical and chemical characteristics of resins											
Softening point [°C]	84.0	89.0	78.0	69.3	73.0	102.5	69.5	80.5	81.5	103.0	51.5
Volatile components at 105 °C [wt%]	0.6^{TGA}	0.4^{TGA}	0.6^{TGA}	0.9	6.8	0.8^{TGA}	0.6^{TGA}	0.9^{TGA}	1.7^{TGA}	5.05	4.0
Moisture [wt%]	0.2	0.3	0.5	0.5	1.2	0.8	0.3	0.9	0.9	2.6	0.5
Ash content at 830 °C [wt%]											
Gravimetric determination	—	—	—	—	3.7	0.2	0.1	0.7	—	1.1	0.3
TGA (in air atmosphere)	0.3	0.2	0.4	0.1	—	0.5	0.0	0.9	0.6	—	—
Coke number [wt%]	24.0	23.9	19.4	13.8	—	20.4	6.9	11.3	17.9	—	—
Content of the main unreacted resorcinols in resins [wt%]											
R	7.7	5.6	5.4	2.1	8.6	0.5	< 0.01	< 0.01	—	—	—
5-MR	—	8.1	10.4	12.1	—	2.8	1.5	2.6	6.4	2.0	—
5-ER	—	2.7	4.4	4.5	—	0.9	0.6	0.7	—	—	—
2.5-DMR	—	—	—	—	—	0.3	0.2	1.3	—	—	56.7
2-MR	—	—	—	—	—	0.1	not found	not found	—	—	—
4-MR	—	—	—	—	—	< 0.01	< 0.01	< 0.01	—	—	—
4.5-DMR	—	—	—	—	—	0.7	0.7	0.7	—	—	—
Water released during the polycondensation process											
Iodine number [g I_2/100g]	0.0	0.0	0.0	67.8	—	0.0	—	—	0.0	—	—
Styrene content [wt% by GC]	0.0	0.0	0.0	—	0.0	—	2.0	3.7	0.0	0.1	0.2

were completely separated. The resulting ether layer was evaporated to a constant weight in an oven at 105 °C and then weighed again. The dry residue was subsequently used for qualitative and quantitative analyses of the resin composition by TLC and GC.

2.3.2. Gas chromatography

The GC method was used to determine the composition of the initial fractions of the oil shale ARs and the residual S content during aralkylation. Before entering the gas chromatographic system, the total ARs residue obtained after extraction, starting material, and aralkylated mixture was silylated with 1.1.1.3.3.3-hexamethyldisilazane (HMDS) (Sigma-Aldrich, USA). 0.004–0.005 g of the mixture to be analyzed was placed in a test tube for derivatization, 0.2 cm^3 of acetonitrile and 0.5 cm^3 of HMDS were added, and the contents were thoroughly mixed. The tube was stoppered with an air condenser, calcium chloride tube, and placed in a thermostat or Labnet dry bath (USA), and maintained for 1 h at 130 °C. The tube was then cooled to room temperature. The contents of the tubes were transferred to vials for chromatography. GC analysis was performed using a Thermo Finnigan TRACE GC chromatograph (USA) equipped with a flame ionization detector with electronic pressure and flow controls. GC conditions: $T_{initial}$ of the thermostat was 150 °C, with a heating rate of 7.5 $°C\ min^{-1}$, and T_{final} of the thermostat was 260 °C., $T_{evaporator}$ and $T_{detector}$ were 260 °C and split 70:1. Separation was carried out on a capillary column Petrocol TM DH ($100m \times 0.25\ mm \times 0.5\ \mu m$) with a non-polar dimethylpolysiloxane phase at a He carrier gas feed rate of 2.5 ml min^{-1}. The sample (volume 0.2 μl) was injected using a Hamilton® syringe for chromatography (HAM80075, Germany).

2.3.3. Gas chromatography mass spectrometry

Gas-liquid chromatography with mass spectrometric detection (GC-MS) was used to identify the compounds formed during the aralkylation of individual ARs (nt. 5-MR, etc.). The analysis was performed using an Agilent 7820 gas chromatograph (Agilent Technologies, USA) with an Agilent 5975 mass selective detector (Agilent Technologies, USA).

The conditions for obtaining the chromatograms and column were identical to those used for the GC. The pumping action was achieved through the electron impact ionization of gas molecules (ionization energy: 70 eV). Mass spectrum measurements were performed in scan mode over the entire m/z range from 10 to 500.

2.3.4. Thin layer chromatography

The qualitative determination of R, 5-MR in the resins, as well as the composition of the resins, was performed by TLC. TLC was run on analytical Silica gel 60 GF_{254} (Sigma-Aldrich) plates using a mixture of toluene, *i*-PrOH and EtOH (85:4:11 $V/V/V$) as a solvent system. The plate was initially treated with hydrogen peroxide, followed by drying in hot air. 2 μl of a solution of the original resin in acetone (1 wt%) was applied to the plate using a microsyringe. It was then placed in a chamber with an eluent. The plates were then air dried. The dried plate was dipped into 1 wt% ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) solution to develop the spots. Subsequently, it was dried again using hot air. The resulting spots were scanned and processed using JustTLC program to determine the *Rf* value.

2.3.5. Softening point

The softening point of the resins was determined by the standard method of Ring and Ball [25] with the replacement of water with glycerin, because the softening points of some resins were above 100 °C.

2.3.6. Resin solubility

The solubility of the obtained polycondensation resins was investigated by dissolving 10 mg of the polymer in 1 ml of solvent containing different compounds (benzene, acetone, distilled water, lower alcohol, etc). The solution was kept at room temperature for two hours, and the contents of the test tubes were occasionally shaken. In the case of partial dissolution or swelling of the resin, its solubility during heating was evaluated. The contents of the tubes were heated in a water bath for 15–30 min at the boiling point of the solution.

2.3.7. Thermogravimetric analysis

Thermal analysis (TG/DTG/DTA) was performed using equipment of Mettler Toledo (Switzerland) and Setaram LabSys (France) in inert gas (N_2 or Ar) and air flow 60 ml min^{-1} at a heating rate of 5 deg min^{-1} with ~ 10 mg of the sample.

2.3.8. Determination of styrene by the iodometric method

The iodine value in the distillate after polycondensation was determined according to the standard method ASTM D1510 [26].

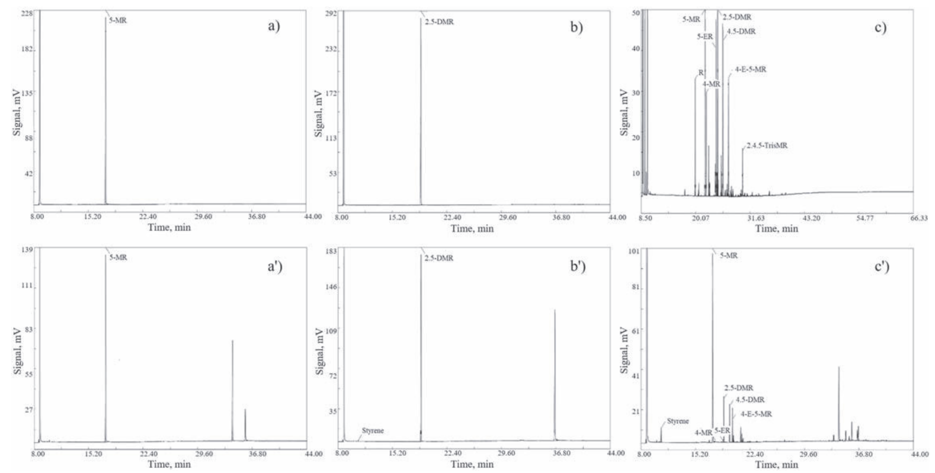


Figure 3. Chromatograms: alkylresorcinols: 5-MR (a), 2.5-DMR (b), oil shale ARs fraction HONEYOL (c); aralkylated alkylresorcinols: 5-MR ($\tau = 45$ min) - (a’), 2.5-DMR ($\tau = 60$ min) - (b’), fraction HONEYOL ($\tau = 45$ min) - (c’).

Table 3. Charge distribution (q_C) in 5-MR, 5-ER, 2.5-DMR molecules [28].

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
5-MR	0.214	−0.131	0.213	−0.106	0.102	−0.117	−0.099	—
5-ER	0.213	−0.119	0.213	−0.110	0.087	−0.110	−0.013	−0.008
2.5-DMR	0.184	−0.055	0.184	−0.107	0.089	−0.108	−0.077	−0.097

3. Results and discussion

The study results show that the aralkylation of oil shale ARs fractions takes twice as long as that of individual ARs [27]. It was determined that S reacts with R within 30 min The reaction of S with 5-MR occurs almost instantly, which explains the higher reactivity of the latter than that of R and other ARs.

The GC, GC-MS, and TLC analyses revealed that the reaction products were mainly monosubstituted resorcinols. From the presented chromatograms (figure 3) in the process of aralkylation of 5-MR and 5-ER, two types of substituted aralkylated molecules were predominantly formed (figures 3–1, 2, 5, 6), with aralkylation of the 2.5-DMR - I type (figure 3–9).

The direction of the ARs aralkylation process is determined by the magnitude of the negative charges on the carbon atoms of the benzene ring. According to the digital values of the charges on carbon atoms [28], the predominant direction of attack of the carbocation is the *ortho*-position 5-MR, 5-ER, and 2.5-DMR, where the carbon atoms have the highest negative charge (table 3).

This does not exclude the possibility of simultaneous formation of para-substituted *ortho*-and para-disubstituted ARs with para-substituted ones.

The possible acid polycondensation products of ARs with F and Ac, leading to the formation of novolac resins, are shown in figure 2. Addition of an aldehyde to the benzene ring occurred at the *ortho*-position. Oligomers with different chain lengths were formed. Presumably, fragments of both the pure R and aralkylated components can be included in the oligomeric chain structure.

The polycondensation reaction of 5-MR with F and Ac proceeded quite rapidly compared with the R and ARs fractions. This is since the rate of interaction of pure 5-MR with F is approximately 80 times greater than R [29]. According to the relative increase in reactivity with F, the alkyl derivatives of R can be placed in the following row:4.5-DMR < 5-ER < 2.5-DMR < 2-MR < 5-MR [30]. It should also be noted that the reactivity of Ac is lower than that of F [31].

The HONEYOL and REZOL fractions contain nitrogen-containing compounds, predominantly pyridine bases [32]. In turn, they interact with sulfuric acid to neutralize it. Therefore, to obtain resins in the formulation in which REZOL and HONEYOL were used, the amount of catalyst was increased in proportion to the volume of the added fraction. An increase in the amount of catalyst by approximately 1.5 times during the

Table 4. Depth of the polycondensation process.

Sample name	Components of the raw mixture	Initial content of free resorcinols [wt%]	Content of free resorcinols in the resin [wt%]	Depth of the polycondensation process [%]
RSF	R	100.0	7.7	92.3
$R_{90}Rez_{10}SF$	R	87.5	5.6	93.6
	5-MR	9.7	8.1	16.5
	5-ER	2.8	2.7	3.6
$R_{70}Rez_{30}SF$	R	66.9	6.4	90.4
	5-MR	25.8	7.8	69.8
	5-ER	7.3	3.5	52.1
$Rez_{100}SF$	R	2.1	2.1	0.0
	5-MR	74.3	12.1	83.7
	5-ER	25.7	4.5	82.5
RSAc	R	100.0	8.6	91.4
$R_{70}Rez_{30}SAc$	R	70.0	0.5	99.3
	5-MR	12.9	2.8	78.5
	5-ER	3.6	0.9	75.0
	2.5- DMR	1.2	0.3	73.3
$Rez_{100}SAc$	R	3.4	0.0	100.0
	5-MR	70.3	1.5	97.9
	5-ER	19.5	0.6	97.0
	2.5- DMR	6.8	0.2	96.8
$Hon_{100}SAc$	R	2.9	0.0	100.0
	5-MR	73.2	2.6	96.5
	5-ER	12.0	0.7	93.9
	2.5- DMR	10.9	1.3	87.7
5-MRSF	5-MR	100.0	6.4	93.6
5-MRSAc	5-MR	100.0	2.00	98.0
2.5-DMRSAc	2.5-DMR	100	56.5	43.5

polycondensation reaction with Ac made it possible to increase the content of the oil shale ARs fraction in the formulation from 10 to 30 wt%. Compared to SF resins, the content of unreacted components in SAc resins decreased by 3–4 times (table 2).

The data in table 4 show that more than 90 wt% conversion of the main components of the fraction (R, 5-MR, and 5-ER) can be achieved when the resin is synthesized using the REZOL fraction and Ac. In 2.5-DMRSAc resin, the conversion of the main component is approximately 44 wt%. This can be explained by the steric factor of the 2.5-DMR molecule. The degree of conversion of 2.5-DMR in the HONEYOL and REZOL fractions ranged from 73 to 97 wt%. The 2.5-DMR content in the REZOL fraction was 2 times less than that in HONEYOL. It can be assumed that, during aralkylation, it does not react with S and remains in its original state. Such a 2.5-DMR molecule has 2 free positions for the reaction with an aldehyde.

Qualitatively, TLC showed that the SF and SAc resins consisted of a set of oligomeric structures (figure 4). It was found that the distillates obtained after polycondensation with Ac contained significantly less unreacted ARs than those obtained after polycondensation with F.

The appearance of unreacted S in the resin and distillate was observed (table 2) when the HONEYOL and REZOL fractions were used in the synthesis. In the case of the $Rez_{100}SF$ resin, the conversion of styrene reached 42 wt%, while in the synthesis of the $Rez_{100}SAc$ and $Hon_{100}SAc$ resins, it was 98 and 97.3 wt%, respectively.

The synthesized SF and SAc resins are solid-colored brittle or plastic substances with softening point of 51.5 °C–103 °C. SF resins have a rich crimson color, SAc - from yellow to crimson. An increase in the proportion of the alkyl resorcinol fraction in the formulation led to a change in the color of the resin to brown. The main characteristics of solid resins used in the rubber industry are their softening point (not lower than 80 °C) and solubility in acetone.

The lowest softening temperature of 51.5 °C is 2.5-DMRSAc resin. The unreacted 2.5-DMR content exceeded 50 wt%. This may be since the addition of the Ac molecule to the aralkylated 2.5-DMR molecule is very difficult owing to the spatial structure of the latter (figure 5).

The softening temperatures of the acetaldehyde resins $R_{70}Rez_{30}SAc$ and 5-MRSAc compared to formaldehyde resins $R_{70}Rez_{30}SF$ and 5-MRSF changed from 78 to 102.5 °C and 81.5 °C to 103.0 °C, respectively.

Replacing 30 mol.% R with the REZOL fraction in the formulation results in an increase in the softening point from 73 to 102.5 °C. This was due to the increase in the molecular weight of the obtained oligomers. The softening temperature of SF resins begins to decrease with an increase in the composition of their fraction of oil shale ARs. The low softening temperature of the $Rez_{100}SF$ and $Rez_{100}SAc$ resins (about 69 °C) is since the REZOL

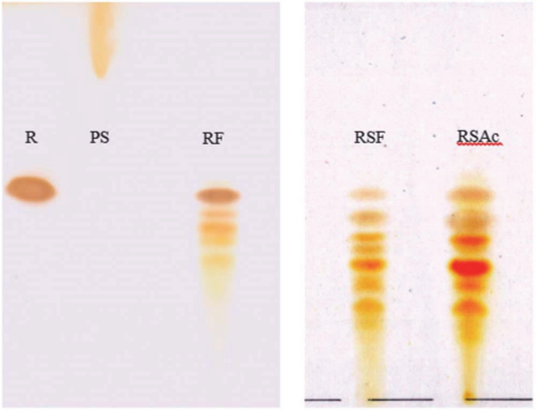


Figure 4. Thin layer chromatography images: resorcinol (R), polystyrene (PS), resorcinol-formaldehyde resin (RF), resorcinol-formaldehyde resin modified with styrene (RSF) и resorcinol-acetaldehyde resin modified with styrene.

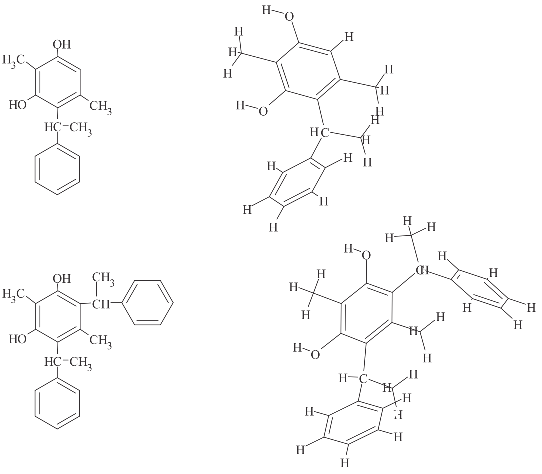


Figure 5. Structure of the 2.5-DMR molecule.

fraction contains ARs, in the structure of which there are long alkyl chains and benzene rings [24], some of which were subsequently aralkylated with S. The polycondensation reactions of such compounds are difficult. According to the literature, the softening point of resins depends not only on the ratio of the initial resorcinol component and aldehyde, but also on the amount of unreacted R present in the resin [10]. For resins based on individual R (RSAc) and its derivatives 5-MR and 2.5-DMR (5-MRSAc, 2.5-DMRSAc), this pattern was preserved (tables 2–5, 10, 11).

The results of the thermal analysis presented in figure 6 highlight that the resins based on (containing) SF behave very similarly. Decomposition takes place in one step at 150 °C–400 °C in an inert atmosphere. The decomposition maxima varied at 27 °C and the total mass loss at 600 °C varied 4 %. The decomposition of SF samples in air occurs in two steps: between 170 °C–350 °C the mass loss is 40%–45% and between 400 °C–600 °C additionally 50%–55%. In the heat flow curves, small endothermic effects were followed at 80 °C–120 °C related to the release of water and volatile components and at 200 °C–270 °C related to melting and decomposition of unreacted components (5-MR, 5-ER *et al*) and low-molecular-weight oligomers. The intensive exothermic effect above 400 °C indicates oxidation reactions of the rest of the resins.

The TA analysis results of RSAc and 5-MRSAc (figure 7) indicate a greater impact of 5-MR on the thermal properties of the Ac resins, despite the lower content of the unreacted part in the resin (table 5). The main decomposition in the inert atmosphere also occurred in one step: for RSAc in the temperature interval of

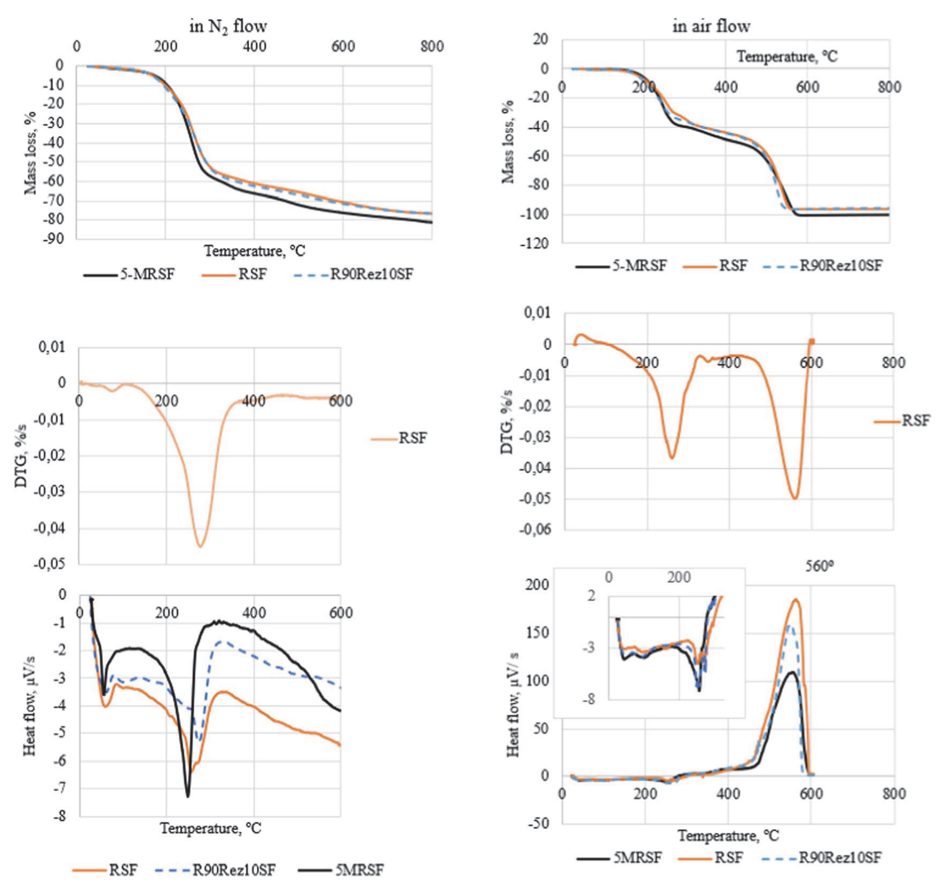


Figure 6. TG, DTG, and DTA curves in inert atmosphere (a) and in air (b) of RSF, $R_{90}Rez_{10}SF$, and 5-MRSF resins.

Table 5. Temperatures of the mass loss levels in inert atmosphere and in the air.

Sample name	Temperature [°C] of mass loss level [τ %]							
	In inert atmosphere				In air atmosphere			
	τ_{10}	τ_{20}	τ_{30}	τ_{50}	τ_{10}	τ_{20}	τ_{30}	τ_{50}
RSF	201	236	255	291	213	246	272	467
$R_{90}Rez_{10}SF$	196	229	253	290	205	235	258	461
$R_{70}Rez_{30}SF$	201	227	247	291	202	228	248	392
$Rez_{100}SF$	196	219	235	268	186	206	222	282
RSAc	165	208	228	275	194	229	278	459
$R_{70}Rez_{30}SAc$	241	261	278	325	237	258	280	387
$Rez_{100}SAc$	224	244	256	291	226	249	264	303
$Hon_{100}SAc$	227	250	266	302	227	250	268	337
5-MRSF	204	231	247	274	214	237	253	422
5-MRSAc	219	243	263	305	238	260	288	421

150 °C–300 °C but for 5-MRSAc up to 400 °C without remarkable thermal effects. The TA curves in air were more complicated and indicated numerous decomposition reactions up to 400 °C, particularly for 5-MRSAc resin. The oxidation reaction, which is more intensive for 5-MRSAc above 400 °C, led to a mass loss of 96 %. The higher mass loss of RSAc at 50 °C–200 °C can be explained by the higher water content (table 2).

The thermal stability of the resins was also evaluated based on the temperatures at certain mass-loss levels, as presented in table 5. In the initial stage of heating in an inert atmosphere, a mass loss of 10 % was achieved at

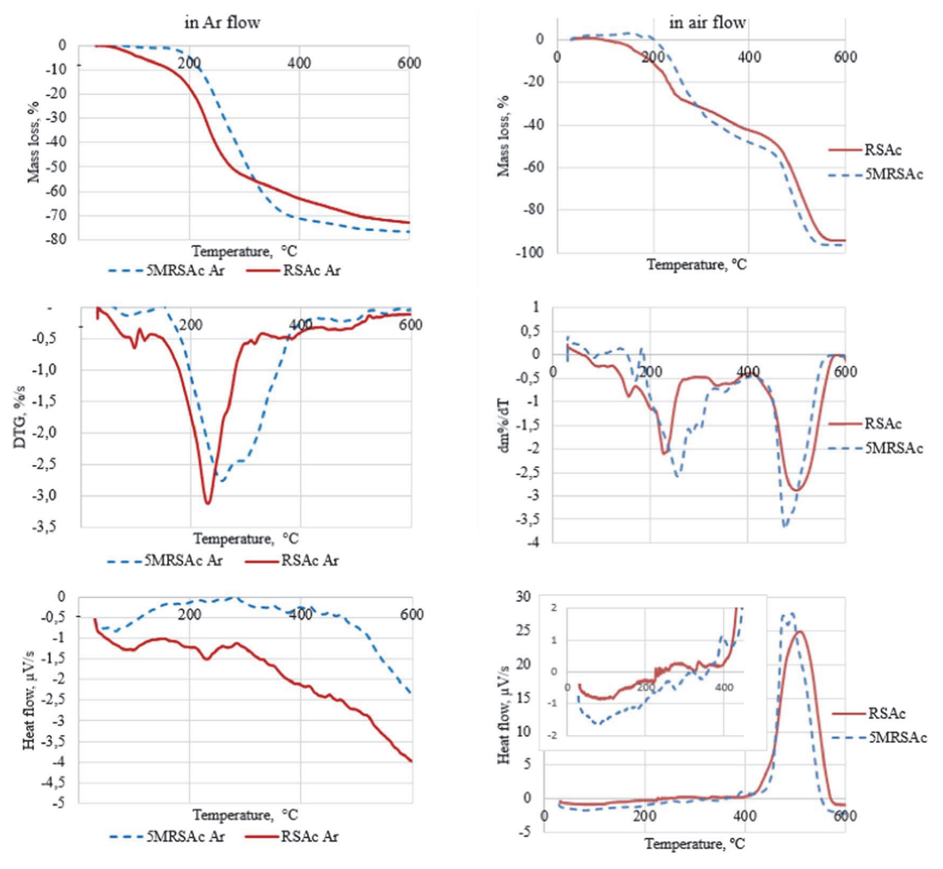


Figure 7. TG, DTG, and DTA curves in inert atmosphere (a) and in air (b) of RSAc and 5-MRSAc resins.

Table 6. Solubility of polycondensation resins in various organic solvents.

Sample name	Solvent					
	Acetonitrile	THF	EtOH	Benzene	Acetone	Water
RSF	++	++	++	—	++	++
$R_{70}Rez_{30}SF$	++	++	++	—	++	+-
$Rez_{100}SF$	++	++	++	—	++	—
RSAc	++	++	++	—	++	+-
$R_{70}Rez_{30}SAc$	++	++	++	—	++	+-
$Rez_{100}SAc$	++	++	++	—	++	—
$Hon_{100}SAc$	++	++	++	—	++	+-
5-MRSF	++	++	++	—	++	+
5-MRSAc	++	++	++	—	++	+-
2.5-DMRSAc	++	++	++	—	++	+-

++ - soluble, + - soluble by heating, +- - partially soluble, – - insoluble

165 °C for RSAc, which is explained by the higher water content. For SF samples, 10 % was achieved at 196 °C–204 °C. The most stable are SAc resins with τ_{10} at 219 °C–241 °C. By the mass loss level τ_{50}, the SAc resins are more stable than the SF resins, except for RSAc. In air, the mass loss level τ_{10} is obtained at 10 °C higher temperatures for SF resins and at 20–30 deg higher temperature for RSAc and 5-MRSAc. For resins with higher REZOL content, the temperature of τ_{10} does not change in different atmospheres. The most stable are SF, RSAc, and 5-MRSAc resins also according to the temperatures of τ_{50} 421 °C–467 °C.

Table 6 shows data on the solubility of resins in various organic solvents. From the presented results, it follows that almost all resins exhibit good solubility in polar (acetone, EtOH), aprotic (acetonitrile) and moderately polar (THF) organic solvents at room temperature. The Rez_{100}SF and Rez_{100}SAc resins, which have low softening points, are insoluble in water. Resins based on R and individual ARs are partially soluble in water. This is caused by the high content of unreacted components with OH-groups in the resin and the presence of oligomers whose molecules do not contain aralkylated components. Partial solubility in water makes possible to introduce them into emulsion systems while maintaining stability. They remain in the aqueous phase and do not migrate into the polymer phase.

To reduce the moisture content and volatile components of the RSAc, 5-MRSF, 5-MRSAc, and 2.5-DMR resins, it is necessary to carefully distill and dry the resin. After aralkylation with S, the resins exhibited reduced hygroscopicity compared to non-aralkylated resins.

4. Conclusions

In the present work, the possibility of aralkylated polycondensation resins synthesis based on R, 5-MR, 2.5-DMR, with partial replacement of R by the oil shale ARs fraction (REZOL), as well as the REZOL and HONEYOL fractions, and aldehyde - Ac, is shown.

The interaction patterns of individual resorcinols (R, 5-MR, and 2.5-DMR) and their mixtures with S were studied. The SF and SAc resins were analyzed using GC, GC-MS, TLC, and TG/DTG/DTA methods. Their various technical characteristics (softening point, moisture content, etc) were determined.

In the aralkylation process, the addition of S to the 5-MR, 5-ER, and 2.5-DMR molecules occurs at the 2-, 4, or 6 positions of the aromatic ring.

It has been found that the use of Ac makes it possible to obtain resins with characteristics that are not inferior to SF resins, and in some cases even better. Resins synthesized with Ac ($R_{70}Rez_{30}$SAc, 5-MRSAc) had a higher softening point than similarly formulated resins with F ($R_{70}Rez_{30}$SF, 5-MRSF).

SAc resins contain 3–4 times less unreacted original resorcinol components compared to SF resins. It has been shown that SF and SAc resins are formed by oligomers with different chain lengths.

All the prepared SF and SAc resins were soluble in organic solvents, such as acetone, acetonitrile, THF, and EtOH. In addition, RSF resins have good solubility in water, whereas SAc resins are only partially soluble in it.

Upon the receipt of SAc resins, the volume of distillation decreases, and accordingly, less waste requires further purification and disposal.

The use of environmentally friendly raw materials, natural shale ARs, and Ac can be considered as alternatives to Ph, R, and F.

The synthesis of resins based on such raw materials will expand their range and improve their properties compared to those of traditional resins. This opens prospects for obtaining not only those listed in the article but also many other multifunctional polymer products. Thus, the presence of reactive functional groups and fragments in the SAc resins makes possible to modify them with other organic compounds. The next steps will be studies introduction of such resins into the industry, considering all the modern requirements. The improvement of properties also leads to the expansion of the use of resins, for example, in the production of adhesive components and additives, electrical, paint, varnish, rubber products, and composite materials.

Thus, obtaining SAc resins based on industrial HONEYOL and REZOL fractions can be considered a very promising direction, which makes it possible to reduce environmental damage during their synthesis and further use in composites.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Funding statement

This research was conducted under the doctoral study of the Tallinn University of Technology.

Ethical compliance

This article does not contain any studies with human participants or animals performed by any of the authors. This article is original. The article has been written by the stated authors, who are ALL aware of its content and approve its submission.

Data access statement

All relevant data are within the paper and its Supporting Information files.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ORCID iDs

Ana Jurkeviciute https://orcid.org/0000-0002-9175-1963
Larisa Grigorieva https://orcid.org/0000-0002-2409-1061

References

[1] Sarika P, Nancarrow P, Khansaheb A and Ibrahim T 2020 Bio-Based alternatives to phenol and formaldehyde for the production of resins *Polymers* **12** 2237

[2] Tang K, Zhang A, Ge T, Liu X, Tang X and Li Y 2021 Research progress on modification of phenolic resin *Materials Today Communications* **26** 101879

[3] Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products (accessed: 2022)

[4] REACH Regulation and Formaldehyde 2022 European Chemical Industry Council

[5] Liteplo R, Beauchamp R, Chénier R and Meek M 2022 *Formaldehyde* (Geneva: World Health Organization)

[6] Robichaud A 2020 An overview of selected emerging outdoor airborne pollutants and air quality issues: the need to reduce uncertainty about environmental and human impacts *J. Air Waste Manage. Assoc.* **70** 341–78

[7] Phenol: health and safety guide 1994 *World Health Organization & International Programme on Chemical Safety* (Geneva: World Health Organization)

[8] Akkerberg I, Blinova E, Veldre I, Karpunin B, Kunamägi H, Parmasto I, Feoktistov G, Schmidt N and Janes H 1970 Toxicology of oil shale products: a methodical letter, Institute of Experimental and Clinical Medicine of the Ministry of Health of the Estonian SSR, Tallinn

[9] Alenkina Z and Grevtseva N N 1990 Study of the toxic properties of the modifier RU-D-2 (Volgograd: Toxicological Laboratory)

[10] Durairaj R B 2005 Resorcinol: Chemistry, Technology and Applications, Indspec Chemical Corporation, Pittsburgh

[11] Dodiuk H and Goodman S H 2014 *Handbook of Thermoset Plastics* (William Andrew, Elsevier Inc.) 3rd edn (https://doi.org/10.1016/C2011-0-09694-1)

[12] Yurkevichyute A, Grigorieva L and Vassiljev V 2016 Synthesis of solid resorcinol-formaldehyde resin modified with styrene with the use of a shale phenol fraction with a boiling temperature higher than 270 °C *Solid Fuel Chem.* **50** 64–8

[13] Harvey T 2008 *Modified Alkylresorcinol Resins and Applications Thereof* US20080090967 USA

[14] Carleton E and Montclair N J 1934 *Resinous Composition From Phenol and Acetaldehyde and Process of Making Same* US1974605A USA

[15] Niederl J B and Vogel H J 1940 Aldehyde-Resorcinol condensations *J. Am. Chem. Soc.* **62** 2512–4

[16] Kanematsu Y, Koyama A, Kuwabara Y, Sone N and Oda H 2008 Control of the porous structure and the surface property of resorcinol – Acetaldehyde carbon cryogels *TANSO* **231** 13–7

[17] Goodrich C, Lawrence J and Smith D 1981 *Internally coated reaction vessel for use in olefinic polymerization* WO1982002555A1 USA

[18] Safronova A S, Vasilyanova L S, Ivanov V V, Gabdrakipov V Z and Arkhipova A 1989 Condensation of phenol with acetaldehyde in various solvents in the presence of HCl *Polymer science USSR* **31** 2095–101

[19] Xu J, Brodu N, Mignot M, Youssef B and Taouk B 2022 Synthesis and characterization of phenolic resins based on pyrolysis bio-oil separated by fractional condensation and water extraction *Biomass Bioenergy* **159** 106393

[20] Lixin H, Xudong L and Hongxing Z 2013 *Preparation method of alkylresorcinol formaldehyde resin* CN103087284A Chinese

[21] Bing Y, Wenming Y and Mingyan W 2013 *Resorcinol aldehyde resin formed by modification of olefin and aromatic hydrocarbon and production process thereof* CN103113541 Chinese

[22] Levanovsky V I, Sobolev V V and Pokonova Y V 1976 Chemistry of oil shale phenols. Leningrad Technological Institute im. Lensoviet, Leningrad, USSR

[23] Lille Y and Bitter L 1971 Methods of preparation and reactivity characteristics of alkylresorcinols *Thematic reviews, Moskow* 4–30

[24] Lille Yu, Bitter L, Kundel H, Murd A, Peinar U and Malko L 1969 On the composition of shale oil diphenols boiling higher than 300 °C *Oil Shale Mining and Processing* **18** 101–12

[25] ASTM D36 / D36M: Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)

[26] ASTM D1510 - Standard Test Method for Carbon Black - Iodine Adsorption Number

[27] Kukushkin Y, Petrov A, Bunina-Krivorukova L, Alexandrova E, Komissarova E and Bogoradovsky E 1982 Improvement of the technical properties of resorcinol- and alkylresorcinol-containing modifiers of rubber compounds based on general-purpose rubbers (Leningrad: Technological Institute)

[28] Vasiliev V V, Komarov V Y, Vetkova L B and Ioniin B I 1982 Chemical shifts of carbon-13 mono- and diatomic phenols *J. Org. Chem.* **52** 524–8

[29] Lille Y, Bitter L, Purre T, Rätsep A, Soo K, Kalde L and Nurske H 1971 Alkylresorcinols. Production methods, properties, and application, TsNIITEneftekhim, Moscow

[30] Freidin A S 1985 Polymer water-based adhesives Chemistry, Moscow

[31] Inoue N and Takayaa M 2019 Reactivity and relative reaction rates of formaldehyde, acetaldehyde, and acetone coexisting with large quantities of acetone on 2,4-dinitrophenylhydrazine-impregnated filters *Anal. Methods* **11** 2785–9

[32] Vasiliev V V 2007 Anticorrosive, waterproofing materials based on non-traditional raw materials – shale oil and oxidized petroleum bitumen: monograph, SPbGIEU, Sankt-Peterburg

Publication III

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, T. Yashicheva, D. Bondarev. “Non-aldehyde resins based on resorcinol and natural alkylresorcinols modified with styrene”, Materials Research Express, 10(10), 105301, 2023 DOI 10.1088/2053-1591/acfd12

IOP Publishing   Mater. Res. Express 10 (2023) 105301   https://doi.org/10.1088/2053-1591/acfd12

Materials Research Express

OPEN ACCESS

RECEIVED
27 May 2023

REVISED
15 September 2023

ACCEPTED FOR PUBLICATION
25 September 2023

PUBLISHED
6 October 2023

PAPER

Non-aldehyde resins based on resorcinol and natural alkylresorcinols modified with styrene

Ana Jurkeviciute[1], **Larisa Grigorieva**[2], **Kaia Tõnsuaadu**[1], **Tamara Yashicheva**[3] **and Dmitrij Bondarev**[4]

[1] Department of Materials and Environmental Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia
[2] Laboratory of Fuels Technology, Virumaa College of Tallinn University of Technology, Järveküla tee 75, 30322, Kohtla-Järve, Estonia
[3] Virumaa College of Tallinn University of Technology, Järveküla tee 75, 30322, Kohtla-Järve, Estonia
[4] Polymer Institute SAS, Dúbravská cesta 9, 84541 Bratislava, Slovakia

E-mail: ana.jurkeviciute@taltech.ee

Keywords: resorcinol, 5-methylresorcinol, natural alkylresorcinols, fraction HONEYOL80, dicyclopentadiene, styrene, non-aldehyde resins

Abstract

The use of natural alkylresorcinols produced in Estonia (5-methylresorcinol, HONEYOL80 fraction) instead of the expensive resorcinol reduces the cost of the synthesized resins while maintaining their high technological characteristics. Resins based on resorcinol (R), 5-methylresorcinol (5-MR), HONEYOL80, dicyclopentadiene (DCPD), and styrene (S) were synthesized in the presence of an acid catalyst. Their physical and chemical characteristics have also been studied. It was shown that depending on the mole ratio of the components of the formulation, resins with different softening temperatures (66 to 97 °C), ash content of 0.04 to 0.39 wt%, and a low content of volatile components at 105 °C, including moisture, were obtained. The best conditions for the synthesis of resins with a softening point of 94 °C–97 °C are molar ratio of R (5-MR): DCPD: S = 1: 0.5: 0.3 at temperature 135 °C–170 °C, synthesis time 5 h 30 min. The synthesized resins did not require additional processing under a vacuum. The presence of unreacted resorcinol and 5-methylresorcinol (quantitatively and qualitatively) in the final product, the homogeneity, and molecular weight characteristics of the resin composition (qualitatively) were determined by TLC and GPC.

Abbreviations

HONEYOL80	fraction of oil shale alkylresorcinols with a boiling point of 270÷320 °C
DCPDS	general designation of resins with dicyclopentadiene
RDS	resorcinol-styrene-dicyclopentadiene resin
5-MRDS	5-methyl-resorcinol-styrene-dicyclopentadiene resin
$Hon80_{100}DS$	alkylresorcinol-styrene-dicyclopentadiene resin based on HONEYOL80 fraction
$R_{70}Hon80_{30}DS$	resorcinol-alkylresorcinol-styrene-dicyclopentadiene resin with the replacement of 30 mol.% resorcinol per fraction
$R_{50}Hon80_{50}DS$	resorcinol-alkylresorcinol-styrene-dicyclopentadiene resin with the replacement of 50 mol.% resorcinol per fraction
TA	Thermal analysis
TGA	Thermogravimetric analysis
TLC	Thin Layer Chromatography
DTG	Derivative thermogravimetry
GPC	Gel permeation chromatography
R	resorcinol
5-MR	5-methyresorcinol

ARs	alkylresorcinols
DCPD	dicyclopentadiene
S	styrene
NaOH	sodium hydroxide
p-TSA	*para*-toluenesulfonic acid
$Na_3[Co(NO_2)_6]$	sodium hexanitrocobaltate (III)
HMDS	1.1.1.3.3.3-hexamethyldisilazane
$T_{\text{start of dec.}}$	start temperature of resin decomposition
T_b	boiling temperature
G’	dynamic modulus of elasticity
tg Δ	dielectric loss angle
$\tau_{10}, \tau_{50}, \tau_{90}$	loss temperature 10, 50, 90 wt%
M_n	number average molecular weight
M_w, MW	weight average molecular weight

1. Introduction

Polymers based on phenol (Ph) and resorcinol (R) condensations are widely used in the chemical industry. They are used in the tire and rubber industry to increase adhesion, preparation of hot- and cold-curing adhesives, sealants, and tire cord impregnation, in medicine, to obtain aerogels, in the manufacture of aerospace and aviation equipment, etc [1–4]. Modification of the polymerization stage or the addition of modifiers to the product can expand their field of application. Composite materials are the most promising materials from the point of view of further development of production technologies and subsequent applications [5–8]. The matrix of polymer composites can be either phenolic [9, 10] or resorcinol-formaldehyde (RF) resins [11, 12].

The resins produced by condensation with formaldehyde (F) have several disadvantages. They are unstable due to increased volatile components content, are hygroscopic, and, accordingly, have a limited storage period. The actual problem is to decrease toxic emissions to the environment [13, 14]. The possibility of replacing F for environmentally and human-friendly acetaldehyde (Ac) was shown in previous studies [15, 16]. However, Ac is difficult to use because of its low boiling point ($T_b \sim 20$ °C). The production of such resins requires specialized equipment with additional cooling.

Polycondensation reactions release low molecular weight substances. In our case, this is water, which can remain in the synthesized resin even after drying. It is bound by hydrogen bonds to the OH-groups of the resin. In the molding process, after breaking these bonds, residual moisture leads to the formation of water vapor in the molten polymer mass. Voids are formed in the composite; therefore, the mechanical properties of the resin are reduced [17, 18].

Currently, environmentally safe technologies for polymer production and manufacturing are becoming a priority [19, 20]. Requirements for the performance characteristics of these materials based on them are becoming stricter every year. To achieve this goal, the introduction of the vinyl compound styrene (S) into the aromatic ring of (alkyl)resorcinols has been investigated [21, 22]. These studies demonstrated the possibility of obtaining modified (alkyl)resorcinol resins with improved technical and environmental characteristics. The addition of S to the polymer matrix of the composite reduced its viscosity. This facilitates the processing of the resin and promotes better dissolution in the butadiene-styrene-rubber base of the composite.

Table 1 shows the comparative properties of vulcanized rubbers derived from R and resorcinol-dicyclopentadiene-styrene resin (RDS) synthesized with different component molar ratios [23]. The results illustrate the curing behavior and physical and mechanical properties of the composite with the addition of individual R and RDS resins.

As turns out from the above data, RDS resins improve the sub-vulcanization time of rubber compounds, with a slight increase in the vulcanization time. Mechanical and dynamic test results show that rubber compounds containing RDS resins have improved properties, such as strength, hardness, and dynamic modulus of elasticity (*G*’). The tangent of the dielectric loss angle (tg Δ) decreased.

Based on patent and literature searches, attempts to synthesize formaldehyde-free resins are considered the most progressive trend [24–26]. A wide range of modifiers [25, 27, 28], including R-based resins [2, 23, 29], make it possible to obtain polymer matrices with improved technical and environmentally safe characteristics. As a substitute for F, dimethoxyethanal [24, 26] and lignin-based aldehyde compounds, such as

Table 1. Test results of rubber compounds [23].

Methylene acceptor:	R	R/DCPD/S(1.0 : 0.4 : 1.0)	R/DCPD/S(1.0 : 0.3 : 1.2)	R/DCPD/S(1.0 : 0.25 : 1.25)
Fuming at 120° C	Very High	None	None	None
Dynamic Properties - 0.2% Strain				
G', MPa	18.92	23.83	23.34	21.93
tg Δ	0.089	0.079	0.085	0.086
Dynamic Properties - 2.0% Strain				
G', MPa	9.96	13.25	12.75	12.03
tg Δ	0.239	0.228	0.244	0.245
Hardness, Shore A	77	80	79	78
Tensile Properties				
100% Modulus, MPa	4.23	4.43	4.24	4.18
300% Modulus, MPa	17.15	17.23	16.35	16.34
Strength, MPa	26.57	26.83	26.65	25.89
Elongation, %	451	459	471	455
Energy to Break, N·m	23.94	24.36	25.37	23.38
Tear Strength (Die-C), KN/M	118.3	129.1	117.0	122.8

4-hydroxybenzaldehyde, vanillin, syringaldehyde [25, 26], glyoxal, furfural, furfuryl alcohol [26], hydroxymethylfurfural [26, 27], and dicyclopentadiene (DCPD) [23, 28, 29] etc are proposed.

One of the drawbacks of resins with a high free resorcinol content is its release during the preparation of some compositions and the appearance of fumes [23]. The use of modifiers consisting of DCPD and S eliminates this disadvantage [23, 29] and allows the production of resins with low R ($<$ 1wt%) use. In addition, mechanical properties such as the elastic modulus and relative elongation were improved. The use of (alkyl)resorcinol increases the level of adhesion between the surfaces of the fibers, cords, and the polymer matrix [2, 22, 29]. The method described in [23] does not produce a large amount of waste and is associated with the use of low temperature and pressure.

Ph and R are typically used for the production of formaldehyde-free resins. However, Ph is a carcinogenic substance with mutagenic properties. R can be used instead. It is mainly synthetically produced. This leads to a significant increase in the cost of the product, despite its advantages over Ph. Natural alkylresorcinols (ARs) can be a substitute for expensive R. [15, 21, 22]. They are obtained during oil shale processing using the Kiviter technology [30]. Replacing R with 5-methylresorcinol (5-MR), a fraction of the total alkylresorcinol HONEYOL80 (Viru Keemia Grupp AS, Estonia), and using DCPD and S opens opportunities to produce new resins in oil shale chemistry plants.

The aim of this study was to investigate the possibility of obtaining an (alkyl)resorcinol-dicyclopentadiene-styrene formaldehyde-free resin with improved characteristics based on industrial oil shale raw materials.

Natural ARs, such as 5-MR and HONEYOL80 oil shale alkylresorcinol fractions, have been used to produce dicyclopentadiene-styrene resins for the first time.

2. Experimental

2.1. Materials used in experiments

The following compounds were used for the synthesis: individual R and 5-MR with basic substance content $>$ 99.9 wt%, natural ARs (commercial fraction HONEYOL80, substances in fraction: R – 0.6 wt%, 5-MR – 88.7 wt%, 5-ER – 5.2 wt%), catalyst - *p*-Toluenesulfonic acid (*p*-TSA) - $>$ 99.9 wt%, S, DCPD, NaOH.

Before the synthesis, S ($>$ 99 wt%, Sigma-Aldrich) and DCPD ($>$ 93 wt%, Sigma-Aldrich) were distilled and purified. The catalyst was neutralized using a 40% sodium hydroxide (NaOH) solution.

In the analytical part, reagents from Sigma-Aldrich (USA) were used with an ACS reagent purity ($\geqslant$ 99.5%).

Commercial fraction HONEYOL80, R and 5-MR, and *p*-TSA were provided by Viru Keemia Grupp AS.

2.2. Synthesis of resins

(Alkyl)resorcinol-dicyclopentadiene-styrene resins were synthesized according to recommendations given in the literature [29]. A block diagram is shown in figure 1.

The raw material for the first three syntheses, R, was used, which was later partially or completely replaced by 5-MR and the HONEYOL80 fraction. The formulations of the synthesized resins are shown in table 2.

R was placed in a four-neck flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and a dropping funnel and heated to 125 °C–135 °C. When R was completely melted, the first portion of the *p*-TSA

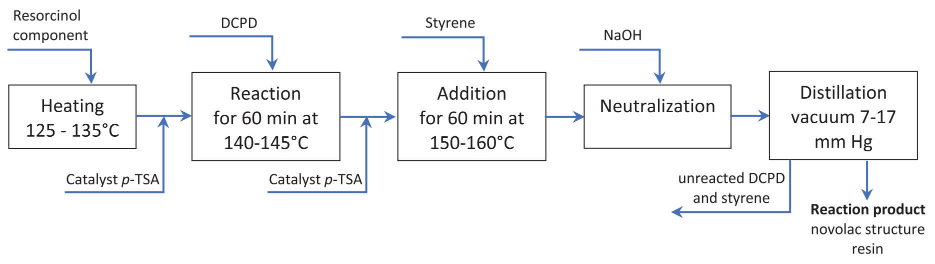


Figure 1. Block-diagram of the synthesis of DCPD resin.

Table 2. Resins formulations and synthesis conditions.

	Compounds, mol						
Sample name	R	5-MR	HONEYOL80	DCPD	Styrene	T, °C	Time
RDS_1	1.0	—	—	0.4	1.0	140–200	8 h
RDS_2	1.0	—	—	0.4	1.0	140–170	6 h 20 min
RDS_3	1.0	—	—	0.4	1.0	125–157	6 h
RDS_4	1.0	—	—	0.5	0.7	125–155	5 h 30 min
RDS_5	1.0	—	—	0.5	0.3	120–155	5 h 40 min
5-MRDS	—	1.0	—	0.5	0.3	135–170	6h30min
$H80_{100}DS$	—	—	1.0	0.5	0.3	128–170	5 h10 min
$R_{70}Hon80_{30}DS$	0.7	—	0.3	0.5	0.3	125–175	5 h10 min
$R_{50}Hon80_{50}DS$	0.5	—	0.5	0.5	0.3	125–165	5 h

catalyst was added, and the mixture was stirred for 5 min. Subsequently, a calculated amount of DCPD was added to the reaction mixture using a drop funnel for 60–90 min at 135°C–145 °C. Then the contents of the flask were incubated at 140 °C–145 °C for an additional 60 min. A second portion of *p*-TSA catalyst was introduced, and styrene was slowly added using a dropping funnel for 60 to 90 min at 140 to 145 °C. The synthesis was continued at 155 °C–160 °C for another 60 min. The reaction temperature was then slightly decreased and an equimolar amount of NaOH (40 wt% solution) was added to neutralize the *p*-TSA catalyst. The removal of unreacted DCPD and S was carried out under vacuum (7–17 mm Hg) at 150 °C–160 °C.

Based on the literature data [2, 29], the synthesis of a formaldehyde-free resin can proceed according to the following scheme (Scheme 1).

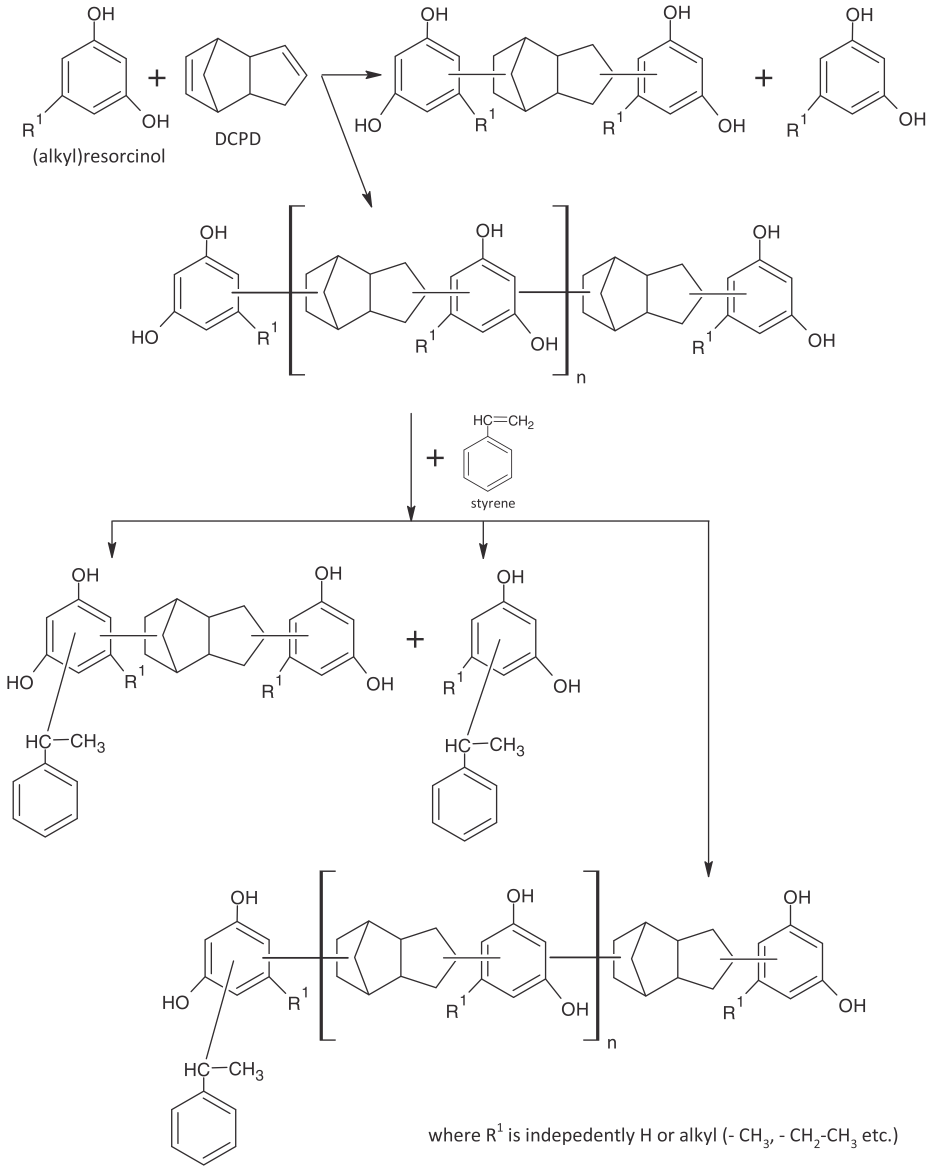
2.3. Methods used in experimental studies

2.3.1. Extraction of unreacted resorcinol and alkylresorcinols in the resins

Unreacted R and ARs were extracted from the resins as follow: 1 g of resin was boiled in 100 ml of distilled water. The suspension was filtered through a blue-ribbon filter. The mass and volume of the filtrate were measured. The pH of the solutions was then checked because in a basic environment, there may be phenolates that are insoluble in diethyl ether. These were destroyed by adding a weak solution of hydrochloric acid to pH 7. Then, a 20 ml aliquot of the filtrate was transferred to a separating funnel, 10 ml of diethyl ether was added, and the mixture was shaken. The ether layer was poured into a bottle and evaporated in air until a constant weight was reached. The resulting residue was used to determine the unreacted R and ARs using GC and TLC.

2.3.2. Gas chromatography

The component composition of the initial (alkyl)resorcinol (R and ARs fractions) was determined using an Agilent Technologies 7890A chromatograph with a PID detector, a DB-1 capillary chromatographic column with an inner diameter of 0.25 mm, length of 50 m, film thickness 0.25 μm. Temperature program: T_{injector} and T_{detector} — 260 °C, T_{initial} — 150 °C (isotherm time — 3 min), T_{end} — 260 °C (isotherm time — 15 min), temperature rise rate — 7.5 °C·min-1, split ratio — 1:70. The mass content of individual components in the sample was calculated automatically using *ChemStation* software. The initial resorcinol components of HMDS were preliminarily derivatized according to the method described in the work [15].



Scheme 1. Synthesis reaction of (alkyl)resorcinol-dicyclopentadiene resins modified with styrene.

2.3.3. Thin layer chromatography

TLC was used to determine unreacted R and 5-MR quantitatively and qualitatively in the resins, as well as to establish the homogeneity of the resin composition. For this, Silica gel 60 GF_{254} plates from Sigma-Aldrich were used. Then, in two test tubes, 0.1 g of R and 5-MR were dissolved in 10 ml of diethyl ether. The solutions were applied using a micro-syringe at a volume of 3 μl per plate and eluted using the ascending method. A mixture of toluene, propanol, and ethanol taken in volume ratios of 46:3:9.5 was used as the eluent. The plates were then air dried. The dried plate was lowered into a developer solution, $Na_3[Co(NO_2)_6]$. Subsequently, it was dried again with hot air until the appearance of brown spots. The resulting spots were scanned and processed using *JustTLC* software to determine the R_f value of the standard and the R and 5-MR extracted from the resin. The obtained R_f retention coefficients were used to calculate the amount of unreacted R and 5-Mr

2.3.3. Softening point

The softening point of the resins was determined using the standard method of Ring and Ball [31] with the replacement of water with glycerol, as the softening points of some resins were above 100 °C.

2.3.4. Resin solubility

Samples of the formaldehyde-free resin were ground to a particle size of 1–3 mm. One gram of crushed sample was placed in test tubes, and 100 g of the solvent (distilled water, acetone, ethanol, toluene, and tetrahydrofuran) was added to a measuring cylinder. The mixture was shaken and allowed to stand for 2 h at room temperature. Periodically shaken, the degree of dissolution indicated fully dissolved, partially dissolved, not dissolved, suspended, or settled particles. In the case of partial dissolution or swelling of the resin, its solubility upon heating was evaluated. To achieve this, the contents of the tubes were heated in a water bath for 15 min at the boiling point of the solution.

2.3.5. Thermal analysis

Thermal analysis (TG/DTG/DTA) was performed using equipment from Setaram LabSys (France) in 80% Ar+20%O_2 flow 60 ml·min^{-1} at a heating rate of 5 deg min^{-1} with ~ 10 mg of the sample. Thermal analyser was coupled with the Pfeiffer OmniStar Mass Spectrometer (Pfeiffer Vacuum Technology AG, Asslar, Germany) by a heated transfer line kept at T = 180 °C. The ion currents of the selected mass/charge (m/z) numbers were monitored in multiple ion detection (MID) mode (Quadera version 4.20 software) with the collection time of 1 s for each channel. The m/z ratios selected for analysis were 12 for C or C_3H_7; 18 for H_2O, 26 and 27 for C_2H_2 and C_2H_3; 44 for CO_2; 45 and 43 for C_3H_7; 52, 78 and 106 for C_6H_6 (styrene).

2.3.6. Determination of styrene and DCPD by the iodometric method

The unsaturated hydrocarbon content in the resin was determined using the standard method of iodometric titration [33].

2.3.7. Gel permeation chromatography

Samples for GPC measurements were dissolved in THF and passed through a 0.22 μm PVDF filter to remove all insoluble material. GPC measurements were performed on an Agilent Technology 1260 Infinity system with a three-column configuration. The column set was provided by *Polymer Standards Services GmbH, Mainz, Germany* and consisted of 8 × 300 mm SDV-type columns with 5 μm beads and porosities of 100000 Å, 1000 Å, and 100 Å, respectively. The system was operated at flow rate 1 ml·min^{-1} at 35 °C. An RI detector, poly(methyl methacrylate) (PMMA), and polystyrene (PS) standards were used. Calibration sets were provided by Polymer Standards Services GmbH (Mainz, Germany).

2.3.8. Volatile and ash content

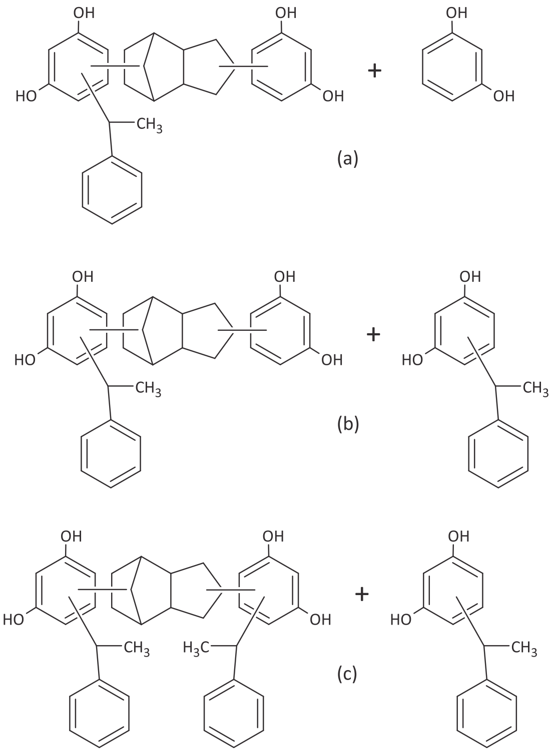
Volatile and ash content were determined using the standard methods [34] and [35], respectively.

3. Results and discussion

The molar ratio of the initial components (table 2) affects both the characteristics of the resins: softening point, ash content, the content of volatile and unreacted components, etc (table 3), and the molecular composition of the final product (Scheme 2). An increase in the mole fraction of the resorcinol fraction in the resin formulation to 30 mol% ($R_{70}Hon80_{30}DS$) led to an improvement in the technical characteristics of the resin. The content of unreacted R (5-MR) decreases from 1.9 wt% (RDS_5) to 0.5 wt% ($R_{70}Hon80_{30}DS$). The degree of conversion of the initial resorcinol components reaches 98.9 wt%. A further increase in the content of the HONEYOL80 alkylresorcinol fraction lowered the softening point and increased the quantity of unreacted components; therefore, the conversion of the initial (alkyl)resorcinols decreased. This is because the alkylresorcinol fraction contains, in addition to the main component 5-MR, also other alkylresorcinols with different side chain lengths, which are less reactive compared to 5-MR [15].

It was established that due to the ratios of the components of the formulations (table 2) during the processing of the resin under vacuum (distillation), the distillate was not formed, and no unreacted unsaturated compounds were present in the resin. Their concentrations were determined by iodometric titration [33]. From this, we can conclude that DCPD and S fully reacted with (alkyl)resorcinol and that the resins obtained by this synthesis method, described in this work, do not require the distillation stage. A comparison of the properties of the resins (free R content and softening point) based on the molar ratio of the components are shown in table 4.

From the data shown in table 4, it follows that the results of the laboratory experiments differ from those in the literature. This can be explained by differences in the quality of the starting substances used in the synthesis.



Scheme 2. The structure of polymer units obtained at different molar ratios of R: DCPD : S—a) 1 : 0.5 : 0.3 [29]; b) 1 : 0.5 : 0.7; c) 1 : 0.4 : 1.

Table 3. Characteristics of samples.

	Characteristics			
Sample name	Softening point, °C	Ash, wt%	Unreacted R or 5-MR, wt%	Conversion, %
RDS_1	64.0	0.06	—	—
RDS_2	71.5	0.1	2.2	94.7
RDS_3	70.5	0.3	1.9	95.4
RDS_4	80.5	0.2	0.9	98.0
RDS_5	97.0	0.4	1.9	96.3
5-MRDS	94.0	0.2	0.6	98.8
$Hon80_{100}DS$	75.0	0.2	1.8	95.8
$R_{70}Hon80_{30}DS$	95.0	0.2	e	98.9
$R_{50}Hon80_{50}DS$	88.0	0.04	2.1	95.6

Table 4. Resin properties depending on the molar ratio of the components.

	Patent data [25]		Experiment data(RDS resins)	
Molar ratio of componentsR: DCPD: S	Content of free R, wt%	Softening temperature, °C	Content of free R, wt%	Softening temperature, °C
1.0: 0.4: 1.0	0.95	95.2	1.87	71.5
1.0: 0.5: 0.7	1.80	113.6	0.88	80.5
1.0: 0.5: 0.3	6.90	127.2	1.94	97.0

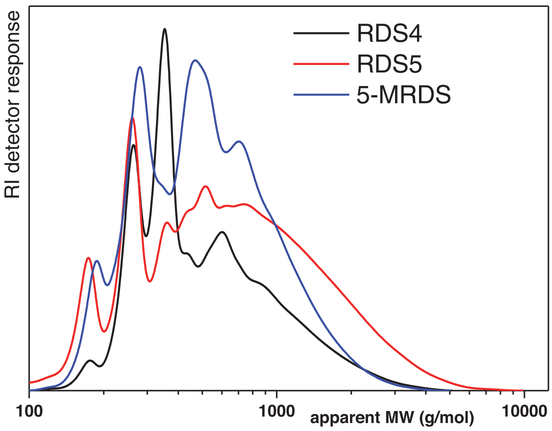


Figure 2. GPC traces of samples RDS$_4$, RDS$_5$ and 5-MRDS converted in MWD distribution by calculation using PS calibration.

Table 5. MW-characteristics of the samples.

Sample name	M_n	M_w	Đ	MW range	Low-MW content (%)
RDS$_4$	430	620	1.44	110–4400	12
RDS$_5$	440	840	1.90	110–6500	16
5-MRDS	420	610	1.45	120–3900	14
R$_{70}$Hon80$_{30}$DS	450	840	1,85	110–7000	25
R$_{50}$Hon80$_{50}$DS	450	790	1.76	110–5700	22
Hon80$_{100}$DS	370	520	1.41	120–2600	30
R$_{70}$Rez$_{30}$SF [15, 18]	320	380	1.20	110–1200	10
R$_{70}$Rez$_{30}$SAc [18]	330	450	1.36	110–1900	20
R$_{70}$Hon$_{30}$DS	450	840	1.85	120–7000	25

However, the softening temperature depends on the molar ratio of the resin components. Changing the molar ratio made it possible to obtain resins with the desired softening point.

Notably, R reacts easily with DCPD in the presence of an acid catalyst at elevated temperatures. In the first stage of the synthesis, resorcinol molecules interacted with DCPD, and a linear oligomer was formed (Scheme 1). In the second stage, S was introduced. S and DCPD bound unreacted resorcinol molecules. The oligomer molecules probably have different structures depending on the molar ratio of the components used for the synthesis (Scheme 2).

The studied resins exhibited moderate molecular weights (table 5), which are typical for this class of materials. By GPC analysis content of molecules with low-MW (180 g·mol^{-1} and 250 g·mol^{-1}) were detected, which can be attributed to the starting compounds R, 5-MR, S, DCPD, or Hon80. Their content can be roughly estimated from GPC. However, any detailed analysis is behind the scope of this study aimed at study of replacement of formaldehyde-based materials with new resins with good/excellent properties.

Figures 2 and 3 shows a comparison of the MW of the samples based on the HONEYOL fraction. The molecular weight of R$_{70}$Hon$_{30}$DS was remarkably higher in comparison with samples R$_{70}$Rez$_{30}$SF and R$_{70}$Rez$_{30}$SAc. Highest MW achieved in the sample with HONEYOL80 was several times higher than for Rez/Ac samples. Dispersity was also higher, which can be explained by the increased ratio of low-M_w compounds (starting materials), which strongly affects the M_n value. The higher values of DCPD and S-containing samples can be explained with increased reactivity of the double bonds and the increased number of possible connections. The second plausible explanation is the different characteristics of the macromolecular architecture. Macromolecules with more linear character show higher molecular weight in GPC than its branched counterparts with identical molecular weight. As shown in Schemes 1 and 2, the introduction of DCPD and S led to the formation of linear segments. The addition of F or Ac leads to branching through methylene bridges.

The first three resins (table 3) were synthesized with the same molar ratio of R: DCPD: S = 1:0.4:1, but at different temperature conditions and process times. The obtained resins exhibit low softening temperatures.

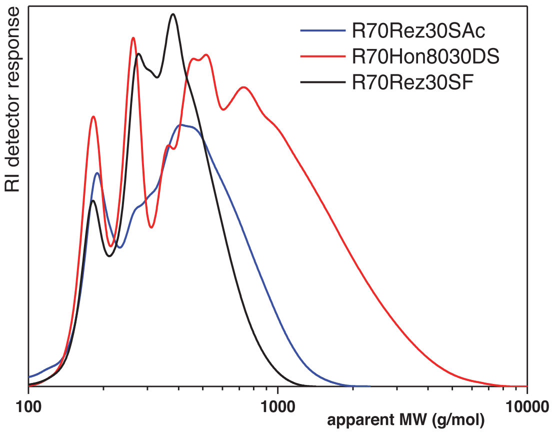


Figure 3. GPC traces of samples $R_{70}Rez_{30}SAc$, $R_{70}Hon80_{30}DS$ and $R_{70}Rez_{30}SF$ converted into MWD distribution by calculation using PS calibration.

The molar ratio of the components was adjusted to increase softening temperature. Table 3 shows that simultaneous increase in DCPD amount from 0.4 to 0.5 mol and decrease in styrene amount from 1.0 to 0.7 mol increase resin softening temperature by 10 °C. The RDS_5 resin synthesized with 0.3 mol of S has a softening point at 97 °C. Varying the molar ratio of the components made it possible to obtain a product with the required softening point. In the subsequent synthesis, 5-MR was used instead of R, which is characterized by increased reactivity owing to the presence of an alkyl group at the *meta*-position of the benzene ring [36]. The introduction of 5-MR instead of pure R hardly reduced the softening point. The complete replacement of R by the HONEYOL80 fraction obtained by Viru Keemia Grupp AS resulted in a reduction of the softening point to 75 °C. This can be explained by the presence of alkylresorcinol compounds with long-chain and cyclic groups, as well as the higher content of pyridine bases in HONEYOL80 [21].

The TA results (figures 4 and 5) shows that the amount of water evolved at temperatures of 70 °C–150 °C is inappreciable quantity, since in this temperature range, there is practically no loss of mass of the resin sample and the release of H_2O ($m/z = 18$). The synthesized resins were stable up to a temperature of 200 °C (table 6). The RDS_5 resin exhibited the highest stability and lowest weight loss among the studied samples. The $Hon_{100}DS$ resin is unstable. Weight loss for all the samples occurred in almost three stages. In figure 4 is seen that because of decomposition of the resin at a temperature of 230 °C–300 °C, light hydrocarbons, as well as styrene, begin to release. The intensity of evolvement depended on the composition of the resin. From stable resins, the release of components with a cyclic structure ($m/z = 78$) (RDS_2, RDS_5 and $R_{50}Hon80_{50}DS$) occurred in the temperature interval of 300–350 to 450 °C. For the unstable resins, this temperature was reduced by approximately 100 °C. Oxidation (burning) was revealed by an exothermic effect in the DTA curve, as well as by the release of CO_2 and H_2O. It becomes dominant for resorcinol resins at approximately 350 °C, but for resins obtained using HONEYOL fraction at 400 °C–430 °C.

The successful application of a polymer material under various conditions depends on its ability to maintain its performance during long-term storage. Using the TGA method, it is possible to make preliminary conclusions regarding the durability of the polymer [32]. The mass loss data convey this information most accurately. As a rule of thumb, the higher the decomposition temperature, the longer is the shelf life of the polymer. The DCPDS resins can be operated at high temperatures. This was indicated by the mass loss temperatures ($\tau_{\%}$) obtained by TGA (table 6).

It should be noted that the obtained resins had low ash content. The ash content index is an important technical characteristic of the resins. This affects the mechanical resistance of both the resin and the composite when the matrix (resin) is added. The lowest values of ash content were noted for RDS, $R_{50}Hon80_{50}DS$ — 0.04 and 0.06 wt%, respectively. Thermogravimetric analysis (TGA) revealed that the volatile compounds in these resins were insignificant.

Partial replacement of R by 5-MR or HONEYOL80 fraction (70/30 or 50/50) allows the synthesis of a product with a softening point of 88°C–95 °C and a small content of unreacted R and 5-MR: $R_{70}Hon80_{30}DS$ — 0.5 wt%, 5-MRDS — 0.6 wt%.

The resins obtained were solid and brittle substances with a dark red or brown color. Red resins were synthesized based on R and 5-MR and brown based on the fraction HONEYOL80. The primary parameters are

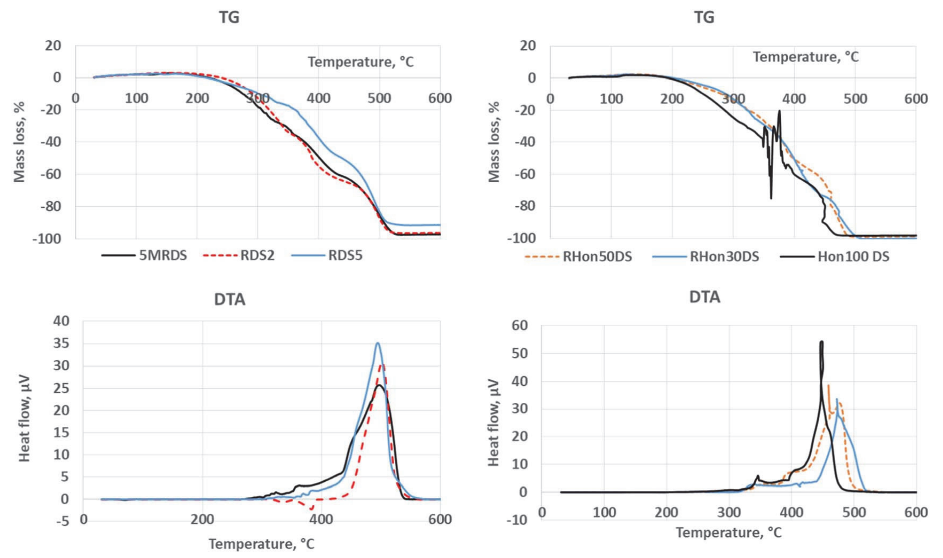


Figure 4. TG and DTA curves of DCPDS resins in Ar+20% O_2 atmosphere at heating rate 5 deg min^{-1}.

listed in table 3. The composition of such resins is more homogeneous than that of resorcinol-aldehyde resins [15, 21]. It should be noted that they practically do not contain volatile components, including moisture, at 105 °C, as shown by the results of TGA results (figure 4).

Resins have different solubilities in various organic solvents. They were soluble in acetone, ethanol, and tetrahydrofuran; slightly soluble in toluene; and insoluble in water. Very good solubility of the resins of all formulations was observed in acetone. It was found that the 1% solutions of the synthesized resins differed sharply in color. This makes it possible to expand their application areas from the tire industry to the paper industry [37, 38]. In the latter, in addition to a decrease of softening point, a low chromaticity of the adhesive additive is required, the role of which is played by the resorcinol resins.

3. Conclusions

Natural alkylresorcinols, such as 5-MR and HONEYOL80 oil shale alkylresorcinol industrial fraction, have been used to produce new non-aldehyde resins (dicyclopentadiene-styrene resins), and their physical and chemical characteristics were determined. It was shown that depending on the mole ratio of the components of the formulation resins with different softening temperatures (66 to 97 °C), ash content of 0.04 to 0.39 wt%, and a low content of volatile components at 105 °C, including moisture, were obtained. The best conditions for the synthesis of resins with a softening point at 94 °C–97 °C are molar ratio of R (5-MR): DCPD: S = 1: 0.5: 0.3 at temperature 135 °C–170°C, synthesis time 5 h 30 min. The best technical parameters have the resin (R70Hon8030DS) obtained using HONEYOL80: softening point 95 °C, ash content — 0.2 wt %, and total content of unreacted R and 5-MR in resins 0.5 wt %.

It has been shown that the synthesized resins do not require additional processing under a vacuum. The negligible water and volatile content in the resins would allow to implement molding without additional ventilation for vapor escape.

Variation in the initial composition is reflected in the MW characteristic of the final material. This is observed in the resins with high double-bond content. Such resins are suitable for replacing synthetic materials with natural ones. It has been proven that the combination of moderate-molecular-weight macromolecules and oligomeric/monomeric fractions corresponds to the proposed chemical mechanisms.

Therefore, it is possible to replace (partial or fully) synthetic R with natural ARs (5-MR) or oil shale ARs industrial fraction (HONEYOL80) in the formulations of non-aldehyde resins. Depending on the molar ratio of the initial components of the formulations, it is possible to synthesize resins with different properties without using a solvent. This makes possible to achieve considerable energy savings.

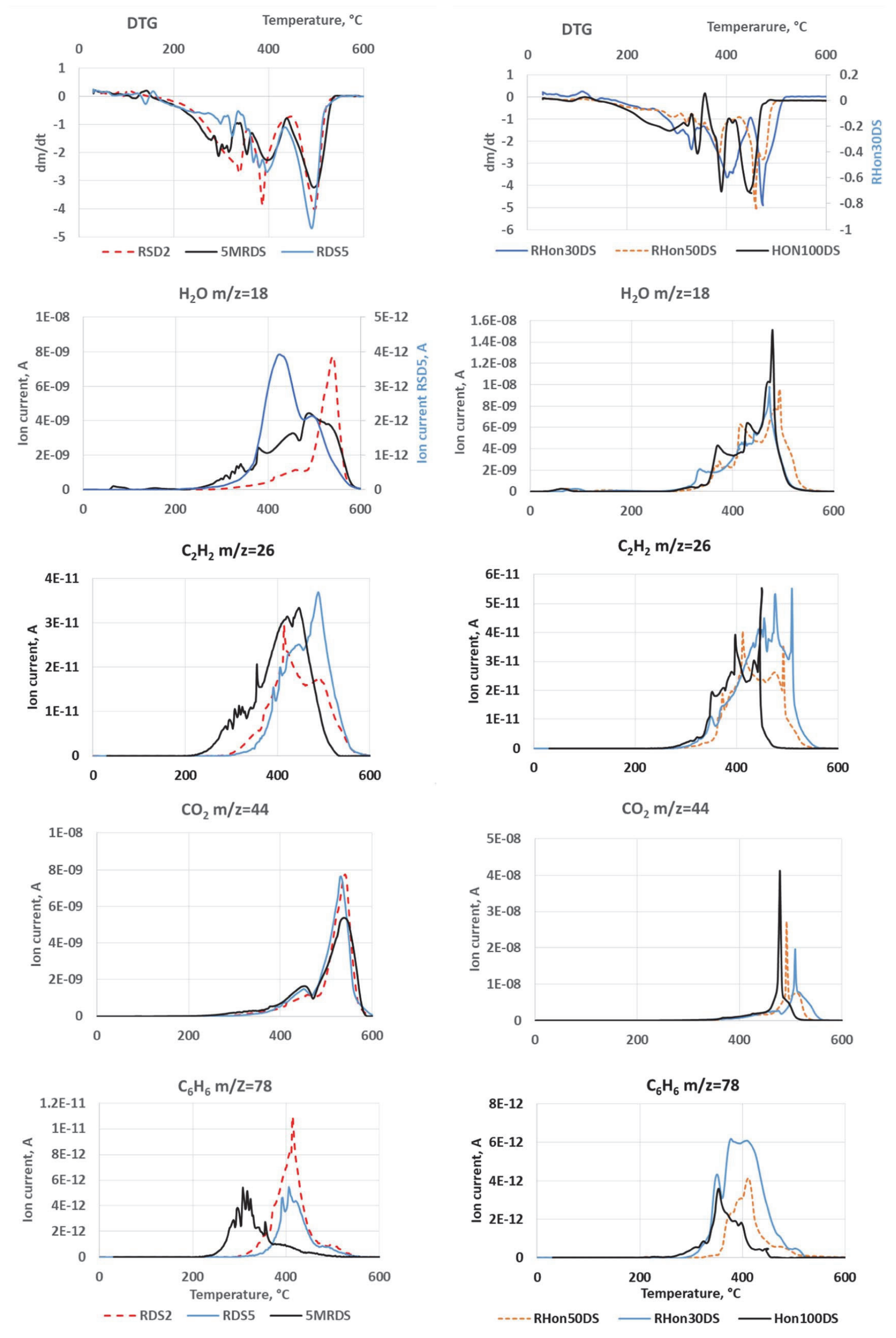


Figure 5. The evolvement of gases at heating of the resins in Ar+20%O$_2$ atmosphere.

Acknowledgments

DB acknowledges the support from project VEGA 2/0161/20.

Table 6. Comparative characterization of the mass loss temperatures of different resins.

	Sample name						
Parameter	RF [15]	RSF [15, 18]	RAc [18]	RDS_5	$R_{90}Rez_{10}SF$ [15, 18]	$R_{70}Rez_{30}SAc$ [18]	$R_{70}Hon80_{30}DS$
$T_{start\ of\ dec}$, . °C	115	155	80	170	155	105	150
τ_{10}, °C	174	213	194	302	205	247	289
τ_{50}, °C	409	467	459	440	461	397	400
τ_{90}, °C	527	565	543	520	554	599	480

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contributions

All authors have read and agreed to the published version of the manuscript.

Funding statement

This research was conducted under the doctoral study of the Tallinn University of Technology.

Ethical compliance

This article does not contain any studies with human participants or animals performed by any of the authors. This article is original. The article has been written by the stated authors, who are ALL aware of its content and approve its submission.

Data access statement

All relevant data are within the paper and its Supporting Information files.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ORCID iDs

Ana Jurkeviciute https://orcid.org/0000-0002-9175-1963
Larisa Grigorieva https://orcid.org/0000-0002-2409-1061

References

[1] Brydson J 1999 *Plastics Materials* (Elsevier Ltd. Butterworth-Heinemann) 7th edn
[2] Dressler H 1994 *Resorcinol: Its Uses and Derivatives* (Springer) (https://doi.org/10.1007/978-1-4899-0999-2)
[3] Yu M 2009 Special polymeric composite materials(Nauchnye osnovy i tekhnology Publ)
[4] Althaqafi K, Satterthwaite J and Silikas N 2020 A review and current state of autonomic self-healing microcapsules-based dental resin composites *Dent. Mater.* **36** 329–42
[5] Asim M, Saba N, Jawaid M, Nasir M, Pervaiz M and Alothman O 2018 A review on phenolic resin and its composites *Current Analytical Chemistry* **14** 185–97
[6] Alieva A 2021 Prospects for obtaining phenol-formaldehyde oligomers *Plasticheskie massy* **9** 22–6
[7] Zastrogina O, Sinyakov S and Serkova E 2021 Materials based phenolformaldehyde oligomers of resol and novolac tipes (review) *Part 1 Federal State Unitary Enterprise «All-Russian Scientific-Research Institute of Aviation Materials» of National Research Center «Kurchatov Institute»b* **10** 58–66
[8] Zang C, Xing Y, Yang T, Teng Q, Zhen J, Zhang R, Jia Z and Han W 2022 The preparation and wear behaviors of phenol-formaldehyde resin/BN composite coatings *Polymers* **14** 4230
[9] Zonghe Yang Z, Liu B, Zhao H, Li J, Guo X, Zhang D and Liu Z 2023 Pyrolysis mechanism of composite binder composed of coal tar pitch and phenolic resin for carbon materials *Anal. and Appl. Pyr.* **169** 105840

[10] Niu Z, Chen B, Shen Sh, Zhang H, Ma X, Chen F, Li L, Xin Y, Zhang Ch and Hou X 2022 Zirconium chelated hybrid phenolic resin with enhanced thermal and ablation resistance properties for thermal insulation composites *Composites Communications* **35** 101284

[11] Zhang K, Ang B, Zhang L, Zhao S and Wu J 2011 Pyrolyzed graphene oxide/resorcinol-formaldehyde resin composites as high-performance supercapacitor electrodes *J. Mater. Chem.* **21** 2663

[12] Wang M, Ni Y and Liu A 2017 Fe_3O_4@resorcinol-formaldehyde resin/Cu_2O composite microstructures: solution-phase construction, magnetic performance, and applications in antibacterial and catalytic fields *ACS Omega* **2** 1505–12

[13] Liteplo R, Beauchamp R, Chénier R and Meek M 2002 *Formaldehyde* (World Health Organization) https://apps.who.int/iris/bitstream/handle/10665/42430/a73769.pdf

[14] Robichaud A 2020 An overview of selected emerging outdoor airborne pollutants and air quality issues: the need to reduce uncertainty about environmental and human impacts *J. Air Waste Manage. Assoc.* **70** 341–78

[15] Jurkeviciute A, Grigorieva L, Tõnsuaadu K and Blum K 2023 Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols *Material Research Express* **10** 035304

[16] Xu J, Brodu N, Mignot M, Youssef B and Taouk B 2022 Synthesis and characterization of phenolic resins based on pyrolysis bio-oil separated by fractional condensation and water extraction *Biomass Bioenergy* **159** 106393

[17] Materials & Processes: Resin matrices for composites. Industry Overivew, Part I: Materials & Processes, Updated on 6/29/2022 Materials & Processes: Resin matrices for composites, Composites World (accessed: 2023)

[18] Aurer J and Kasper A 2003 *Unsaturated Polyester Resins. Polymers with Unlimited Possibilities, Mediaservice GmbH, Buchloe, Germany*

[19] Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products (accessed: 2023)

[20] REACH Regulation and Formaldehyde. European Chemical Industry Council (accessed: 2023)

[21] Yurkevichyute A, Grigorieva L and Vassiljev V 2016 Synthesis of solid resorcinol-formaldehyde resin modified with styrene with the use of a shale phenol fraction with a boiling temperature higher than 270 °C *Solid Fuel Chem.* **50** 64–8

[22] Harvey T 2008 *Modified Alkylresorcinol Resins and Applications Thereof.* Patent US20080090967

[23] Durairaj R and Peterson A 2002 *Nonformaldehyde, Nonfuming Resorcinolic Resins and Methods of Making and Using the Same* Patent US6472457B1

[24] Despres A, Pizzi A, Vu C and Delmotte L 2010 Colourless formaldehyde-free urea resin adhesives for wood panels *Eur. J. Wood Wood Prod.* **68** 13–20

[25] Foyer G, Chanfi B-H, Boutevin B, Caillol S and David G 2016 New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors *Eur. Polym. J.* **74** 296–309

[26] Chrobak J, Iłowska J and Chrobok A 2022 Formaldehyde-free resins for the wood-based panel industry: alternatives to formaldehyde and novel hardeners *Molecules* **27** 4862

[27] Xu C, Zhang Y and Yuan Z 2015 *Formaldehyde-Free Phenolic Resins, Downstream Products, Their Synthesis, and Use.* Patent US20160355631A1

[28] Hsiue G-H, Wei H-F, Shiao S-J, Kuo W-J and Sha Y-A 2001 Chemical modification of dicyclopentadiene-based epoxy resins to improve compatibility and thermal properties *Polym. Degrad. Stab.* **73** 309–18

[29] Durairaj R B 2005 *Resorcinol: Chemistry, Technology and Applications* (Indspec Chemical Corporation)

[30] Baerends E, Grigor'eva L and Ostroukhov N 2021 Extraction of Total Water-Soluble Alkylresorcinols from the Tar Water of the Kiviter Process with Methyl Isobutyl Ketone *Solid Fuel Chem.* **55** 177–186

[31] ASTM D36-06 Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus)

[32] Pavlov N 1982 Aging of plastics in natural and artificial conditions, Chemistry, Moskow,

[33] GOST 2070 Light petroleum products. Methods for determination of iodine numbers and content of unsaturated hydrocarbons

[34] ISO 11358-1 Plastics - Thermogravimetry (TG) of polymers - Part 1: General principles

[35] ASTM D5630 Standard Test Method for Ash Content in Plastics

[36] Lille Y, Bitter L, Purre T, Rätsep A, Soo K, Kalde L and Nurske H 1971 Alkylresorcinols. Production methods, properties, and application(TsNIITEneftekhim)

[37] Sinha A 2021 A novel manufacturing process of paper composite using recycled old newspaper sheets and phenol formaldehyde resin *Quarterly Journal of Indian Pulp and paper Technical Association* **33** 13–7

[38] Ahmed W, Sagir M, Tahir S and Ullah S 2019 Phenol Formaldehyde Resin for Hydrophilic Cellulose Paper *Advances in Sustainable and Environmental Hydrology, Hydrogeology, Hydrochemistry and Water Resources* (Springer) CAJG 2018, Advances in Science, Technology & Innovation (https://doi.org/10.1007/978-3-030-01572-5_22)

Curriculum vitae

Personal data

Name: Ana Jurkevičiūtė
Date of birth: 31.07.1978
Place of birth: Estonia
Citizenship: Lithuanian

Contact data

E-mail: ana.jurkeviciute@gmail.com

Education

2015–2023	Tallinn University of Technology – PhD
2012–2014	Tallinn University of Technology, Virumaa College – MSC (*Cum laude*)
2005–2011	Tallinn University of Technology, Virumaa College – Higher applied education (*Cum laude*)
1998–2001	Kohtla-Järve Polytehnikum – Secondary education
1993–1998	Kohtla-Järve Polytehnikum – Secondary education

Language competence

Russian	Native speaker
Estonian	Fluent
English	Fluent

Professional employment

2019–present	Estonian Standardization and Accreditation Center, Lead Assessor
2019–2019	Tallinn University of Technology, School of Engineering, Virumaa College, Early Stage Researcher, Master's Programme Director, Teaching
2017–2019	Tallinn University of Technology, School of Engineering, Virumaa College, Chemical Engineer, Master's Programme Director, Teaching
2011–2017	Tallinn University of Technology, Virumaa College, Laboratory of Fuels Technology, Chemical Engineer, Quality Manager
2008–2011	Tallinn University of Technology, Virumaa College, Lecturer in Chemical Technology, Laboratory Assistant

Defended dissertations

Master's Degree, 2014, The research of the possibility of a modified solid alkyl-resorcinol-formaldehyde upgraded resin production by using REZOL fraction. Supervisor: Larisa Grigorieva (PhD), Co- Supervisor Valentin Vassiljev (DScTech)

Involvement in research projects

IUT33-19 – "Fundamentals of multicomponent mineral-organic systems: Chemistry, modeling and sustainable processing. (01.01.2015–31.12.2020)"

SEF5 – “New technologies, including ICT application in the development of study programmes in Belarus. (01.09.2018–31.12.2020)”

Creative work

2008 BeST project, e-course “Polymer Chemistry and Physics”

Awards

2022	Kristjan Jaak Scholarships https://blogi.harno.ee/kristjan-jaagu-stipendium-lennutas-taisse/
2015	Laureate of 68. All-Russian scientific and technical conference of students, undergraduates and graduate students of higher educational institutions with international participation. Yaroslavl State Technical University, Yaroslavl
2014	AS VIRU KEEMIA GRUPP Master’s grant
2014	Kohtla-Järve Municipal Government grant
2012	Kohtla-Järve Municipal Government grant
2006	AS VIRU KEEMIA GRUPP applied higher education grant

Participation in conferences

2023	Attendance with poster presentation at “Composites 2023 International Conference”, Bangkok, Thailand
2022	Attendance with poster presentations at “Baltic Polymer Symposium 2022”, Tallinn, Estonia
2022	Attendance with poster presentation at Graduate School of Functional Materials and Technologies (GSFMT) scientific conferences, Tallinn, Estonia
2018	Attendance with poster presentation and as a moderator at World Congress on Oil, Gas and Petroleum Refinery, Abu Dhabi, UAE
2016	Attendance with oral presentations at 69th All-Russian Scientific and Technical Conference of Students, Undergraduates and Postgraduates of Higher Educational Institutions with International Participation, Jaroslavl, Russia
2015	Attendance with oral presentations at 68th All-Russian Scientific and Technical Conference of Students, Undergraduates and Postgraduates of Higher Educational Institutions with International Participation, Jaroslavl, Russia
2014	Attendance with poster presentation at 34th International Oil Shale Symposium, Colorado, USA
2014	Attendance with oral presentations at 67th All-Russian Scientific and Technical Conference of Students, Undergraduates and Postgraduates of Higher Educational Institutions with International Participation, Jaroslavl, Russia
2014	Attendance with poster presentation at International Oil Shale Symposium, Jordan
2008	Attendance with oral presentations at II-nd International scientifical and practical conference for students and post-graduatess “Current problems of oil and gas chemical complex and alternative sources of energy”, Saint-Petersburg State University of Engineering and Economics, Saint-Petersburg, Russia

Supervised dissertations

Kristina Blum, Master’s Degree, 2019, (juh) **Ana Jurkeviciute**, Synthesis and properties of polycondensation polymers based on oil shale alkylresorcinols, Tallinn University of Technology, School of Engineering, Virumaa College

Igor Demidovich, Master’s Degree, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, Optimization of shale oil gasoline fraction condensation process at the Enefit280 oil plant, Tallinn University of Technology, School of Engineering, Virumaa College

Jelena Derbneva, Master’s Degree, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, The final stage of the condensation process modernization at the Enefit280 oil plant, Tallinn University of Technology, School of Engineering, Virumaa College

Roman Šestakov, Master’s Degree, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, Elimination of Process Fluctuations at Enefit280 Shale Oil Plant, Tallinn University of Technology, School of Engineering, Virumaa College

List of publications

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, T. Yashicheva, D. Bondarev. “Non-aldehyde resins based on resorcinol and natural alkylresorcinols modified with styrene”, Materials Research Express, 10(10), 105301, 2023 DOI 10.1088/2053-1591/acfd12

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, K. Blum. “Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols”, Materials Research Express, 10(3), 035304, 2023, DOI 10.1088/2053-1591/acc0e1

A. Yurkevichyute, L. Grigorieva, V. Vassiljev. “Synthesis of Solid Resorcinol-Formaldehyde Resin Modified with Styrene with the Use of a Shale Phenol Fraction with a Boiling Temperature Higher Than 270 °C”, Solid Fuel Chemistry, 50(1), 64-68, 2016, DOI 10.3103/S0361521916010122

А. Юркевичюте, Л. Григорьева, В. Васильев. Синтез твердой резорцино-формальдегидной смолы, модифицированной стиролом, с использованием фракции сланцевых фенолов с температурой кипения выше 270 °С, ХИМИЯ ТВЕРДОГО ТОПЛИВА, 2016, № 1, с. 66–70. DOI: 10.7868/S0023117716010126

Additional information

https://www.etis.ee/CV/Ana_Jurkeviciute/eng/

Elulookirjeldus

Isikuandmed

Nimi:	Ana Jurkevičiūtė
Sünniaeg:	31.07.1978
Sünnikoht:	Eesti
Kodakondsus:	leedulane

Kontaktandmed

E-post:	ana.jurkeviciute@gmail.com

Hariduskäik

2015–2023	Tallinna Tehnikaülikool – PhD
2012–2014	Tallinna Tehnikaülikool, Virumaa Kolledž – MSC (*Cum laude*)
2005–2011	Tallinna Tehnikaülikool, Virumaa Kolledž – Rakenduskõrgharidus (*Cum laude*)
1998–2001	Kohtla-Järve Polütehnikum – Keskeriharidus
1993–1998	Kohtla-Järve Polütehnikum – Keskeriharidus

Keelteoskus

Vene keel	emakeel
Eesti keel	kõrgtase
Inglise keel	kõrgtase

Teenistuskäik

2019–praegune	MTÜ Eesti Standardimis- ja Akrediteerimiskeskus, peaassessor
2019–2019	Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž, doktorant-nooremteadur, magistriõppekava programmijuht
2017–2019	Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž, keemiainsener, magistriõppekava programmijuht
2011–2017	Tallinna Tehnikaülikool, Virumaa Kolledž, Kütuste tehnoloogia teadus- ja katselaboratoorium, keemiainsener, kvaliteedijuht
2008–2011	Tallinna Tehnikaülikool, Virumaa Kolledž, Keemiatehnoloogia lektoraat, laborant

Kaitstud väitekirjad

Magistrikraad, 2014, Parendatud kvaliteediga modifitseeritud tahke alküülresortsinoolformaldehüüdvaigu saamise võimaluse uurimine kasutades REZOL fraktsiooni. Juhendaja: Larisa Grigorieva (PhD), kaasjuhendaja: Valentin Vassiljev (DScTech)

Teadusprojektid

IUT33-19 – "Multikomponentsete mineraal-orgaaniliste süsteemide käitlemise alused: keemia, modelleerimine ja kestlik kasutus. (01.01.2015–31.12.2020)"

SEF5 – "Uute tehnoloogiate, sh IKT rakendamine õppekavaarenduses Valgevenes. (01.09.2018–31.12.2020)"

Tunnustused

2022	Kristjan Jaagu stipendium https://blogi.harno.ee/kristjan-jaagu-stipendium-lennutas-taisse/
2015	Laureaat, 68. Ülevenemaaline teaduslik-tehnilise konverents õpilastele, magistrantidele ja aspirandile rahvusvahelise osalusega, Jaroslavli Riikliku Tehnikaülikool, Jaroslavl
2014	AS VIRU KEEMIA GRUPP magistriõppe stipendium
2014	Kohtla-Järve Linnavalitsuse magistriõppe stipendium
2012	Kohtla-Järve Linnavalitsuse stipendium
2006	AS VIRU KEEMIA GRUPP rakenduskõrgharidusõppe stipendium

Osalemine konverentsidel

2023	Posterettekannetega esinemine "Composites 2023" rahvusvahelisel konverentsil, Bangkok, Tai
2022	Posterettekannetega esinemine Balti Polümeeri sümpoosiumil, Tallinn, Eesti
2022	Posterettekandega esinemine Funktsionaalsete materjalide ja tehnoloogiate doktorikooli (FMTDK) teaduskonverentsidel, Tallinn, Eesti
2018	Posterettekandega ja moderaatorina Maailma nafta-, gaasi- ja naftatöötlemistehaste kongressil, Abu Dabhi, Araabia Ühendemiraadid
2016	Suuliseettekandega esinemine 69. Ülevenemaalisel teaduskonverentsil õpilastele, üliõpilastele ja magistrantidele rahvusvahelise osalusega, Jaroslavli Riikliku Tehnikaülikool, Jaroslavl, Venemaa
2015	Suuliseettekandega esinemine 68. Ülevenemaalisel teaduskonverentsil õpilastele, üliõpilastele ja magistrantidele rahvusvahelise osalusega, Jaroslavli Riikliku Tehnikaülikool, Jaroslavl, Venemaa
2014	Posterettekandega esinemine 34. Rahvusvahelistel Põlevkivi sümpoosiumil, Colorado, USA
2014	Suuliseettekannetega esinemine 67. Ülevenemaalisel teaduskonverentsil õpilastele, üliõpilastele ja magistrantidele rahvusvahelise osalusega, Jaroslavli Riikliku Tehnikaülikool, Jaroslavl, Venemaa
2014	Posterettekandega esinemine Rahvusvaheline Põlevkivi sümpoosiumil, Jordaania
2008	Suuliseettekandega II rahvusvahelisel teadus- ja praktilisel konverentsil üliõpilastele ja magistrantidele "Nafta- ja gaasikeemiakompleksi ja alternatiivsete energiaallikate aktuaalsed probleemid", Peterburi Riiklik Tehnika- ja Majandusülikool, Sankt-Peterburg, Venemaa

Juhendatud lõputööd

Kristina Blum, magistrikraad, 2019, (juh) **Ana Jurkeviciute**, Polükondensatsiooni polümeeride süntees ja omadused põlevkivi alküülresortsinoolide alusel, Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž

Igor Demidovich, magistrikraad, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, Põlevkiviõli bensiinifraktsiooni kondensatsiooniprotsessi optimeerimine Enefit280 õlitehases, Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž

Jelena Derbneva, magistrikraad, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, Põlevkiviõlitehase Enefit280 kondensatsiooni viimase etapi moderniseerimine, Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž

Roman Šestakov, magistrikraad, 2019 (juh) **Ana Jurkeviciute**, Aleksei Zaidentsal, Põlevkiviõlitehase Enefit280 protsessi kõikumiste elimineerimine, Tallinna Tehnikaülikool, Inseneriteaduskond, Virumaa kolledž

Teaduspublikatsioonid

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, T. Yashicheva, D. Bondarev. “Non-aldehyde resins based on resorcinol and natural alkylresorcinols modified with styrene”, Materials Research Express, 10(10), 105301, 2023 DOI 10.1088/2053-1591/acfd12

A. Jurkeviciute, L. Grigorieva, K. Tõnsuaadu, K. Blum. “Comparative analysis of the qualitative characteristics of formaldehyde and acetaldehyde resins based on styrene-modified oil shale alkylresorcinols”, Materials Research Express, 10(3), 035304, 2023, DOI 10.1088/2053-1591/acc0e1

A. Yurkevichyute, L. Grigorieva, V. Vassiljev. “Synthesis of Solid Resorcinol-Formaldehyde Resin Modified with Styrene with the Use of a Shale Phenol Fraction with a Boiling Temperature Higher Than 270 °C”, Solid Fuel Chemistry, 50(1), 64–68, 2016, DOI 10.3103/S0361521916010122

А. Юркевичюте, Л. Григорьева, В. Васильев. Синтез твердой резорцино-формальдегидной смолы, модифицированной стиролом, с использованием фракции сланцевых фенолов с температурой кипения выше 270 °С, ХИМИЯ ТВЕРДОГО ТОПЛИВА, 2016, № 1, с. 66–70. DOI: 10.7868/S0023117716010126

Lisainfo

https://www.etis.ee/CV/Ana_Jurkeviciute/est/

ISSN 2585-6901 (PDF)
ISBN 978-9916-80-112-3 (PDF)