

Thermo-Viscous Properties of Phenolic Resin with Different Formaldehyde to Phenol Molar Ratio

Ahmedi Asraf^{1,2}, Ariadne Lakshmidevi Juwono^{1*}, Bagus Hayatul Jihad², Yudi Nugraha Thaha³

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Indonesia (UI), 16424, Depok, Indonesia

²Research Centre for Rocket Technology, National Research and Innovation Agency (BRIN), 16350, Bogor, Indonesia

³Research Centre for Metallurgy, National Research and Innovation Agency (BRIN), 15314, South Tangerang, Indonesia

*Corresponding Author: ariadne.laksmidevi@ui.ac.id

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Abstract: Phenolic resin is widely used as a matrix in composite material. Understanding the thermo-viscous properties of the resin is essential because the viscosity is one of the main factors determining the success of the composite material fabrication. In this study, we synthesized the resin with formaldehyde to phenol molar ratio (F/P) of 1.1, 1.2, 1.3, and 1.4 and analyzed their viscosity as a function of temperature from 17 °C to 25 °C. The resin's Arrhenius activation energy with an F/P value of 1.1, 1.2, 1.3, and 1.4 was found to be 88.8 kJ/mol, 96.5 kJ/mol, 86.1 kJ/mol, and 81.4 kJ/mol, respectively. It suggests that the fiber wetting or impregnation process using these resins during composite material fabrication can be done from 21 °C to 25 °C. However, the temperature must be maintained strictly to ensure the quality of the composite because the resin viscosity is quite sensitive to temperature change. Furthermore, the differential scanning calorimetry (DSC) analysis was conducted on all resins. The endothermic reaction due to water evaporation was found to be dominated at a temperature of around 100 °C, and the curing reaction peak of all resins took place at 150 °C.

Keywords: Arrhenius equation, Formaldehyde, Phenol, Phenolic resin, Viscosity.

INTRODUCTION

Phenolic resin is a thermoset polymer with a great mechanical property, dimensional stability, flame retardancy, and corrosion resistance. In its application, the resin acts as a matrix in polymeric composite used in construction, agriculture, military, automotive, and electronic industries (Pesci et al., 2021; Poloni et al., 2023; Ren et al., 2023; Zanjanijam et al., 2023).

One technique that is widely used to produce various polymeric composite materials is the vacuum infusion technique. The technique involves the infusion of a resin through an inlet by reducing the pressure under the vacuum bag (Wang et al., 2023; Zénone et al., 2018). The success of the composite material fabrication largely depends on temperature, vacuum level, and the viscosity of the infused resin (Lionetto et al., 2020). The viscous resin results in a long filling time and low fiber volume fraction during the composite manufacturing process. When highly viscous resin is used, viscosity reduction is necessary. It can be done by heating or combining viscous resin with a low-viscosity resin (Chokka et al., 2021). Advanced composite material is also fabricated by stacking the composite prepregs. Viscosity is one of the most important parameters in the prepreg manufacturing process. Improper fiber

wetting will be obtained when the viscosity of the resin is too high. Relative low viscosity will cause the resin to bleed. Both of these conditions cause a reduction in the final properties of the produced composite (Somarathna et al., 2024).

Resole phenolic resin is synthesized by reacting phenol with excess formaldehyde under basic conditions. The reaction during the synthesis is shown in Figure 1 (Lian et al., 2021). Methylene glycol, the form of formaldehyde in an aqueous solution (Albert et al., 2000), reacts with phenol to form methylol phenol that contains a hydroxymethyl functional group at the ortho and para side. Further reactions between the methylol phenol and methylene glycol might result in trimethylol and dimethylol phenol formation. The methylol phenol and the unreacted phenol will condense when heat is added to form the methylene bridge. Ether bridge is also formed via the condensation reaction between methylol phenol groups. Water forms as a by-product of the condensation reaction. As the reaction progresses, the ether bridge will be converted to a methylene bridge by releasing the formaldehyde molecule (Xu et al., 2019). Ortho-para methylene, para-para methylene, and ortho-ortho methylene are the possible types of methylene bridges that can be formed (Zhang et al., 2024).

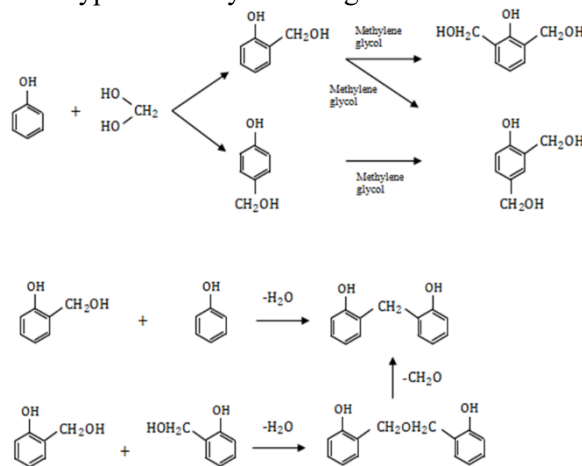


Figure 1. Reaction during the synthesis of resole type of phenolic resin

The synthesis of phenolic resin involves competition of many side reactions, depending on the synthesis parameters (Kamarudin, Radiah Awang Biak, et al., 2020). The initial F/P value influences phenolic resin's polymerization kinetics and significantly influences its properties and molecular structure (Astarloa Aierbe et al., 2000). Viscosity reflects the molecular behavior of resin (Baimukhametov et al., 2024). Thermo-viscous characteristic of phenolic resin influences the fiber's flow ability and wetting ability during the polymeric matrix composite manufacturing process. Phenolic resin's molecular structure also affects its curing process (Ma et al., 2013).

Phenolic resin is stored at sub-ambient temperature for stability, laying up at room temperature, and cured at high temperature (Guo et al., 2024; Raju et al., 2020). Understanding its viscosity at different temperatures is essential to comprehend the effect of composition on the variability and stability of the resin during the laying-up process. The success of the composite material's fabrication mainly depends on this feature. Because formaldehyde to phenol molar ratio (F/P) affects the final properties of phenolic resin, it can be synthesized with various F/P according to specific requirements. However, the thermo-viscous characteristic of the phenolic resin with different formaldehyde to phenol molar ratios

(F/P) in the temperature range of 17 °C to 25 °C has not been reported. This paper aims to determine the phenolic resin's thermo-viscous properties having 1.1, 1.2, 1.3, and 1.4 F/P values. Differential scanning calorimetry analysis was also performed to study their curing characteristic.

RESEARCH METHODS

Materials

Formaldehyde solution (37 wt%) and phenol were purchased from Smartlab Indonesia. Sodium hydroxide was purchased from Merck. All are analytical reagent grade.

Methods

Resin Synthesis

Four types of phenolic resin were synthesized in this study. The F/P values were 1.1, 1.2, 1.3, and 1.4; these resins are called resin 1.1, 1.2, 1.3, and 1.4, respectively. NaOH to phenol molar ratio (OH/P) of each resin was 0.1. All resins were synthesized using the same procedure to prevent the influence of variables other than the F/P value.

They were synthesized by pouring phenol, formaldehyde, and sodium hydroxide (40wt%) into a three-necked flask equipped with a cooling condenser. The system was stirred during the synthesis using a magnetic stirrer at 300 rpm. The synthesis was performed for two hours. The temperature was increased to 90 °C at the first 40 minutes and maintained for the rest of 80 minutes. After that, the resins were distilled in a vacuum-degassing apparatus for two hours to reduce their water content.

Characterization

The resin's structure was analyzed using UV-Vis spectroscopy and Fourier transform infrared spectroscopy (FT-IR) (Bruker ALPHA II). Brookfield viscometer was used to measure their viscosity. The viscosity was measured from 17 °C to 25 °C. The measurement was performed at each temperature for 25 seconds, and the data were collected at each second. The reported data were the average of the last five collected data. The solid content S of the resin was calculated using (Q. Liu et al., 2022):

$$S = \frac{m_f - m_m}{m_i - m_m} \quad (1)$$

where m_f , m_m , and m_i are the mass of the mold containing the resin after cured, the mass of the mold, and the mass of the mold containing the resin before cured. The reported solid content of each type of phenolic resin was the average from three samples. The curing process used was two hours at 80 °C, followed with 95 °C for 3 hours, followed with 100 °C for 2 hours, and the last two hours at 130 °C. Differential scanning calorimetry (DSC) analysis was conducted in a nitrogen environment with a heating rate of 10 °C per minute from 25 °C to 300 °C.

RESULTS AND DISCUSSION

UV-Vis and FTIR Spectrum

Figure 2 displays the phenolic resins' UV-Vis spectra. The absorption band between 200 to 320 nm is related to $\pi \rightarrow \pi^*$ transition of the aromatic rings (Kaya & Yilmaz, 2017). A weak absorption peak at 345 nm and a broad band peak at the visible region of 400-700 nm is also observed. These absorption peaks are related to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transitions of carbonyl groups in quinone (Vân Anh & Williams, 2012). The difference in

absorption in the 255 nm - 260 nm range is related to the different $\pi \rightarrow \pi^*$ systems due to the different degrees of condensation.

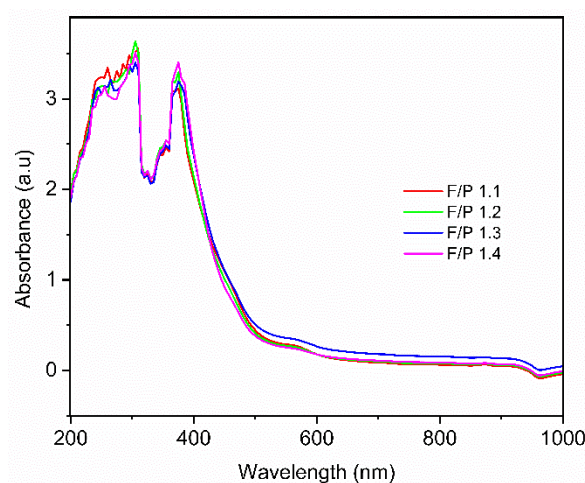


Figure 2. UV-Vis spectrum of phenolic resin

Figure 3 displays the FTIR spectrum of resin 1.1, 1.2, 1.3, and 1.4. All samples exhibit similar FTIR spectra, which differ from each other by their intensity. These FTIR spectra indicate that the as-synthesized resins exhibit similar functional groups in their structure. Hydroxymethyl functional groups are observed, indicated by the absorption around 992 cm^{-1} (Xiong et al., 2023). The absorption peak around 1597 cm^{-1} is related to the carbon double bond in the benzene ring. The methylene bridges are also observed. The absorption peaks around 1478 cm^{-1} and 1455 cm^{-1} are related to the para-para methylene and ortho-para methylene, respectively. Ether bridges also exist, as indicated by the peak of around 1063 cm^{-1} (Hu et al., 2022). The $2800 - 3600\text{ cm}^{-1}$ absorption is related to O-H bond vibration (Palencia, 2018). It also shows the existence of water molecules in resin.

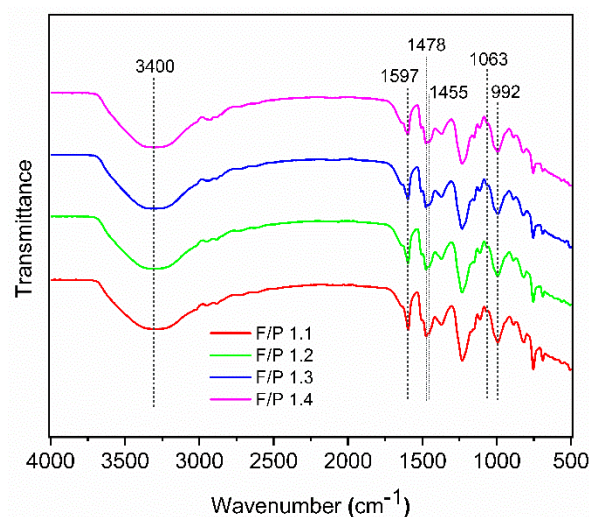


Figure 3. FTIR spectrum of phenolic resin

The concentration of the methylene bridge, ether bridge, and hydroxymethyl functional group can be described using index of para-para methylene $MI_{(p-p)}$, index of ortho-para methylene $MI_{(o-p)}$, index of ortho-ortho methylene $MI_{(o-o)}$, index of total methylene MI_{total} , index of ether EI, and index of hydroxymethyl HI. These indexes were estimated by the following relation (Hu et al., 2022):

$$MI_{(p-p)} = \frac{A_{(1478)}}{A_{(1610)}} \quad (2)$$

$$MI_{(o-p)} = \frac{A_{(1455)}}{A_{(1597)}} \quad (3)$$

$$MI_{(o-o)} = \frac{A_{(1440)}}{A_{(1597)}} \quad (4)$$

$$EI = \frac{A_{(1063)}}{A_{(1597)}} \quad (5)$$

$$HI = \frac{A_{(992)}}{A_{(1597)}} \quad (6)$$

$$MI_{total} = MI_{(p-p)} + MI_{(o-p)} + MI_{(o-o)} \quad (7)$$

where $A_{(1597)}$, $A_{(1478)}$, $A_{(1455)}$, $A_{(1440)}$, $A_{(1063)}$, and $A_{(992)}$ are the height of the peak at wavenumber of 1597 cm^{-1} , 1478 cm^{-1} , 1455 cm^{-1} , 1440 cm^{-1} , 1063 cm^{-1} , and 992 cm^{-1} .

Table 1 presents the result of the calculation. The concentration of para-para methylene is higher than that of ortho-para methylene. Both types of methylene bridges increase due to the increasing F/P value, suggesting that the total methylene index and the average molecular weight also increase. The ortho-ortho methylene index is zero due to the ortho-ortho methylene suggested by the peak at wavenumber 1440 cm^{-1} is not observed. The hydroxymethyl functional group concentration increases as the F/P value becomes larger. However, the ether bridge concentration of resins 1.1 and 1.2 is higher than that of 1.3 and 1.4. This indicates that the methylol phenols of resins 1.3 and 1.4 have a greater tendency to react with free phenol to form a methylene bridge.

Table 1. Index of Methylene, index of ether, and index of hydroxymethyl of phenolic resin

F/P	$MI_{(p-p)}$	$MI_{(o-p)}$	MI_{total}	EI	HI
1.1	0.266	0.091	0.357	0.344	0.867
1.2	0.310	0.118	0.429	0.306	0.961
1.3	0.339	0.153	0.492	0.267	1.073
1.4	0.342	0.187	0.530	0.302	1.206

Solid Content

Solid content is related to the proportion or mass fraction of the resin converted to solid after curing. A low solid content indicates a high fraction of water in the phenolic resin. Viscosity can decrease as the solid content gets lower. Low solid resin's water content increases the distance between the molecular chains (Y. Liu et al., 2020). Due to the increase in inter-molecular distance, the molecules have more space to move freely (Bista et al., 2020).

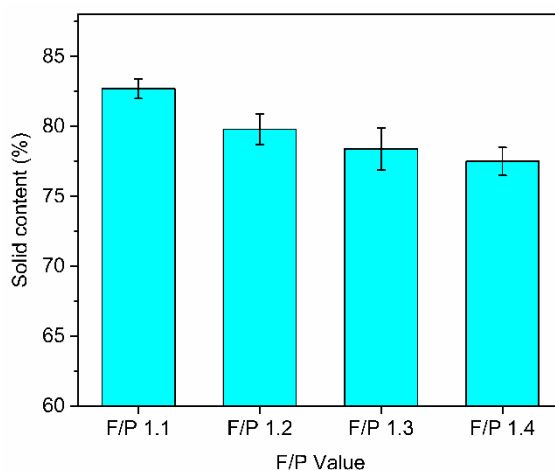


Figure 4. Resin solid content as a function of F/P value

Phenolic resin is cured at elevated temperatures. High temperatures will cause the water content to evaporate. The resin will get denser as a crosslink increases during the curing process. It makes a portion of evaporated water and other volatiles to be entrapped. As a result, voids are formed in a cured phenolic resin. A high fraction of water will tend to produce more voids in the resin after being cured (Choi et al., 2023). Due to the voids fraction affecting the properties of the cured resin or its composite, a high solid content resin is preferable.

The solid content of the phenolic resin is strongly influenced by the F/P ratio, as shown in Figure 4. It reveals that the solid content gets smaller with the increases in the F/P ratio. The solid content of the resin 1.1, 1.2, 1.3, and 1.4 are 82.7%, 79.8%, 78.4%, and 77.5% respectively. This is because the formaldehyde was a solution with water as its solvent. The concentration of the hydroxymethyl functional group also contributes to the solid content of phenolic resin. The condensation reaction between methylol phenol will produce water molecules to form ether bridges, and the ether bridges will be converted into methylene bridges by releasing formaldehyde molecules.

Viscosity

Figure 5 displays the viscosity of the phenolic resin as a function of the temperature from 17 °C to 25 °C. The viscosity of resin 1.1 decreases from 703 cP to 257 cP with the increasing temperature. Resin 1.2 exhibits a higher viscosity than resins 1.1, 1.3, and 1.4. Its value decreases from 915 cP to 329 cP. It shows that the resin's viscosity does not depend only on its solid content. The viscosity of resins 1.3 and 1.4 decreases from 603 cP to 232 cP and 601 cP to 253 cP, respectively.

The difference in viscosity can also be attributed to the difference in resin average molecular weight and the interaction between long-chain polymers. As found by Hu et al. (Hu et al., 2021), the number of the average molecular weight increases with the increase in F/P value. It is consistent with the increase in the total methylene index, as shown in Table 1. The increase in the average molecular weight contributes to the increase of the resin viscosity (Astarloa Aierbe et al., 2000). However, the viscosity of resins 1.1 and 1.2 is higher than that of resins 1.3 and 1.4, possibly due to their higher solid content and the difference in molecular weight distribution.

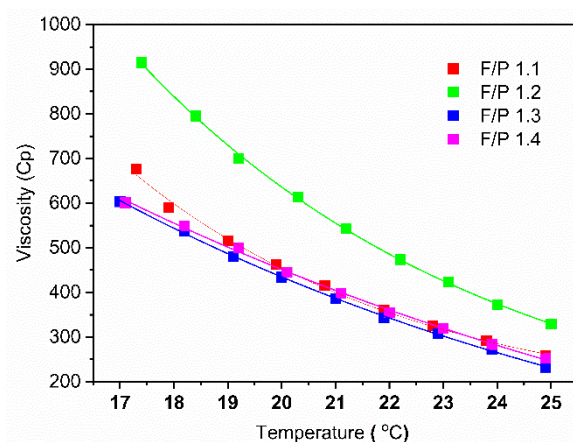


Figure 5. Graph of Viscosity vs temperature

The relation between the viscosity and the temperature of a liquid can be described using Arrhenius equation below (Giap, 2010):

$$\eta = Ae^{E_a/RT} \quad (8)$$

where η , A , E_a , R , and T are dynamic viscosity (Pa.s), pre-exponential factor (Pa.s), Arrhenius energy of activation (J/mol), Universal gas constant (J/(mol. K)), and Temperature (K). Taking the natural logarithm of both side of the equation leads to (Alzamil, 2021):

$$\ln \eta = \left(\frac{E_a}{R} \right) \frac{1}{T} + \ln A \quad (9)$$

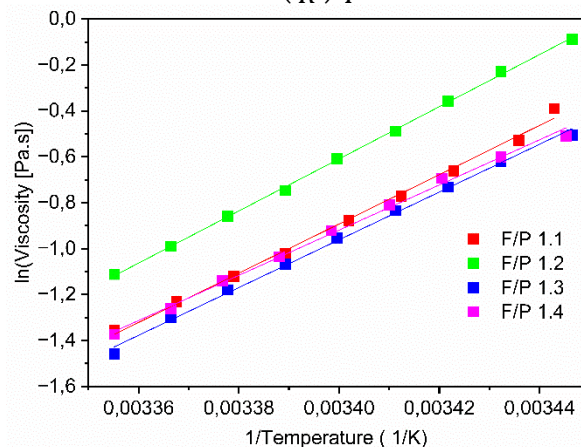


Figure 6. Graph ln(viscosity) vs 1/T

The relation between $\ln \eta$ and $(1/T)$ of the resins is shown in Figure 6. By applying the linear regression to the $\ln \eta$ vs. $(1/T)$ data and comparing the results to the equation (9), the pre-exponential factor and the Arrhenius energy of activation can be obtained as shown in Table 2.

Though the relation between $\ln \eta$ and $(1/T)$ of the resins is linear with an R-squared value of the regression of about 0.99, all resin exhibits different slopes, indicating that the F/P value affects the Arrhenius activation energy. According to equation 8, the Arrhenius energy of activation describes how sensitive the viscosity is to temperature. The lower its value, the lower the heat needed to change the viscosity of the phenolic resin.

Therefore, temperature must be strictly maintained during composite fabrication using resin with a relatively high Arrhenius activation energy.

Table 2. Pre-exponential factor, Arrhenius energy of activation, and R-squared of the regression

F/P	A (Pa · s)	E_a (kJ/mol)	R-squared
1.1	6.88×10^{-17}	88.8	0.9963
1.2	3.93×10^{-18}	96.5	0.9996
1.3	1.91×10^{-16}	86.1	0.9972
1.4	1.37×10^{-15}	81.4	0.9966

The vacuum infusion process is commonly performed at room temperature. The viscosity of the resins used varies. Acosta used the resin with a viscosity of 205 cP at room temperature (Acosta et al., 2023). Another literature recommends that the viscosity for laying up during the manufacturing process of composite materials is about 400 to 600 cP (Kamarudin, Awang Biak, et al., 2020). This means the resin with a viscosity range of 200 cP to 600 cP can fabricate the composite material. The fiber wetting process or impregnation using resins 1.1, 1.2, 1.3, and 1.4 can still be done from 21 °C to 25 °C because their viscosity is still between 200 cP to 600 cP. However, the temperature must be maintained strictly to ensure the quality of the composite because the resin viscosity is quite sensitive to temperature change, as indicated by the Arrhenius energy of activation.

DSC Analysis

Differential scanning calorimetry was used to examine the chemical and physical change of the phenolic resin during the thermal heating process. Figure 7 displays the DSC thermogram of resin 1.1, 1.2, 1.3, and 1.4. The endothermic reaction is observed at a temperature of 100 °C. It was caused by the evaporation of water existing in the resin, excess free formaldehyde, and the water produced during the polymerization process (Shaghaghi et al., n.d.). The higher the water content, the more endothermic the reaction. This is indicated by the endothermic peak of the DSC thermogram, which gets broader and higher as the F/P value becomes larger.

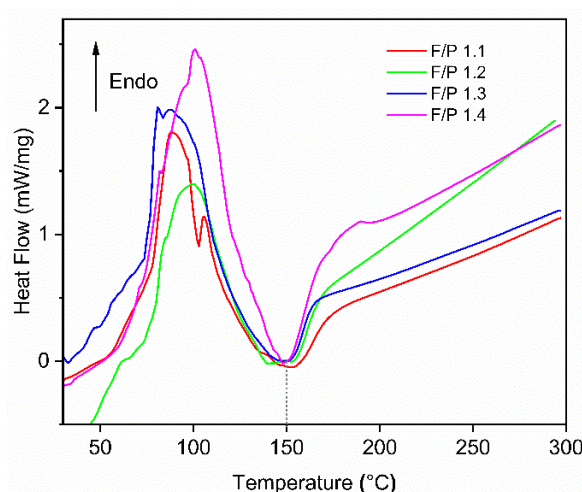


Figure 7. DSC graph of phenolic resin

The peak of the curing process of all resin happened at the same temperature, about 150°C. The exothermic peak becomes sharper when the F/P value gets larger. It reveals that polymerization becomes faster due to the increase in F/P. In the range of 150°C to 170°C, the slope of the curve becomes higher as the F/P value increases, indicating that the fraction of the residual of uncured resin is lower in the higher F/P resin. So, resins 1.1 and 1.2 need more heat and time to cure completely.

The F/P effect on phenolic resin's curing kinetic was also reported by Ma et al. (Ma et al., 2013). They found that the activation energy of the resin gets smaller with the increase of the F/P ratio, suggesting that the polymerization process becomes faster as the F/P ratio increases. The increase of polymerization process kinetics with the increase of F/P value was also reported by Kamaruddin et al. (Kamarudin, Awang Biak, et al., 2020). The hydroxymethyl functional group plays an important role during the polymerization process. The group is responsible for forming the methylene bridge and ether bridge. Due to its concentration increasing as the F/P gets larger, the more possibility of the condensation reaction occurring, leading to the decrease of the polymerization activation energy at a higher F/P value.

CONCLUSIONS

Several rheological experiments were conducted to determine the thermo-viscous properties of resole phenolic resins 1.1, 1.2, 1.3, and 1.4. Their viscosity was characterized at temperatures ranging from 17°C to 25°C. Resin 1.2 exhibited the highest viscosity, followed by resins 1.1, 1.4, and 1.3, respectively. As the temperature increased from 17°C to 25 °C, the viscosity of these resins decreased as follows: resin 1.1 from 915 cP to 329 cP, resin 1.2 from 703 cP to 257 cP, resin 1.3 from 603 cP to 232 cP, and resin 1.4 from 601 cP to 253 cP. The relationship between the natural logarithm of viscosity and the reciprocal of temperature for the synthesized phenolic resins was found to be linear. The Arrhenius energy of activation for resins 1.1, 1.2, 1.3, and 1.4 were measured at 88.8 kJ/mol, 96.5 kJ/mol, 86.1 kJ/mol, and 81.4 kJ/mol, respectively. This suggests that the fiber wetting process using resins 1.1, 1.2, 1.3, and 1.4 can be effectively performed at temperatures between 21°C and 25°C. However, it is essential to maintain a consistent temperature to ensure the quality of the composite, as resin viscosity is sensitive to temperature changes.

Furthermore, differential scanning calorimetry analysis revealed that the endothermic reaction associated with water evaporation predominated around 100°C. The exothermic peak of the polymerization process for all resins occurred at 150°C. The peak became sharper with an increasing fiber-to-phenolic (F/P) ratio, indicating that the activation energy for polymerization decreases as the F/P ratio increases. This is attributed to the higher concentration of hydroxymethyl groups present in resins with a greater F/P ratio.

This study demonstrates that the F/P value significantly affects the properties of phenolic resin. Given that the resin can serve as a matrix in composite materials, future research should explore how the F/P ratio influences the fabrication process and the final properties of composites made from these resins.

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