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Synthesis of Natural Phenolic Compound Contained Alkaline Phenolic Foundry Resin and Its Performance Evaluation on Casting

A.E. Güvendik [a], K. Ay * [b]
[a] Çukurova Kimya Endüstrisi A.Ş., Turkey
[b] Manisa Celal Bayar University, Turkey
* Corresponding author: Email address: kadir.ay@cbu.edu.tr

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Abstract

In foundry, metal casting can be done with various methods. One of the most important methods preferred around the world is sand casting. Ester curable alkaline phenolic resins have produced to make sand molds by No-bake systems. They must have specific properties to make sand casting efficient and reliable. Production of these resins depends on some fossil raw-materials like phenol. To investigate more sustainable and green resin synthesis method, lots experiment have been done by substitution of phenol with renewable alternative phenolic materials like resorcinol, lignosulphonates and tannic acid and its derivatives. Different properties of resins were produced with competitive performance with the market product, ÇKE Alfanol A 72 No-Bake Resin. Without loss of performance, calcium lignosulfonate was used in polymer synthesis at the rate of 15% instead of phenol. On the other hand, the reaction in which lignin and resorcinol were combined instead of phenol by reducing it by 25% gave better results in terms of mechanical and thermal properties. Thermal properties were investigated for resorcinol and lignin modified resins by using TGA-DSC and mechanical performance of cured sand core sample were tested by Simpson Sand Strength Testing Machine as compression strength as N/cm$^{2.}$. After laboratory testing casting performance of new resins are compared with two different companies' resins in steal casting demo. Experimental results were matched with casting trail and no defect was detected.

Keywords: Phenolic resins, Lignin, Sustainability, Foundry, No-Bake

1. Introduction

Phenolic resins have been using as a binder on sand casting due to its thermal and mechanic properties [1]. Sophisticated alkaline phenolic resin can be cured with ester and this provides no-bake casting system that makes able to arrange striping time after mixing and shaping of sand mixture [2]. Cured sand shapes should give high strength and flexibility to separate from molds than carry and cast with melted metals. In this study, phenolic resin polymer was modified with different natural phenolic substance to make more renewable binder that gives required properties for metal casting. Some of the similar studies have been done to substitute phenol with natural phenolic substance [3-12]. However, these studies have been made for the modification of resins used in sectors other than the foundry industry.

There are generally two main concerns in research conducted to evaluate alternatives to phenol and formaldehyde. The first is concern for the health hazards of free phenol and formaldehyde in finished product [13-15]. The other is the fact that the consumption of fossil resources is increasing day by day with environmental damage and the limited resources will end one day after [16,17]. In the targeted phenolic resin, since the amount of free monomer is currently very low, economic and ecological gains have been prioritized by saving phenol.

Phenolic resin synthesis was divided two different steps which are adding and condensation reaction as shown in literature [18,19]. Calcium and Sodium lignosulfonate, tannic acid and its derivatives and resorcinol were added synthesis to substitute phenol as much as possible. Physical and chemical properties of successfully synthesised resins were determined as gelling time with ester hardener, viscosity, pH, solid content and free formaldehyde amount in modified resins. Compression strength of 2% resin added and cured samples were measured and compared with standard no-bake ester curable resins, Çukurova Kimya Alfanol A 72 and similar resin of another resin producer companies(X). Competitive modified resins were chosen to characterize thermal properties of their ester and heat cured structure with TGA-DTA instrument. Results discussed before casting demo according to phenol substitution ratio, mechanic and thermal performance.

Resorcinol modified resins shows excellent binding performance and TGA-DTA results showed decomposition points of cured samples are higher than non-modified and lignin modified resins however this modification makes also gelling time higher and it's known that this material has higher cost than phenol. On the other hand lignin modification does not affect mechanical properties with 15% phenol substitution ratio and also lignosulphonates are cheaper than phenol. Most cost efficient modified resin is obtained with 10% sodium lignosulphonate modification with not less mechanical properties than Alfanol A 72 resin. Maximum substation is reached up to 25% by combine resorcinol and lignin materials in different synthesis steps. Other phenol alternate materials show negative effect on binding performance. Result of steal casting demo does not show difference between two modified resin and two market resin therefore most phenol substituted resin and only lignin modified resin have been found suitable for the foundry use.

Also morphological behaviour of lignin and resorcinol modified resins that cured by dibasic ester and triacetin and only heat observed under SEM. Modification type does not give much more different results than ester type. Dibasic ester gives needle like structure but triacetin makes more smooth structure due to their functional ester group coordination.

2. Experimental

2.1. Materials

ÇKE Alfanol A 72 no-bake and another company' similar purpose resin were used to compare with studied new resins. Çukurova Kimya raw materials, which are suitable for use in factories; phenol (91%), formalin (37%), calcium lignosulfonate, urea, resorcinol, potassium hydroxide (80%) were used in synthesis. Also, Sodium lignosulfonate purchased from Likit Kimya, 65% tannic acid from AR-TU Kimya A.Ş. the acorn and valeks factory were used. ÇKE AS 8 Alfanol Serter was used as hardener in sand core strength measurement test. Triacetin and dibasic ester were purchased from Brenntag. Chinese originated Colatan GT 10 and CF 2 tannic acids modified with phenol and formaldehyde were tried as modification substance.

Glass flasks and laboratory glassware in 500-2000 mL volumes, electronic stirrer, jacket heater, condenser, thermometer, weight and time measuring equipment and other auxiliary laboratory equipment were used in Research Facility of Çukurova Kimya Endüstri Co. to synthesis new resins, Simpson brand electronic strength measurement device and Fort Cup 4 Viscosity Measurement tool and FT-IR and TGA-DTA and other chemical characterization test devices were used in ÇKE Quality Control Facility. For other instrumental measurements, TGA-DSC, scanning electron microscope, which is under DEFAM, has been serviced. Steel casting trail was done in foundry of Manisa Döküm.

2.2. Resin Synthesis

Ester curable alkaline resins were synthesis with ÇKE original procedure. Reactions were carried out in alkaline condition until reaching standard gelling time with triacetin. To substitute phenol, total phenol mass reduced as addıtion amount of new phenolic material consider as its purity. The diagram of resin synthesis is shown in Fig. 1.

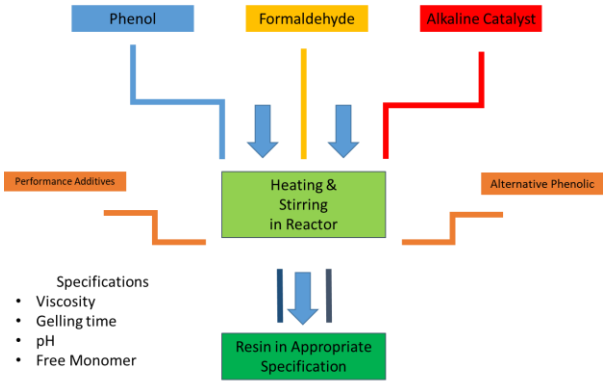

Fig. 1. Alkaline phenolic resin production diagram

Calculated amount of alternative phenolic materials were added to reaction in the begging of the first stage which is addition reaction or second stage which is condensation reaction[18,19]. New resins were coded with their modification type, order and applied some other materials like urea or extra KOH. New resins were named as firstly their modification ratio than code modification type and lastly adding step of modification showed as for beginning of reaction "B", for second step "S" if there is second modification, this name code repeat as this order. Resorcinol modification was coded as "RES", sodium lignosulphonate "LIG1", calcium lignosulphonate "LIG2", non-modified tannic acid "TAN1", phenol modified tannic acid

Colatan GT 10 “TAN2” and formaldehyde modified tannic acid Colatan CF 2 “TAN3”. Also additional modification of KOH were showed “(k)” and for urea “U”. For example, synthesised new resin which 15% calcium lignosulphonate added in the beginning of reaction than in the second step 10% resorcinol added with extra KOH and urea was coded as 15LIG2 B 10RES S(k) U.

2.3. Measurements

2.3.1. Chemical and Physical Characterization

ISO 11402/2004 standard was used to determine the amount of free formaldehyde (s.f %). Solids content is a method that measures the concentration of phenolic resin that can evaporate at the test temperature during the test period, and was performed according to the ISO 8618 standard. Viscosity of resins were measured by using Fort Cup 4 (hole radius 4.12 mm) flow time with DIN 53211 standard. Gelling time is a control method for estercurable resins that should be in the range of current resin’s specification. 50.0 g of resin is weighed on a balance in a cup. The cup with resin is placed in the fixative in the water bath at 20 °C. When the resin temperature is fixed at 20 °C, 7.5 g of triacetin is added on it and the stopwatch is started. Time is stopped with solidification of liquid resin. pH value was measured by using standardized electronic pH meter.

2.3.2. Compressive Strength Test

2.0 kg of dry and clean sand (45-50 AFS) is loaded into the mixer. The resin in the proportion of 2% of the sand is weighed into beakers. The hardener ÇKE AS 8 in ratio of %20 of resin is added and mixed with sand. The weighed resin is added to this mixture and after 1 minute mixing stopwatch is started. 150-160 grams of this mixture is loaded into metal mold and pressed under sand rammer for 3 times. A total of four pressed molds are prepared to measure 1 h, 2 h and 3 h and 24 h compressive strength. When the pressed sand is hard enough to be peeled off the mold, the stripping time measured by stopping the stopwatch. The samples that are due are tested on the Simpson device and values are noted as N/cm^2 .

2.3.3. Sample Preparation for TGA-DTA/DSC

ÇKE Alfanol A 72, 10% lignosulfonate modified resin and 10% resorcinol modified resin were cured separately with heat, triacetin and dibasic ester. Total nine cured materials were dried by using vacuum heater at 50 °C for 5 h. Thermal characterization of all dried samples were analysed by TGA-DTA between 30 °C to 900 °C temperature under inert nitrogen atmosphere in ÇKE. Char yield and decomposition points were determined.

Liquid Alfanol A 72 and most modified (15% lignin + 10% Resorcinol) resins’ thermal characterization were done by using TGA-DSC between 30 °C to 600 °C temperature under inert nitrogen atmosphere in Manisa DEFAM. Glass transition temperature of new resin was compared with standard resin.

2.3.4. Sample Preparation for SEM

As previous sample preparation for TGA-DTA, there was applied also same curing and drying techniques. Standard resin and modified resins cured with heat, dibasic ester (DBE) and triacetin then all nine samples were dried under vacuum and mild temperature in order to get SEM image. For surface conductivity, fine powdered samples were coated with Au-Pd in Manisa Celal Bayar University-Applied Science Research Center (DEFAM). Surface characterizations of the samples were done with SEM-EDX instrument with Ph.D. İsmail Katı the researcher of DEFAM, Under/above 20 micron images were made in various regions of the samples.

2.3.5. Casting Trail

Casting trail performed in Manisa Döküm foundry with the helps of experienced foundry workers. Experimental results had been compared before casting trail in order to select the best performance new resin. After all, 10% resorcinol + %15 Ca.Lignosulphonate modified 15LIG2B10RES S (k) U coded resin which has the most substitution of phenol and 15LIG2B U coded resin that has moderate performance with low cost were chosen as two best option for foundry. In trail, simple shapes were used to model a standard sand casting with No-Bake system to evaluate performance of resin by examination of casted metal surface [20]. Standard model figure is shown in the Fig. 2.

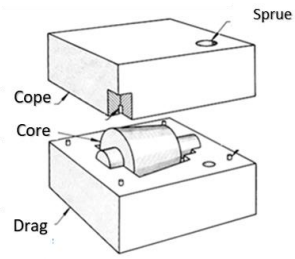

Fig. 2. Model for basic sand molding to evaluate casting performance [18]

The new resins and ÇKE Alfanol A 72 and another No-Bake resin were used to make sand cores. Foundry sand and required amount of hardener were mixed together and resin about 2% by weight of the sand was added to the mixture. Cured cores were placed in the middle of model. The preparation of the molds is shown in the images below, Fig. 3.

Fig. 3. Foundry workers are filling the drag than placing the core model

After the alphanol resin, sand and serter mixture was automatically mixed and poured into the mold, the compressed

sand hardened completely in approximately 20 minutes. It was flexible enough to allow the shape placed in the cured molding sand to be removed. The placement of the cores is shown in the cavities created in Fig. 4.

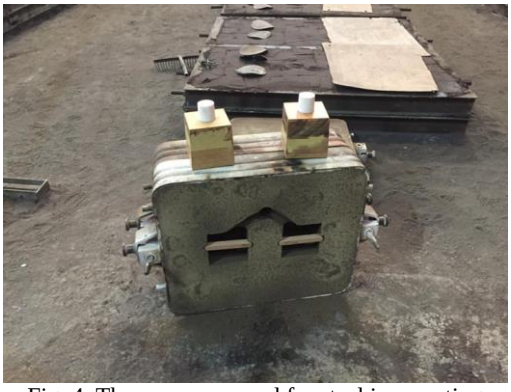

Fig. 4. The cope, prepared for steel iron casting

After drag and cope parts were brought together and fastened tightly, the molten metal was poured into the mold from the open space. Steel GS 60, a type of molten alloy prepared in Manisa Döküm casting, came out of the furnace at 1665 °C and filled the molds at 1550 °C. After the parts obtained with cores resisting these temperatures and the pressure created by the metal cooled, additional processes were applied. Sand mold has shaken out after casting and the metal parts obtained are shown in Fig. 5.

Fig. 5. Cooled steel parts after shake out

Casting parts go through a series of processes to remove burrs and sand from the surface after casting. These processes mean extra expense and workload for the foundry. After demo casting, steel parts, which will show the performance of a total of 4 different resin samples consisting of 2 parts, were inserted only into the ball bombardment device (Fig. 6)

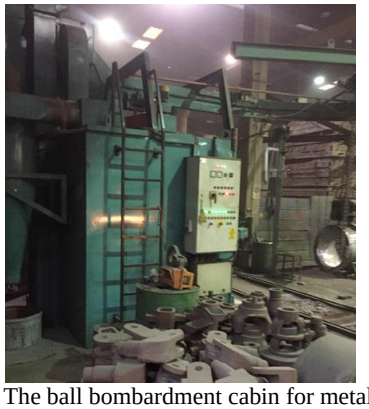

Fig. 6. The ball bombardment cabin for metal parts

3. Results

In the results section, the results from the properties of the synthesized resins to the casting trial with the resins found successful are listed. During this whole process, the thermal and morphological properties of the new polymers were also tried to be enlightened and the important findings obtained were shared.

3.1. Chemical and Physical Properties of Resins

The gel time, flow time in seconds, viscosity FC4 V as second, solid matter content, free formaldehyde percentage F.F%, pH, alkali percentage measurements of the synthesized resins are given in the Table 1.

3.2. Compressive Strength Test Results

Mechanical performance of resin bonded sand cores are in the Table 2. As an important parameter, striping time (cure time of the core) is shown reliability for foundry No-Bake process. Minimum requirements for compressive strength for general ester curable No-Bake process list in the bellow of table. The values obtained are the average values for the tests performed. It was repeated that some results deviated from the mean in accordance with GOST standards. The low strength resins obtained were eliminated at this stage.

Table 1.
Chemical and physical test results of resins

	Gel Time (Min.)	FC4 V.	Solid%	F.F%	pH	Alkali %
A 72 STD U	13	23	52.01	0.1	13	12.0
A 72 No-Silane	13	22	51.88	0.1	13	12.0
10LIG1 STD B	16	26	53.56	0	12.9	11.2
15LIG2 STD B	14	38	54.91	0	12.6	10.6
20LIG1 STD B	15	35	54.09	0	12.8	10.8
10LIG1 STD B U	15	28	53,88	0	12.8	11.1
10LIG1 STD+ B U	15	33	54.24	0	12.7	11.3
10RES STD S	25	25	52.86	0	12.4	11.3
20TAN2 STD B	16	25	52.24	0,1	12.6	12.2
10RES STD S(k)	18	24	52.61	0	12.9	11.6
15RES STD S(k)	29	25	52.42	0	12.6	11.3
10TAN1 STD S	11	23	51.42	0	12.8	11.9
10TAN3 STD S	6	24	52.21	0	12.9	11,8
10LIG2B10RES S	17	27	53.23	0,1	12.7	10.8
15LIG2B10RES S	33	52	55.58	0	12.0	10.5
15LIG2B10RES S(K)	18	60	55.38	0	12.2	10.6
Spect.	14-18	20-30 sec	50-54%	Max1%	12.0-13.2	11.0-13.2

Table 2.
Sand core strength test, unit for 1/2/3/24 hours is N/cm^2

	Striping, min.	1 Hours	2 Hours	3 Hours	24 Hours
A 72 No-Silane	14	8	10	14	15
A 72 STD	13	23	30	35	48
A 72 STD U	13	22	31	34	45
10LIG1 STD B	16	22	25	32	43
20LIG1 STD B	15	15	19	20	32
10LIG2 STD B	16	18	20	23	36
10LIG1 STD S	12	20	25	30	40
10LIG2 STD S	14	18	23	25	35
20LIG2 STD S	15	14	20	23	28
10LIG1 STD B U	15	20	25	34	40
10LIG1 STD+ B U	15	23	30	35	45
15LIG2B10RES S(k)	20	22	33	37	50
15LIG2B10RES S(k)U	16	21	32	36	48
10RES STD S	25	20	34	35	55
20TAN2 STD B	16	6	8	8	10
Specifications	9 - 16	17	20	24	35

Tannic acid modified alkaline modified resins shows very low bonding performance. Only measurable result of general tannic acid and its derivatives mod. resin was 20TAN2 STD B

Shelf life for alphanol resins is determined by the decrease in the binding performance with the increase in viscosity, and it is determined as 6 months for storage conditions at an average degree of 20 °C. Since the initial viscosity value for the new resin is higher than the standard resin, at the end of 6 months the direct sand test was made with the standard resin reciprocally and the following results were obtained. As a result, a similar shelf life for the new resin is set as 6 months. After 6 months for future studies, the effect on its use for casting can be investigated.

Table 3.
Shelf life prediction for new resin, 15LIG2B-10RES-S (k)-U

	1 h	2 h	3 h	24 h
ÇKE A 72 at 6th months	15	23	25	30
New Resin 6th months	16	22	25	32

3.3. TGA-DTA/DSC Analysis Results

After the synthesis process there was many new resins but only some of them were applicable for foundry core making process. These resins were modified with resorcinol or

lignosulfonate or both of them. Thermal behaviour of these new phenolic modification agents were investigate with standard Alfanol A 72 resin. The results obtained by using TGA-DSC instrument within DEFAM and Perkin Elmer STA 8000 belonging to ÇKE are given in the Table 4. The measurement charts where the results are obtained are included in the appendices.

Table 4.
TGA-DTA results, getting from graphs that in appendix

Sample #	Resin Code	Cure	Loss %	Peak1	Peak2
1	**A 72 STD**	Heat	39.31	425.37	523.16
2	**A 72 STD**	Triacetin	57.63	293.72	379.66
3	**A 72 STD**	DBE	52.49	450.78	492.66
4	**15LIG2STDB**	Heat	41.00	356.99 /394.5	519.47
5	**15LIG2STDB**	Triacetin	57.9*	321.21	383.34
6	**15LIG2STDB**	DBE	55.81	463.82	-
7	**15RESSTDS**	Heat	36.47	452.50	522.78
8	**15RESSTDS**	Triacetin	56.95	443.49	496.06
9	**15RESSTDS**	DBE	52.76	439.35	-
10**	**A 72 STD**	No-cure	62.81	80~	450~
11**	**15LIGB10RESS**	No-cure	64.20	80 /120~	450~

* Description is available in the Appendix. ** are made in DEFAM.

3.4. SEM Images

Cured and dried three different alkaline phenolic resins were examined under SEM in DEFAM and it was noticed that the morphological structure changed depending on the curing factor. Structures of the materials were homogeny and continuous in the image so it made examination easier. Categorized according to the size of the images and the type and curing of the sample from which they are obtained, are given below.

- **Images larger than 20 microns**

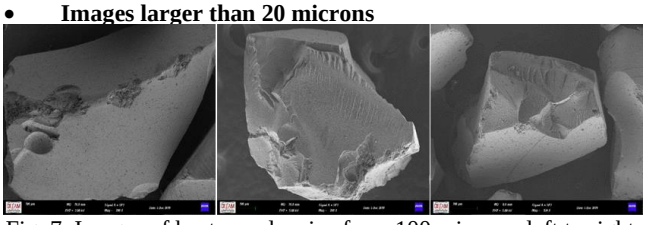

Fig. 7. Images of heat cured resins from 100 microns, left to right, respectively; Standard Alfanol (200X, 2 kV, 10 mm) Lignin mod.(208X, 5kV, 10 mm) and Resorcinol mod. (326X, 5kV, 6.6 mm)

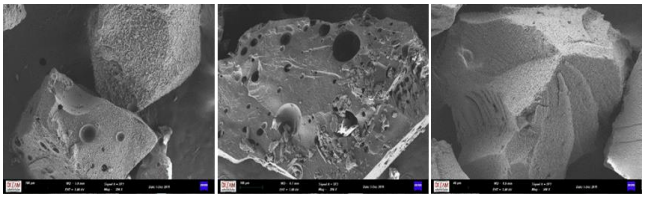

Fig. 8. Images of DBE cured resins from 100 microns, left to right, respectively; Standard Alfanol (294X, 5kV, 5,9 mm), Lignin mod. (298X, 7kV, 6.7 mm) and Resorcinol Mod. (500X, 5kV, 6.6 mm)

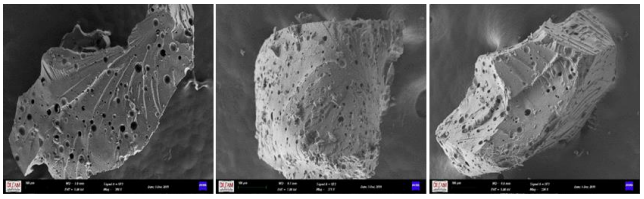

Fig. 9. Images of DBE cured resins from 100 microns, left to right, respectively; Standard Alfanol (300X, 5kV, 5.9 mm), Lignin mod. 371X, 7kV, 6.7 mm) and Resorcinol Mod. (324X, 5kV, 6.6 mm)

- **Images smaller than 20 microns**

When comparing all other cured structures in scales where nano dimensions can be observed, it is more easily understood that the morphological structure is primarily shaped by the curing effect. These images are given together in Fig. 10. It was observed that there were variations in the morphological structure among micron scale resins.

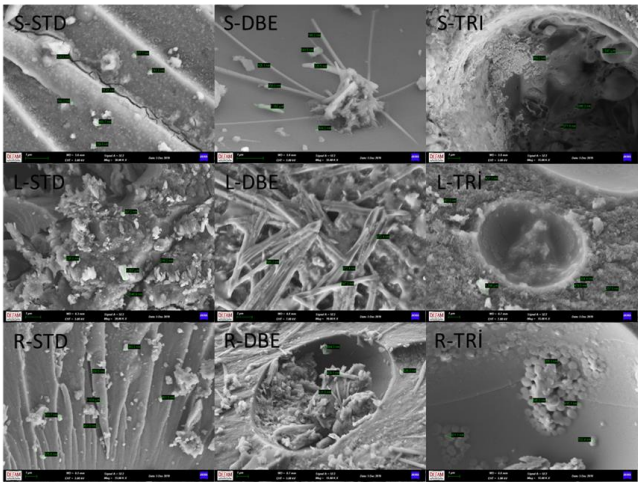

Fig. 10. SEM images of different resins, Alfanol (S), Lignin Mod. (L), Resorcinol Mod. (R) cured by temperature (STD), dibasic esters (DBE), and triacetin (TRI), are shown, S-STD (30K X, 5kV, 5.6mm), S-DBE (35K X, 5kV, 5.9mm), S-TRI (15K X, 5kV, 5.9mm), L-STD (20K X, 5kV, 6.3mm), L-DBE (10K X, 7kV, 6.8mm), L-TRI (15K X, 7kV, 6.7mm), R-STD (15K X, 5kV, 6.5mm), R-DBE (15K X, 5kV, 6.7mm), R-TRI (15K X, 5kV, 6.6mm)

In the images taken by zooming into the same cured structure, it was determined that the structures formed were formed in nano-

dimensions. Among these needles like structures, images of resorcinol modified alkali phenolic resins cured with DBE agent are shown in Fig. 11.

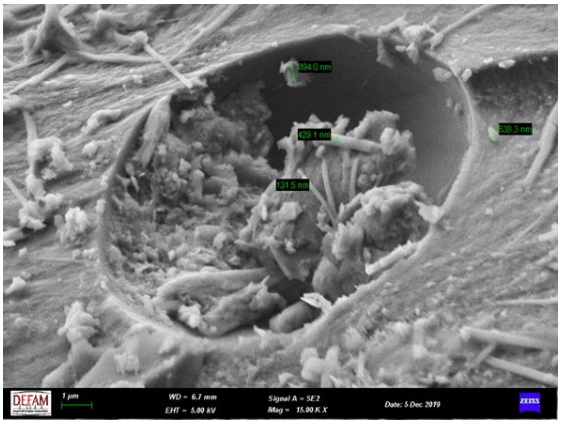

Fig. 11. The image of the resin structure cured with DBE at a scale of 1 micrometer (15K X, 5kV, 6.7mm)

When these needle-like structures are examined in detail with SEM-EDX, the image and elemental distribution obtained are given in Fig. 12. The material on the surface was found to have the elements in a combination that coincided with the resin content and the surface coating. In the structure of the resin modified with Kraft Lignosulfonate, elements such as sulphur, sodium, potassium, as well as phenolic structures and curing agent dibasic esters, high amounts of carbon and oxygen were found. The presence of sulphur in needle-like structures indicates that these structures belong not only to the crystals of the compounds formed by the reaction of ester and alkali materials, but to fiber-like structures caused by the polymer structure.

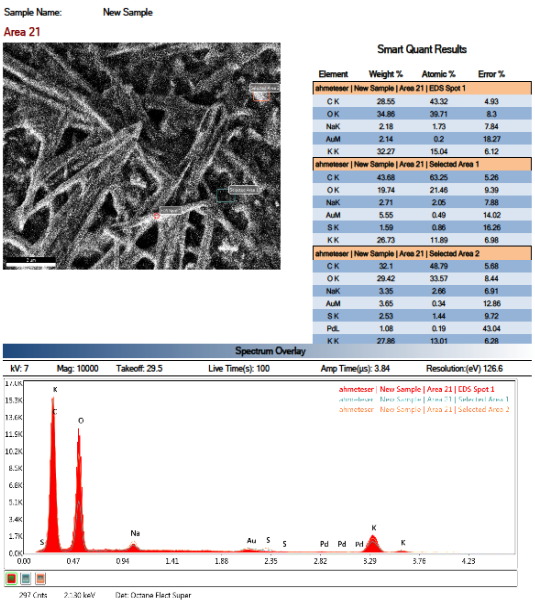

Fig. 12. SEM-EDX image of DBE cured lignin mod resin and distribution of element groups

3.5. Casting Results

Resins with codes 15LIG2B U and 15LIG2B10RES S (K), which were determined from the synthesized casting resins, two resins, lignin modification and lignin-resorcinol modification, were produced by Çukurova Kimya End. A.Ş. resin was observed in a casting trial with Alfanol A 72 and another company's no-bake molding resin. The surfaces of the cores obtained with four different casting resins obtained after cleaning the attachment points of the cores in the parts removed from the bombardment cabinet to the mold are shown in Fig. 13.

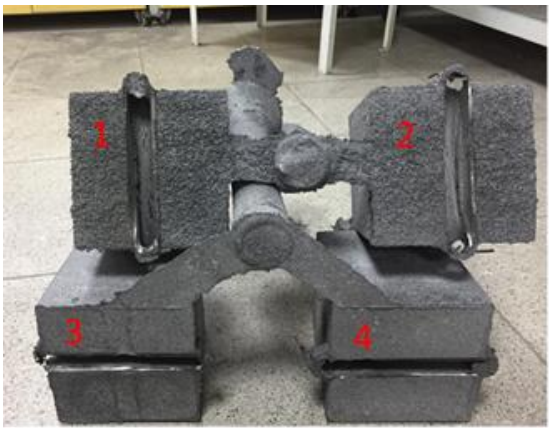

Fig. 13. Casting parts containing the cavities of the cores prepared with 4 different resin samples cleaned after casting. 1: 15LIG2B U, 2: 15LIG2B10RES S (K), 3: A 72 STD (Alfanol A 72), 4: Resin of another company

No negativity has been notified to us by the user. No surface defects were found in the parts whose surface examination was performed. No breakage or leakage during casting indicates that new resins can compete with Alfanol A 72 and the other resin.

4. Discussion

Many modifications were tried in this study. The success of the modification process is not only evaluated by the completion of the reaction but also is based on the performance of the current product. After the synthesis process, the information that is considered to be positive or scientific value for future studies on the resins tested with chemical and physical tests was re-evaluated, and the resin was synthesized again with small changes and additions, and the effect of these changes was investigated.

It is known that the polycondensation of phenol and formaldehyde consists of two main parts. Addition, where relatively lower temperature and pH is applied, and the preferred condensation reaction at higher temperature and pH [1]. While other conditions are the same, the size distribution, orientation numbers and polymerization degrees of the polymers that will be obtained as a result of polymerization reactions that take place at different temperatures or in environments with pH will vary [18]. The importance of the 2 main parts separated in the literature selected for the phenolic modification process has been more evident especially in phenolic materials with different reactivity

compared to phenol. The reactivity of resorcinol, which was reported in 1979 by Pizzi et al. [7], that its propensity to react was 12 times that of phenol, created a problem when it was used in the 1st step during our synthesis processes and caused the resin to gel early and cancel the trial. The 10RES STD B coded study, in which 10% resorcinol was added at the beginning had a dense consistency between 40 and 50 °C during the process of raising the temperature of the first step to 60 °C and it gelled in the first half hour of the waiting process at 60 °C. This can be explained by the fact that the reactivity of resorcinol after binding with formaldehyde is higher than phenol and other phenol-formaldehyde compound structures. Products with higher usage percentages could not be taken into the trial as they would gel again, and lower percentages were not tested when it was seen that resorcinol was added to the reaction at percentages of 10% or more later, that is, in the second step, creating positive results. Resorcinol, which is added to the reaction later, may react with methylol functional groups of the phenol-formaldehyde polymer chain since there is not enough formaldehyde in the environment. This situation, which does not go to the gel and gives a positive effect on the performance, shows that resorcinol is included in the resin system properly.

Lignin and its derivatives have a structure similar to the PF polymer structure and have been the focus of studies for many years to be considered as a renewable resource [8]. Contrary to resorcinol, higher strength values were obtained when the water-soluble calcium and sodium lignosulfonate, which is less reactive than phenol [9], was included in the reaction environment in the first step of the polymerization reaction. This has been explained by Kuo et al. [10] that the complex lignin structure contains sterically hindered phenols [10], and it has been tried to be overcome by hydroxymethylation with alkali formaldehyde [11,12]. The case of incorporation with formaldehyde and phenol into the alkaline medium, which increases the strength values of the alkali resin that can be cured with the esters targeted in the project, coincided with the literature studies. No big difference was found between sodium and calcium lignosulfonate, but because calcium lignosulfonate was used as an agent in other products, it was easier to transport and use it in high-volume production. The effects of silane modification were also investigated, as it has a very important effect on performance that shown in Table 2.

The tests were carried out under laboratory conditions where temperature and humidity were under control. Except for the resin change, if the deviation between the minimum parameters is higher than 10%, the test repetition was continued. Few experiments have taken place that generally exceeds this margin of deviation. The method used in practice complies with GOST guidelines, a Russian standard with very high validity [21]. The average value of all results was taken and recorded in the comparison table. While the trials that caused out-of-the-standard results were eliminated, modified resins that were within or close to the specification values were reconsidered, and it was provided to save more phenol in more appropriate ways. Although the high usage rates obtained in studies on the use of lignin and its derivatives could not be achieved with lignin alone in this study, it was concluded that lignin could be used within certain limits without impairing the performance of the resin. Increasing this limit with resorcinol, the other alternative phenolic raw material, and saving up to 25% of phenol cumulatively was another important point reached.

Lower limits for strength performance were determined in line with foundry needs as 17/20/24/35 N/cm^2 for 1/2/3/24 hours after mold formation, using 2% resin and a sufficient amount of hardener AS 8 hardener. The stripping time, on the other hand, was determined as 9-16 minutes by using AS 8 harder 20% of the resin in accordance with the curing time range offered by the hardener to be chosen by the user. This period depends on the resin and may change with the effect of temperature, but if it is too short or too long, it creates the risk of disrupting foundry planning and work flow.

A thermal gravimetric analyser was used to provide thermal characterization of resins, which were found suitable for casting, having separate lignin and resorcinol content, and to better understand these modifications. TGA measurements are one of the methods that provide the easiest idea about the thermal character of the material. Throughout the study, although the main purpose was a more environmentally friendly, sustainable and cost-effective resin synthesis that could keep up with the market, the morphological, chemical and thermal effects caused by different esters in the cured structure were also studied throughout the study. Therefore, the structures cured separately with triacetin and dibasic ester were compared with the alkali resin cured by heat only as a control group.

The original versions of the TGA curves are given in the appendices. Although the large amount of water in the resin is thrown away after curing with heat, it remains in the structure after curing with esters. This moisture was completely removed from the environment after curing with the ester, by drying the samples that were ground every other day at 50 °C for 5 hours in a vacuum oven. The purpose of this process is to observe whether structures cured with esters will subsequently cure with heat. It is known that phenolic resins cure with heat, releasing water as a result of the combination of methylol ends. Considering the intervals determined in the study conducted by Bouajila et al in 2002 [22], the solvent in the range of 30-120 °C and the water vapours after the condensation were determined by the secondary instruments used during the TGA analysis. It was observed that the structures cured with esters did not release water by forming an additional crosslink up to 150 °C and did not lose mass up to this temperature. The loss of mass after 150 °C was interpreted as the etheric bridges transformed into methyl bridges and released water.

When all the results were evaluated, the most important difference was that the resin, which hardened only by temperature, without the addition of esters, remained unburned at 900 °C, more than 60%. This is due to the KOH value of the alkaline resin, approximately 13%, and the high carbon yield of the phenolic structure. If a rough calculation is made, the amount of solid matter is taken as 52% on average in table 4 in the previous section and if the KOH% amount is accepted as 12%, it is expected that the inorganic material that cannot be gassed as a result of combustion is only 23% in the heat cured structure, but the total protected mass is It seems to be much higher. As a result of the TGA test performed in an inert environment, the amount of material remaining in the structure without decomposition with the effect of temperature shows how high the ash yield is in phenolic resins.

As mentioned in the work of J. Bouajila et al., The maximum burning loss was observed in the range of 300-500 °C, but the positions of the peaks in this range differed according to the modification and curing type. Organic materials included in the structure during curing with esters increased the burning loss. The reason why structures curing with triacetin in inert environment cause more burning loss can be thought as the fact that triacetin carries more oxygen in the structure of a higher percentage compared to dibasic esters. The thermal characteristics of the two different resins obtained as a result of the modifications made by reducing the phenol in equal proportions showed differences when considering the curing types as the same. The reason for this was thought to be that calcium lignosulfonate brought more impurities to the structure than resorcinol, and that these impurities generally consist of oxygen-containing structures such as sugar and hemicellulose.

Considering the studies in the literature, it is thought that esters form some kind of bridges between polymer structures that are alkalized [1, 23, 24]. Considering that the structures that will be obtained as a result of the formation of these bridges will have differences and wondering what effect the modification will have on the morphological structure, it has been focused on obtaining SEM images. The first condition of capturing images with scanning electron microscopy is that the material must be stable and conductive enough to be able to capture images with electrons from the surface, making it the most difficult requirements for a polymer structure that shows thermosetting and insulating properties and reveals water while curing. These requirements were fulfilled by drying the polymer material for a long time after fully cured with the ester and surface coating with conductive material after powdering.

When the images were examined in detail, it was seen that the first striking structural differences were due to the type of curing and the ester used as the main factor. These differences were seen to be the same for all types of resin in 20 microns and above images, but it was determined that there was some change according to the modification of the polymer in images below 20 microns. It was observed that the structures cured with temperature in structures above 20 microns were broken in linear lines with crystal-like particles and contained small salt-like whiter crystals on the surface. The reason for this was explained by the fact that the phenolic polymer forms its cross-links more regularly with a uniform bonding. When looking down to images below 20 microns according to the type of resin, the great similarities in the macro structure were reduced by detecting the much rougher surface differences for the structures modified with lignosulfonate under micron. The fact that lignosulfonates caused more complex structures during crosslinking was also detected in the structures formed as a result of curing with esters. In structures modified with resorcinol, the surfaces are almost the same with the standard resin both in images above and below 20 microns.

The biggest morphological difference detected in SEM images is the different structures formed due to the curing factor. The biggest difference between the mixture of hardeners, triacetin and dibasic ester, which are both esters, is the number of ester groups they have. Triacetin has three ester groups and causes much more oval structures than dibasic ester mixture with two ester groups. Triacetin, which creates spherical spaces in the macro structure, also contains these spherical structures in the micro structure. In DBE, as cashmere-like surfaces in macro structure got closer, they turned into structures knitted with fibers. When these structures are examined with EDX, they have the same elemental composition with the structures that remain in the background, perhaps because the surface image cannot be taken clearly. DBE react with alkaline phenolic polymers and cause the structures to be linear while forming cross-links. Triacetin, on the other hand, causes the formation of spherical structures with its tetrahedral shape and the ester groups at these ends and alkali phenolic polymer. These spherical structures are almost the same size in submicron images and are 300 to 900 nm in size. It is thought that the phenol-formaldehyde polymer length distribution is effective in these structures.

A lot of information was collected during the casting in which one of the most important parts of the research, the practical trial, was made. The commercially available ÇKE Alfanol 72 resin for casting, that is, and the resin from another company, which is shown as its equivalent, together with the final lignin and resorcinol modified resin and only a high proportion of lignin modified resin, a total of four resins with the same hardener in the same proportions used together. Thin long cores for casting were prepared one day in advance with the use of 2% different resins and 2% and it was aimed to examine the performance of these cores against molten metal in the casting glaze. When the surfaces obtained after a series of processes shown in the “Results” section were examined more closely, it was found that all parts had slight burrs. These burrs are caused by not applying casting paint and could not be completely removed as they remained inside the bombardment. However, when we compare these burrs in number and the area they cover, it is seen that there is no big difference. These surface defects, which are mostly based on the reaction of the silicon in the sand with the metal, could be reduced to zero thanks to the refractory feature of the casting paint. No sulfur-related error occurred on the surfaces over time. Since sulfur is an oxidizer like oxygen, it can create undesirable effects on metal surfaces. When the surface defects were examined observationally in accordance with the literature [25-26], no major defects were found to prevent casting.

It is seen that the cost of the product with 15% lignin modification instead of phenol is 4.85% lower than the standard product when calculated by converting the raw material costs into unit cost. The negative effect of the use of 15% lignin on the strengths was compensated by increasing the silane modification a little, and as a result, a successful product was obtained with an equivalent casting performance. The addition of resorcinol, which improves the strength and binding performance, raised the cost a little alone, but this was offset by the modification with lignin. The resin, which is suitable for use in casting and provides the highest phenol savings, is at a level to compete with the products on the market in terms of cost.

5. Conclusion

As a result, in the study, it was found suitable for the market by showing equivalent performance with the product produced and the resins available in the market. A product cost comparison study for different formulations was carried out with the Çukurova Kimya Purchasing team and it was determined that the use of lignosulfonate could reduce cost by 5-10% without loss of

performance, but binding performance was increased by resorcinol modification with increasing the cost by up to 15%. The comparison of the equivalent final product and the standard product in terms of general features is given in the graphic in figure X. In terms of strength performance (N/cm^2), the new resin, which is very close to the standard resin but offers better properties in long-term strength, came at a value outside the value ranges specified for alphanol resins, due to the impurities whose viscosity was included in the resin during lignin modification and increased the percentage of solid matter. This situation did not cause any negativity during the casting demo. It was observed that the 25% phenol-saving working product, in which both raw materials were used together, was balanced with the products in the market by balancing the raw material costs. In terms of performance and advantages, the study goal was achieved with the production of 15LIG2B-10RES-S (k) -U.

Table 5.
Standard ÇKE A 72 and New resin15LIG2B-10RES-S (k)-U. as hourly binding performance(N/cm^2), viscosity(FC4), gel time(minute)

	1 h	2 h	3 h	24 h	Gel t.	Visc.
ÇKE A 72	22	31	34	45	13	23
New Resin	22	32	36	48	18	56

Other important takeaways during the research were that the curing structures of the materials change depending on the curing agent. This change is due to the number of functional groups the ester has. In SEM images, this difference was seen as the formation of more oval and smooth structures in the triacetin, while the structures became more needle-like structures with DBE.

Table 6.
Standard ÇKE A 72 and New resin 15LIG2B-10RES-S (k)-U. as solid content(%), phenol saving(%) and cost comperassion (%)

	Solid Cont.	Phenol Save	Cost Comp.
ÇKE A 72	52.01	As Reference, 0	As Reference,100
New Resin	54.98	25	102

Declaration of conflicting interests

The authors declare that there is no conflict of interest.

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