

## Advances in Synthesis, Characterization, and Industrial Applications of Phenol Formaldehyde Resins

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**Abstract** – In this research, it has been determined that the ratio of phenol to formaldehyde is an important factor in determining the properties of the resulting resin. In experimental studies, a molar ratio (1/1.5) of phenol/formaldehyde is used. With higher phenol ratios, resins with better thermal stability and chemical resistance are obtained. However, considering production costs, optimization studies have been carried out according to the final product's desired characteristics and the application's special requirements. It appears that the amounts of phenol and formaldehyde used in the production process depend on the phenol/formaldehyde ratio selected according to the desired properties. In the reaction between phenol and formaldehyde to form phenol formaldehyde resin (PFR), high temperature, and pressure can be preferred to facilitate the reaction and achieve higher yield. In this study, physical interactions and chemical reactions are monitored at atmospheric pressure at temperatures of 70 °C, 80 °C, 90 °C, and 100 °C. According to the results obtained the bulk density of PFR decreases as the production temperature increases. Additionally, increasing the production temperature increases Shore D hardness of PFR. At low production temperatures, the thermal conductivity of PFR is also low. Sulfuric acid is used to catalyze the chemical reaction between phenol and formaldehyde. The manufacturing process of PFR is often optimized through experimental trials to maximize resin yield, quality, and cost-effectiveness. The production of PFR depends on the ratio of phenol to formaldehyde, amounts of reactants, reaction conditions, catalyst selection, and optimization parameters. According to these factors, efficient and cost-effective resin production is envisaged in industrial applications.

**Keywords** – Phenol Formaldehyde, Reaction Parameters, Resin Properties, Characterization, Optimization

### I. INTRODUCTION

A polymer is a solid made up of numerous component sand units that are chemically connected or that come together to form a solid by bonding. Because of their many useful properties such as being light and having good physical, chemical, thermal, optical, and mechanical properties polymers are substances that are used widely in a variety of industries, including biotechnology, chemistry, food, materials, and cosmetics [1]. Materials in the polymer group can be categorized into four primary groups: fibers, processed rubber, elastomers, and plastics. The two sub-branches of plastics are thermoplastics and thermosets, and the two sub-branches of elastomers are natural and synthetic rubber [2]. The thermoset polymers that hold significant commercial value are categorized as epoxy, unsaturated polyester resins,

urea-formaldehyde, phenol-formaldehyde, and melamine formaldehyde [3]. The matrix of polymer composites made of thermosetting and thermoplastic resins is becoming more and more common. Composite resins have a significant market share and are utilized in a variety of industries, including electronics, construction, automotive, sustainable energy, and space flight [4]. Because of their advantageous chemical and mechanical qualities, resins organic materials have become widely used in a variety of industries, including the construction, paper, plastics, textile, electrical, electronics, and paint sectors. There are two categories for resins: natural and synthetic. The majority of resins, both natural and artificial, are soluble in organic solvents like toluene, propanol, butanol, chloroform, and chlorobenzene but insoluble in water [5].

Synthetic resins are a class of polymers made up of simple molecules or monomers that are used to make a variety of thermoplastic and thermoset resins. They have a broad range of applications in numerous disciplines. Epoxy, alkyd, poly-amide, vinyl, poly-urethane, poly-styrene 4, acrylic, phenolic, and ketonic resins are the most popular synthetic resins now in use and knowledge. Because of its many applications, phenolic resins are a versatile material that is inexpensive, highly durable, and resistant to heat and chemicals [6-7]. The first synthetic plastic was phenol-formaldehyde resin, which Leo Bakel and created in 1907 and was also referred to as [8]. The non-conductive "Bakelite" phenol-formaldehyde resin is mostly utilized in adhesives. It is employed in the creation of bakelite composites as a matrix. In comparison to other synthetic polymers, phenol-formaldehyde resin exhibits better chemical and physical qualities. It also has good thermal stability, insulation, flame retardant, and corrosion resistance [9-10]. Formaldehyde and phenol derivatives react to generate structures that make up the broad family of thermoset polymers known as phenolic resins. Phenol and formaldehyde were the primary ingredients in PFR [11]. For outdoor applications, phenolic resins are typically utilized as wood adhesives. Another interesting feature of phenolic resins is their replacement of metal with them. Their usage regions are expanding annually due to their smaller weight and reduced cost. Furthermore, phenolic resins have long been employed as binders [12]. Chemically speaking, phenol-formaldehyde resins fall into two primary categories [13]. Condensation processes yield these polymers, as do resol reactions with basic catalyst and novolac phenolic resin reactions with acidic catalysts [14]. The type of resin produced depends on the formaldehyde-to-phenol ratio and the catalyst utilized in the phenol aldehyde reaction [15].

The catalyst, free monomer residues, reaction conditions, and monomer ratio all affect the composition of phenolic resin. The qualities of the chemicals obtained are greatly influenced by the temperature and pH of the formaldehyde and phenol reactions. Owing to their considerable diversity, phenolic resins can be produced at temperatures ranging from above 280 °C for resins modified with natural resins to as low as 20 °C for hydroxyl methyl phenol [16-18].

Today, PFRs are important polymers with a wide range of industrial uses. These resins are synthesized by reacting chemical substances such as phenol and formaldehyde under certain conditions. Such resins are known as high-performance polymers with thermosetting properties. Industrial applications of PFRs include the production of composite materials, coating materials, adhesives, electrical insulation, and laminates. There are many studies in the literature on the synthesis, properties, and applications of PFRs. Research is becoming widespread to understand the role of these important polymer materials in their industrial use and to guide future research [19,20]. Phenol formaldehyde resins are an important branch of polymer chemistry and have a wide range of industrial uses. These resins are synthesized by the chemical reaction of components such as phenol and formaldehyde. Such resins are used as binders, coatings, and laminating materials in various applications [21].

PFRs have superior properties such as thermal and mechanical durability, fire retardant, and water resistance. For this reason, they are the preferred materials in various industrial sectors. An important industrial application of PFRs is the production of composite materials. These resins are reinforced with reinforcing fibers such as glass fiber or carbon fiber to obtain high-strength and lightweight composite materials. These composite materials are used in the production of structural components in many industries such as automotive, aerospace, marine, and construction. They are also widely preferred in areas such as electrical insulation, electronic components, furniture, and flooring [22]. Research on the

synthesis and properties of PFRs continually provides new opportunities for materials science and industrial applications. The focal points of this research include the development of synthesis methods, improvement of resin properties, discovery of recyclable and environmentally friendly alternatives, and exploration of new application areas [23].

Phenol ( $C_6H_5OH$ ), formaldehyde ( $CH_2O$ ), and phenol are the components in the production of formaldehyde resin. In this chemical interaction, the methylene group ( $CH_2$ ) of formaldehyde reacts with the hydroxyl group ( $OH$ ) of phenol. This reaction usually takes place in an acidic environment and is accelerated in the presence of a catalyst (usually an acid or base). As a result of this reaction, phenol formaldehyde oligomers or polymers are formed. Formaldehyde can also polymerize on its own, and this reaction occurs by condensation of formaldehyde molecules to each other. However, this chemical reaction occurs mostly in an acidic environment [24,25].

In the synthesis of phenol formaldehyde resin, phenol, and formaldehyde as well as catalysts and other additives react. These additives are used to determine resin properties and are often required to optimize reaction conditions. Some catalysts can increase the reaction rate, while other additives can improve the mechanical strength or chemical resistance of the resin. The reactions of phenol and formaldehyde determine the properties of phenol-formaldehyde resin and eventually provide the desired products. These reactions represent an important production process that enables PFRs to be widely used in industrial applications. Phenol formaldehyde resins constitute an important family of polymers with a wide range of industrial applications [26,27].

In this study, the components, ratios, production optimization, and characterization of PFR have been examined. In addition to the main components of the resin, phenol and formaldehyde, catalysts and various additives play a critical role in determining the properties of the resin. During the production process, the ratios of these components and reaction conditions are optimized. This optimization increases production efficiency by providing the desired resin properties while also reducing operating costs. During the characterization phase, the physical, chemical, and mechanical properties of the resin are comprehensively analyzed. These analyses are very important to evaluate the suitability of the resin for end-use areas. This study provides a detailed review to provide a comprehensive understanding of optimizing the production process and end products of phenol formaldehyde resin. In this research, topics such as components used in the synthesis of PFRs, reaction mechanisms, production optimization, characterization methods, and industrial applications have been discussed. Also, an evaluation is presented on the future importance of PFR for current and potential application areas. This study is designed to highlight the importance of PFR in materials science and to guide future research.

## **II. MATERIAL AND METHOD**

### **Materials**

Phenol and formaldehyde resin components were supplied from Polisan Kimya. Sulfuric acid (Merck) with 96% purity is used as a catalyst. The components used are stored under appropriate laboratory conditions. Phenol, a petroleum-derived compound, is one of the main components of the resin and provides durability and hardness to the structure of the resin. Formaldehyde is a crosslinker that reacts with phenol and initiates the polymerization of the resin, allowing the resin to form a hard and durable bond to the materials.

### **The production method of PFR**

The production of phenol-formaldehyde resin generally takes place in an acidic (sulfuric acid) environment. Sulfuric acid is generally used as the catalyst of this process. Catalytic amounts of acid are added to the mixture of phenol and formaldehyde. This acid initiates the polymerization reaction between phenol and formaldehyde, increasing the reaction rate. Under acid catalysis, formaldehyde reacts with phenol to form methylol derivatives. Methylol derivatives form polymer chains by cross-linking with each other and with phenol molecules, and the resin cures over time. The temperature is controlled to increase the reaction rate and ensure proper polymerization of the resin [28-30]. Figure 1 shows the

production scheme of phenol formaldehyde resin. Figure 2 shows the phenol-formaldehyde resin production mechanism [31,32].

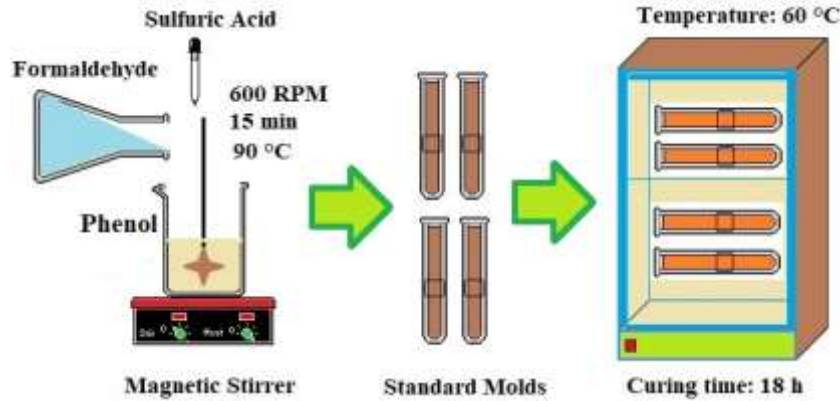


Figure 1. Production scheme of PFR

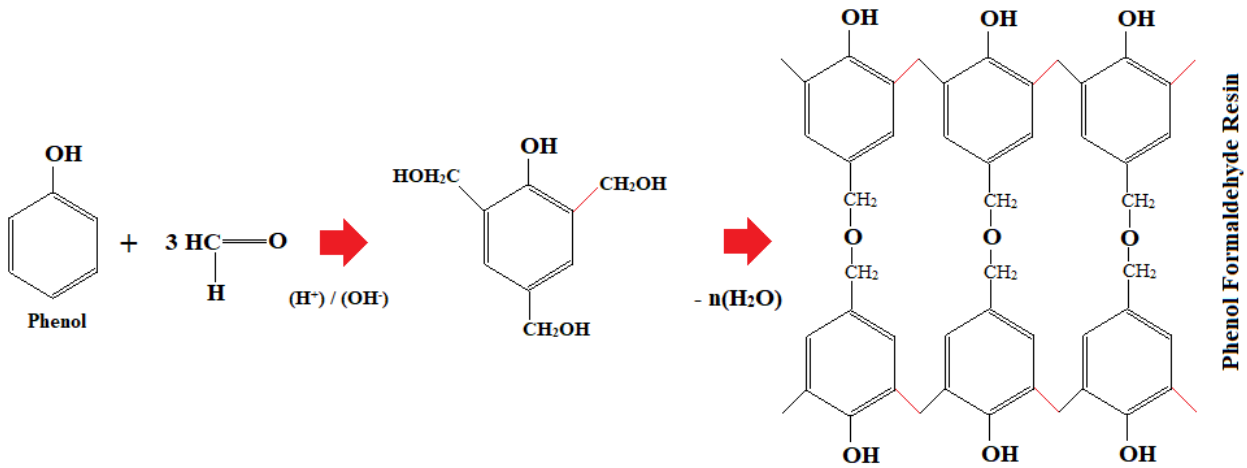


Figure 2. Chemical reaction mechanism of PFR

### Bulk density of PFR

The dimensions of the cured PFR removed from a standard mold are controlled using a digital caliper. The approximate volume of the rectangular prism-shaped sample is calculated. After determining its mass using a precision balance, bulk density is calculated from the mass/volume ratio [33].

### Shore D hardness of PFR

The surface hardness of the resulting composites is determined by taking the average of 5 measurements with the Shore D device. Measurements are taken in different areas on the flat surface of the phenol-formaldehyde resin [34].

### Thermal conductivity coefficient of PFR

The thermal conductivity coefficient of PFR has been determined using the thermal conductivity measuring device. Average results are obtained after the measurements are repeated three times. The thermal conductivity coefficient of PFR samples has been measured at room temperature with Thermtest TLS-100 [37].

### Fourier transform infrared (FTIR) analysis of PFR

Measurements are made with the Shimadzu QATR-S spectrophotometer in the wavelength range of 400–4000  $\text{cm}^{-1}$  with a scanning period of 45 seconds [38].

### III. RESULTS AND DISCUSSION

#### Bulk density results of PFR

The molar ratio of phenol/formaldehyde resin is determined as 1/1.5 and the bulk density of the resin is found by changing the temperature of the prepared mixture. As seen in Figure 3, the density of the resin decreases as the production temperature increases. The density of PFR decreases as the production temperature increases. The increase in reaction temperature affects the chemical structure and molecular matrix of the resin. As the production temperature increases, the phenol-formaldehyde reaction rate generally increases and may cause more cross-linking and polymerization to occur. Therefore, a resin with a larger molecular weight and larger molecular sizes can be produced. This results in fewer molecules per unit volume and therefore a lower density. Additionally, the increase in reaction temperature may affect the crystal structure of the resin, thus resulting in a less dense structure.

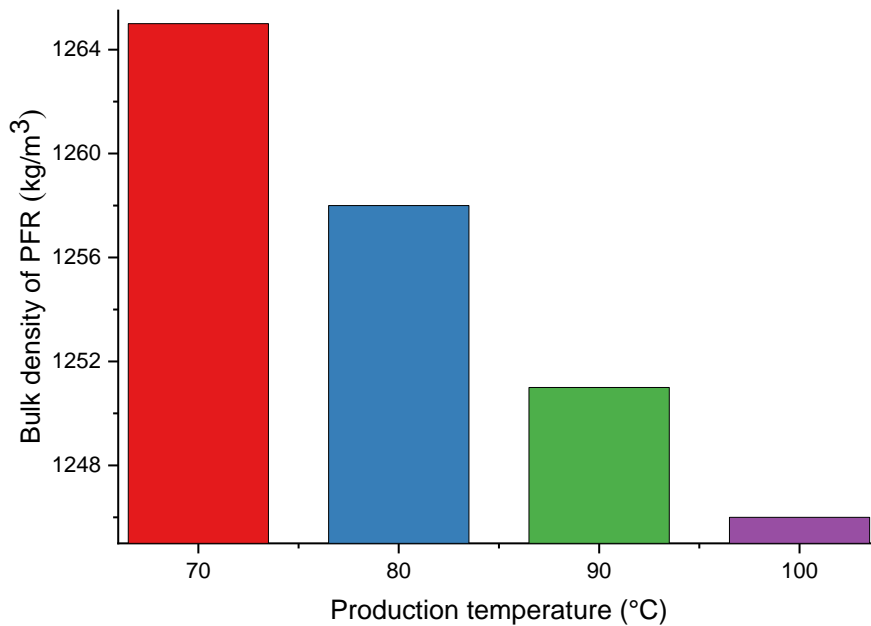


Figure 3. Effect of PFR production temperature on bulk density

#### Hardness results of PFR

The increase in the production temperature of PFR has an obvious effect on the hardness of the resin, as seen in Figure 4. This is because the molecular matrix and internal structure of the resin are affected by temperature changes. As the production temperature increases, the chemical reaction rate increases, and the reaction process occurs faster. Therefore, it can lead to the formation of a resin with larger molecular weight and larger molecular sizes. Larger molecules generally tend to have a harder and more durable structure. Additionally, higher temperatures promote greater cross-linking and polymerization during the reaction. This causes the resin to become harder and more durable. According to the results obtained, it can be said that the increase in production temperature generally has an increasing effect on the hardness of PFR.

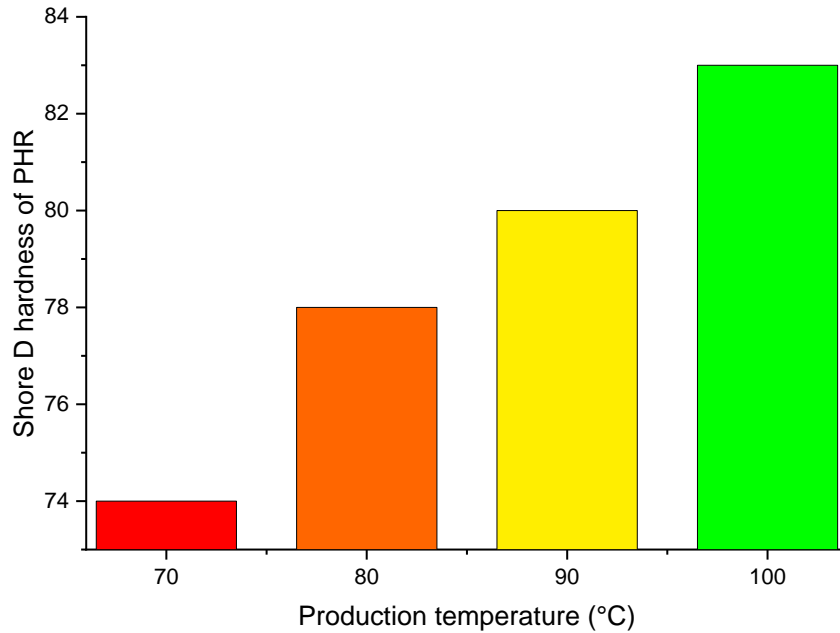


Figure 4. Effect of PFR production temperature on the hardness

### Thermal conductivity coefficient results of PFR

As seen in Figure 5, the thermal conductivity coefficient of PFR increases as the production temperature increases. This may be because high temperatures increase the molecular mobility within the resin, thus creating a structure that conducts heat better. As the production temperature increases, the reaction rate increases, and larger molecular networks can form in the resin. Thus, it means more molecular contact area and more thermal energy transmission. However, if the temperature is too high, uncontrolled reaction conditions may lead to undesirable results. In this case, irregular pores and changes in resin color may be observed.

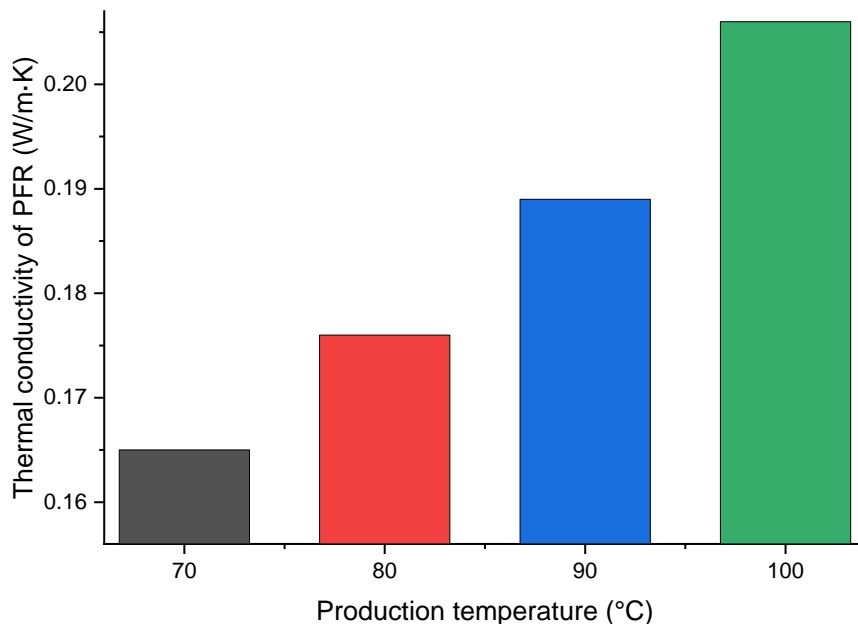


Figure 5. Effect of PFR production temperature on the thermal conductivity coefficient

### FTIR analysis results of PFR

Fourier transform infrared (FTIR) spectroscopy provides information about the molecular structure and composition of PFR (Figure 6). A three-dimensional polymer structure is formed by cross-linking through

a chemical reaction. PFR contains phenyl rings, which are characteristic aromatic structures found in phenol molecules. These rings are typically seen in the wavelength range of  $1600\text{-}1500\text{ cm}^{-1}$ . Stretching vibrations of C-H group bonds in phenyl rings and other aliphatic groups give peaks in the  $3000\text{-}2800\text{ cm}^{-1}$  region. Stretching vibrations of C-O bonds in phenol formaldehyde are observed in the wavelength range of  $1200\text{-}1000\text{ cm}^{-1}$ . Stretching vibrations of C=O bonds in aldehyde groups of formaldehyde are seen in the wavelength range of  $1700\text{-}1650\text{ cm}^{-1}$ . Stretching vibrations of hydroxyl (OH) groups in phenol also appear as a broad peak around  $3500\text{-}3300\text{ cm}^{-1}$  [35,36].

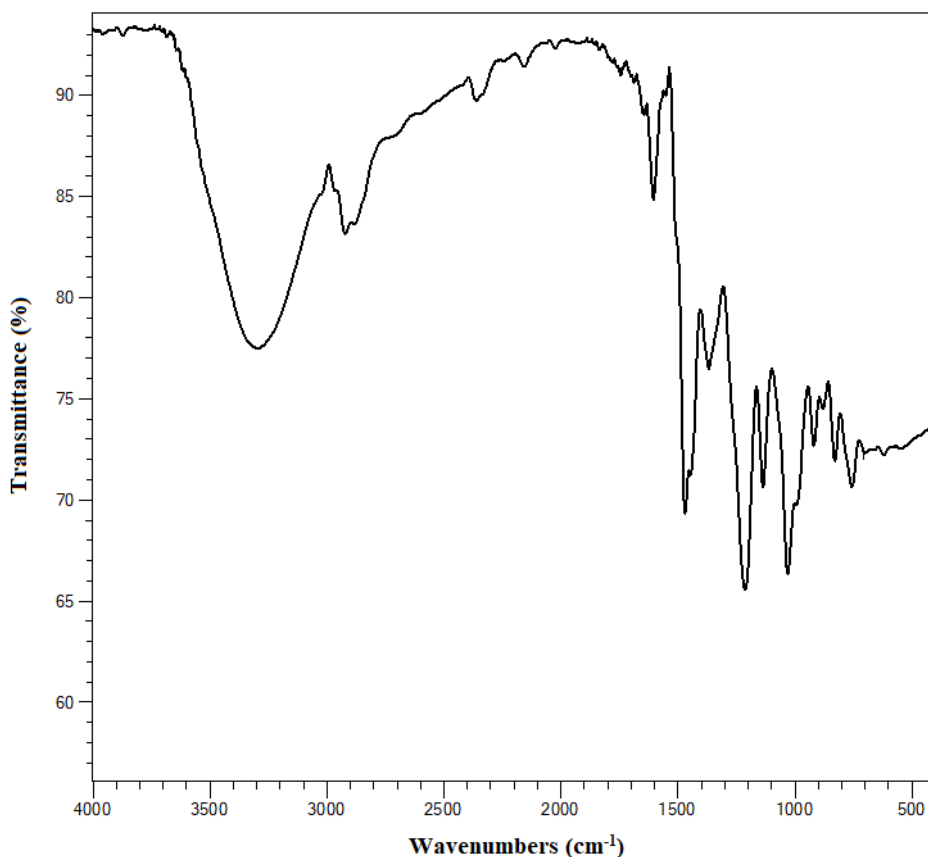


Figure 6. FTIR analysis of PFR

## CONCLUSIONS

As a result, several factors appear to be of critical importance in the production of phenol-formaldehyde resins. These factors include phenol/formaldehyde ratio, amounts of reagents used, reaction conditions, catalyst selection, and optimization parameters. In this research, the effective parameters of the process used in the production of PFR are emphasized.

Experiments show that high phenol ratios contribute to obtaining resins with desirable properties such as better thermal stability and chemical resistance. However, taking into account production costs, optimized studies were carried out in line with the desired properties of the end product and the specific requirements of the application.

The bulk density of PFR decreases with increasing production temperature, according to the obtained results. In addition, Shore D hardness of PFR increases with increasing manufacturing temperature. PFR has a low thermal conductivity coefficient at low manufacturing temperatures.

High temperature and pressure may be preferred to increase the speed of the reaction and increase the yield; however, this can also result in increased energy consumption and equipment costs. Catalysts are frequently used to increase the reaction rate and increase resin production efficiency. This study monitors physical interactions and chemical reactions using sodium hydroxide catalysts.

Optimization studies have been carried out to improve the efficiency, quality, and cost-effectiveness of PFR. Effective and cost-effective resin production in industrial applications requires careful management of the components, reaction conditions, and optimization parameters used in the production of PFRs. This research has taken a step towards understanding the complexity and diversity of phenol-formaldehyde resins and has laid an important foundation for guiding future industrial applications.

## REFERENCES

- [1] Khaha, H. M., Soleimani, O., *Properties and Applications of Polymers: A Mini Review*. Journal of Chemical Reviews, 2023: 5(2), 204-220.
- [2] Bartlett, E. P., Anderson, L. W., Curry, D. M., *An evaluation of ablation mechanisms for the Apollo heat shield material*. Journal of Spacecraft and Rockets, 1971: 8(5), 463-469.
- [3] He, G., Yan, N., *<sup>13</sup>C NMR study on structure, composition and curing behavior of phenol-urea-formaldehyde resole resins*. Polymer, 2004: 45(20), 6813-6822.
- [4] Ravindran, L., MS, S., Kumar S, A., Thomas, S, *A comprehensive review on phenol formaldehyde resin based composite sand foams*. Polymer Composites, 2022: 43(12), 8602-8621.
- [5] Naidu, U. A., & Dinda, S. *Development of ketonic resin by polymerization reaction: A critical review*. Polymer, 2015: 61, 204-212.
- [6] Xu, Y., Guo, L., Zhang, H., Zhai, H., Ren, H. *Research status, industrial application demand and prospects of phenolic resin*. RSC advances, 2019: 9(50), 28924-28935.
- [7] Hirano, K., Asami, M. *Phenolic resins 100 years of progress and their future*. Reactive and functional polymers, 2013: 73(2), 256-269.
- [8] Baekeland, L. H. *The synthesis, constitution, and uses of Bakelite*. Industrial & Engineering Chemistry, 1909: 1(3), 149-161.
- [9] Gardziella, A., Pilato, L. A., Knop, A. *Phenolic resins: chemistry, applications, standardization, safety and ecology*. Springer Science & Business Media. 2013.
- [10] Lee, D. C., Jang, L. W. *Preparation and characterization of PMMA-clay hybrid composite by emulsion polymerization*. Journal of Applied Polymer Science, 1996: 61(7), 1117-1122.
- [11] Park, J. K., Kang, T. J. *Thermal and ablative properties of low temperature carbon fiber-phenol formaldehyde resin composites*. Carbon, 2002: 40(12), 2125-2134.
- [12] Özbay, G., Atar, M., Ozcifci, A. *Synthesis of phenolic resin reinforced with TiO<sub>2</sub> nanoparticles and its effect on combustion performance of laminated veneer lumber (LVL)*. Drvnaindustrija, 2023: 74(1), 13-20.
- [13] Dick, J. S. (Ed.). *Rubber technology: compounding and testing for performance*. Carl Hanser Verlag GmbH Co KG, 2020.
- [14] Granger, F. S. *Condensation of phenols with formaldehyde*. Industrial & Engineering Chemistry, 1937: 29(10), 1125-1129.
- [15] Qureshi, S. P., *Phenolic resins*, 2001.
- [16] Pilato, L., *Phenolic resins: 100 Years and still going strong*. Reactive and functional polymers, 2013: 73(2), 270-277.
- [17] Poljanšek, I., Šebenik, U., Krajnc, M. *Characterization of phenol-urea-formaldehyde resin by in line FTIR spectroscopy*. Journal of Applied Polymer Science, 2006: 99(5), 2016-2028.
- [18] Gindl, W., Schöberl, T., Jeronimidis, G., *The interphase in phenol-formaldehyde and polymeric methylene di-phenyl-di-isocyanat glue lines in wood*. International Journal of Adhesion and Adhesives, 2004: 24(4), 279-286.
- [19] Sarika, P. R., Nancarrow, P., Khansaheb, A., Ibrahim, T., *Bio-based alternatives to phenol and formaldehyde for the production of resins*. Polymers, 2020: 12(10), 2237.
- [20] Asim, M., Saba, N., Jawaid, M., Nasir, M., Pervaiz, M., Alothman, O. Y., *A review on phenolic resin and its composites*. Current Analytical Chemistry, 2018: 14(3), 185-197.
- [21] Gollob, L., *The interaction of formulation parameters with chemical structure and adhesive performance of phenol-formaldehyde resins*, 1982.
- [22] Ravindran, L., MS, S., Kumar S, A., Thomas, S., *A comprehensive review on phenol-formaldehyde resin-based composites and foams*. Polymer Composites, 2022: 43(12), 8602-8621.
- [23] Sarika, P. R., Nancarrow, P., Khansaheb, A., Ibrahim, T., *Bio-based alternatives to phenol and formaldehyde for the production of resins*. Polymers, 2020: 12(10), 2237.
- [24] Dorieh, A., Ayrilmis, N., Pour, M. F., Movahed, S. G., Kiamahalleh, M. V., Shahavi, M. H., Mehdinia, M., *Phenol formaldehyde resin modified by cellulose and lignin nanomaterials: Review and recent progress*. International Journal of Biological Macromolecules, 2022: 222, 1888-1907.
- [25] Asim, M., Saba, N., Jawaid, M., Nasir, M., Pervaiz, M., Alothman, O. Y., *A review on phenolic resin and its composites*. Current Analytical Chemistry, 2018: 14(3), 185-197.
- [26] Ibeh, C. C., *Phenol-formaldehyde resins*. Handbook of thermoset plastics, 1998: 2, 23-71.
- [27] Demirpolat, A. B., Aydoğmuş, E., *Development of Composite Materials from Phenol Formaldehyde Resins and Evaluation of Their Uses*. International Journal of Advanced Natural Sciences and Engineering Researches, 2023: 7(4),



- 158-162.
- [28] Hong, S., Gu, Z., Chen, L., Zhu, P., Lian, H., *Synthesis of phenol formaldehyde (PF) resin for fast manufacturing laminated veneer lumber (LVL)*. *Holzforschung*, 2018: 72(9), 745-752.
- [29] Sprengling, G. R., Freeman, J. H., *The reaction of phenol with formaldehyde*. *Journal of the American Chemical Society*, 1950: 72(5), 1982-1985.
- [30] Bender, H. L., Farnham, A. G., Guyer, J. W., Apel, F. N., Gibb, T. B., *Purified chemicals and resins from phenol and formaldehyde*. *Industrial & Engineering Chemistry*, 1952: 44(7), 1619-1623.
- [31] Ravindran, L., MS, S., Kumar S, A., Thomas, S., *A comprehensive review on phenol-formaldehyde resin-based composites and foams*. *Polymer Composites*, 2022: 43(12), 8602-8621.
- [32] Martin B. Hocking, *Commercial Polycondensation (Step-Growth) Polymers*, *Handbook of Chemical Technology and Pollution Control*, 2005: 689-712
- [33] Karataş, M., Aydoğmuş, E., *Obtaining Pectin Reinforced Polyester Composite and Investigation of Thermophysical Properties*. *European Journal of Science and Technology*, 2023: (48), 64-66.
- [34] Demirel, M. H., Aydoğmuş, E., *Waste Polyurethane Reinforced Polyester Composite, Production, and Characterization*. *Journal of the Turkish Chemical Society Section A: Chemistry*, 2022: 9(2), 443-452.
- [35] Pullichola, A. H., Varghese, L. A., Gopalakrishnapanicker, U., Das, K. M., *Fourier transform infra-red spectroscopy to determine formaldehyde to phenol ratio of phenol formaldehyde resole*. *Journal of Elastomers & Plastics*, 2022: 54(4), 593-604.
- [36] Jiang, H., Wang, J., Wu, S., Yuan, Z., Hu, Z., Wu, R., Liu, Q., *The pyrolysis mechanism of phenol formaldehyde resin*. *Polymer degradation and stability*, 2012: 97(8), 1527-1533.
- [37] Orhan, R., Aydoğmuş, E., Topuz, S., Arslanoğlu, H., *Investigation of thermo-mechanical characteristics of borax reinforced polyester composites*. *Journal of Building Engineering*, 2021: 42, 103051.
- [38] Aydoğmuş, E., Dağ, M., Yalçın, Z. G., Arslanoğlu, H., *Synthesis and characterization of waste polyethylene reinforced modified castor oil-based polyester biocomposite*. *Journal of Applied Polymer Science*, 2022: 139(27), e52526.