

Research Article

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Optimizing curing agent ratios for high-performance thermosetting phthalonitrile-based glass fibers

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Abstract: Phthalonitrile (PN) is a highly promising material in the field of high-performance thermosetting polymers due to its ability to maintain its properties even at extremely high temperatures. The goal of this study was to investigate the effects of varying curing agents on the thermal properties of cured PN resin. The curing agents were found to effectively cure the resin, as indicated by the increasing ratio of N and S contents and decreasing the C content as the proportion of curing agents increased, as observed by scanning electron microscopy and energy dispersive X-ray spectroscopy data analyses. Moreover, thermogravimetric analyses revealed that the sample with 20% curing agent showed the highest thermal decomposition rate among the 2, 5, 10, and 20% curing agent dosages. These properties can be further improved by incorporating glass fibers. Overall, these results demonstrate the successful use of curing agents to create an efficient and functional polymer with superior thermal properties that are suitable for use in harsh environments. The findings of this study are a significant step forward in advancing the use of PN as a high-performance thermosetting polymer.

Keywords: thermosetting resin, phthalonitrile, curing agent

1 Introduction

In recent years, there has been a growing interest in the application of high-performance thermosetting resins, which possess remarkable properties such as low water

absorption, outstanding corrosion resistance, and flame retardancy. The key characteristics of high-performance thermosetting resins include high aromatic content, glass temperature ($T_g > 150^\circ\text{C}$), and thermal decomposition temperature ($T_d > 400^\circ\text{C}$) [1]. Epoxy resins are one of the most widely used high-performance thermosetting resins due to their superior mechanical and chemical properties [2,3]. Epoxy resins are synthesized through a reaction between epichlorohydrin and bisphenol-A, yielding a highly durable material that exhibits notable resistance to impact, heat, and chemicals. This trait renders epoxy resins ideal for adhesives, coatings, and composites. Similarly, phenolic resins are formulated through a reaction between phenol and formaldehyde, resulting in a material that possesses remarkable heat and chemical resistance [4,5]. Phenolic resins are commonly employed in the fabrication of high-strength composites, electrical laminates, and molded parts, owing to their exceptional mechanical properties and low flammability. Polyester resins are synthesized by the reaction of dibasic acids and glycols, which can be further augmented with a variety of additives to enhance their mechanical and chemical properties [6].

Among the emerging high-performance thermosetting resins, phthalonitrile (PN) resin has received significant attention due to its exceptional thermal stability [7–11]. Its heterocyclic macromolecular structure sets it apart from other resins, making it ideal for use at high service temperatures. These resins have become essential in various industries, including aerospace, microelectronics, composite materials, and more [12–14].

One of the most promising applications of PN is in the field of aerospace [15–18]. Due to its high thermal stability, PN can withstand extreme temperatures, making it an ideal material for use in aircraft engines and other high-temperature applications. It has been used to manufacture heat shields, exhaust nozzles, and other components in aerospace engines, where it provides outstanding resistance to thermal and mechanical stresses. Another significant application of PN is in the field of electronics [19–21].

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The polymer is used to create printed circuit boards that have superior thermal stability and are resistant to high temperatures, making them suitable for use in harsh environments. Additionally, PN is also used as an insulating material for high-voltage power cables due to its excellent dielectric properties. PN is also being explored as a potential replacement for traditional materials in the automotive industry [22,23]. The polymer can be used to create lightweight components that are resistant to heat and chemical damage. Another exciting application of PN is in the field of 3D printing [24]. The polymer's excellent thermal stability and chemical resistance make it an ideal material for use in 3D printing applications that require high-temperature resistance. PN-based 3D printing filaments are already available, and they have been used to create complex parts that can withstand high temperatures and harsh environments. In the field of energy, PN is being utilized to develop high-performance membranes for use in fuel cells [25]. These membranes are used to separate the fuel and oxygen in the fuel cell, so they have to be durable, stable, and possess high conductivity. PN-based membranes have demonstrated excellent performance in this application, showing high thermal stability and high proton conductivity. Although efforts have been made to improve the processability of PN resin, its high production costs remain a significant challenge [26–28].

The primary goal of our investigation is to meticulously examine the impact of adjusting the ratio of curing agents on the thermal properties of PN resin. Our study has shown that manipulating the proportion of curing agents can substantially improve the thermal properties and the yield of the final product. Additionally, we have also observed that the surface characteristics of the PN resin exhibit marked variations with differing ratios of curing agents. This conclusively demonstrates that the ratio of curing agents plays a crucial role in determining the thermal properties and surface characteristics of the PN resin. Our research underscores the importance of diligently controlling the ratio of curing agents to optimize the thermal properties of PN resin. Furthermore, our findings suggest that this resin holds immense potential for expanded utilization in diverse industrial applications. This article is structured as follows: Section 2 provides a comprehensive overview of the synthesis methodology for the PN resin, along with a detailed description of the relevant experimental apparatus. In Section 3, various ratios of curing agents are employed on the PN resin at reduced heating temperatures and durations compared to previous studies with the aim of enhancing energy efficiency. To achieve this, five distinct heating profiles are pre-examined to determine the optimal processing conditions. The physicochemical

properties of the resulting samples are subsequently compared, and the sample exhibiting the highest temperature resistance is selected for further application in glass fiber.

2 Experimental

All of the starting materials were of reagent grade and were used without purification. PN resin was synthesized by the following route [29]. A mixture of 4-fluorobenzonitrile (200 g, 1.65 mol), benzoyl chloride (93 g, 0.66 mol), ammonium chloride (106 g, 1.98 mol), and aluminum chloride (106 g, 0.79 mol) was heated to 150°C for 24 h. Cold water (1 L) was then added to the mixture dropwise until the temperature reached 0°C. Afterward, hydrochloric acid (36.5%, 200 g) was added to the cooled mixture. The resulting mixture (Compound 1) was filtered and washed with distilled water. To obtain compound 2, 4,4'-dihydroxybiphenyl (82 g, 0.44 mol), calcium carbonate (82 g, 0.58 mol), 1-methyl-2-pyrrolidone (600 mL), and toluene (600 mL) were added to the mixture in one portion, and heated until the temperature reached 150°C. The toluene was then removed through a Dean-Stark apparatus. The mixture without toluene was then allowed to cool to room temperature. The former compound (76 g, 0.22 mol) and 1-methyl-2-pyrrolidone (500 mL) were added to the mixture at 190°C for 3 h. Then, 4-nitrophthalonitrile (89 g, 0.51 mol) and 1-methyl-2-pyrrolidone (500 mL) were added to the mixture at 50°C. The mixture was stirred overnight at 80°C and then cooled to room temperature. The resulting compound was neutralized using sodium hydroxide (5%, 6 L), and a yield of 122 g (60%) was successfully obtained. The chemical structures of the synthesized compounds were verified by scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) microanalysis using an FEI Quanta 650 FEG SEM (ThermoFisher Scientific). With a high glass transition of nearly 400°C, differential scanning calorimetry results were omitted since there was no significant peak observed. Fourier-transform infrared spectrometer (FT-IR) was employed to support the curing process observed via EDX (TENSOR27, Bruker). Thermal properties were determined by time-domain thermogravimetric analysis using TGA8000 (PerkinElmer).

3 Results and discussion

The curing process involves the reaction of the PN resin with a curing agent, which leads to the formation of covalent bonds between the polymer chains. The curing

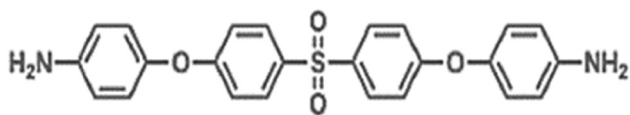


Figure 1: The chemical structure of the curing agent used in this work.

temperature determines the rate and extent of this reaction, as it affects the activation energy required for the reaction to occur. One hindrance to the utilization of PN resin is its requirement for high curing temperatures [30,31]. In this work, we applied a curing stage under 400°C. The compound with varying amounts of the curing agent was heated incrementally, starting at 200°C for 2 h, then 250°C for 1 h, 300°C for 4 h, and finally 350°C for 12 h (Figure 1).

The ratio of the curing agent to the PN resin is also a fundamental parameter that plays a pivotal role in the preparation of these resins. The curing process is a chemical reaction between the curing agent and the PN resin, leading to the formation of crosslinks among the polymer chains. The stoichiometric ratio of the curing agent to the PN resin defines the extent of crosslinking in the final resin, thus influencing its mechanical and thermal characteristics. A curing ratio that exceeds the optimal amount leads to an over-abundance of curing agents, inducing over-crosslinking and brittleness in the final resin. Conversely, if the curing ratio is insufficient,

a reduced degree of crosslinking results, leading to decreased mechanical and thermal properties of the PN resin. Moreover, the curing ratio modulates the rate of the curing reaction. Higher curing ratios generally facilitate a quicker curing process, given that more curing agent is available for the reaction. However, excessive curing ratios instigate a rapid exothermic reaction that promotes thermal degradation of the resin, and in severe cases, may even cause a fire. Therefore, the optimal curing ratio must be carefully determined. In this work, the curing ratio was in the range of 2–20%. To the best of our knowledge, investigations into the thermal properties of PN comprising a 20% concentration of curing agent have been scarcely explored in previous studies. For simplicity, the samples in this work are referred to as curing ratio-PN.

Figures 2 and 3 depict the SEM images and EDX microanalyses of the samples, respectively. Analyzing the data set, it is evident that all the samples contain significant amounts of C and O, which is a common feature of the PN resin (Table 1). Interestingly, there is a discernible increase in the N and S content in the samples as the proportion of curing agents is increased. This trend becomes more apparent when comparing the 2-PN sample to the 20-PN sample. The former, with the lowest proportion of curing agents, also has the lowest N and S content. On the other hand, the latter with a higher proportion of curing agents displays the highest N and S content. The S content

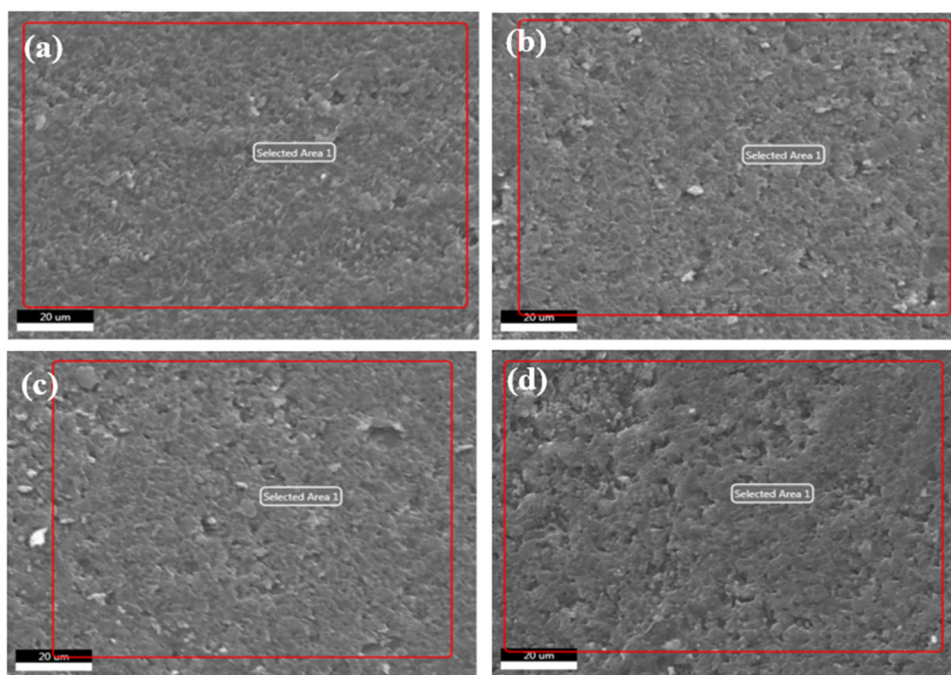


Figure 2: Scanning electron microscopic images of PN resins with the curing agent proportion of (a) 2%, (b) 5%, (c) 10%, and (d) 20%. EDX microanalyses (red box) are shown in Figure 3.

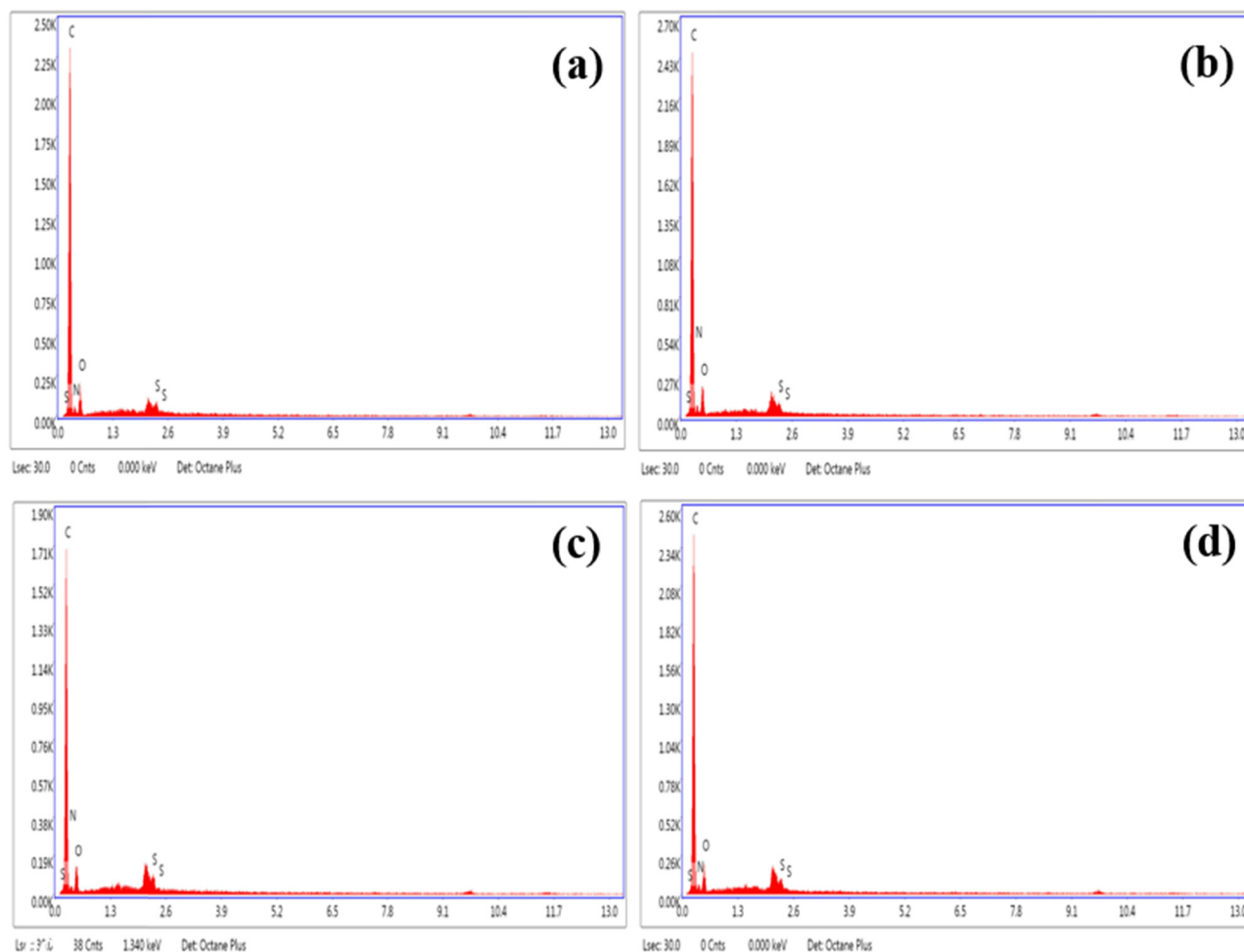


Figure 3: EDX microanalyses of PN resins with the curing agent proportion of (a) 2%, (b) 5%, (c) 10%, and (d) 20%.

Table 1: Elemental characteristics of samples

Curing agent (%)	Element	Weight (%)	Atomic (%)
2	C	80.22	84.27
	N	6.53	5.88
	O	11.73	9.25
	S	1.52	0.60
5	C	79.06	83.33
	N	7.45	6.74
	O	11.62	9.20
	S	1.87	0.74
10	C	76.24	81.15
	N	8.13	7.42
	O	12.98	10.37
	S	2.65	1.06
20	C	74.37	79.57
	N	9.22	8.41
	O	13.07	10.43
	S	3.34	1.59

is mainly due to the curing agent. The S-containing curing agent can act as co-catalysts to accelerate the curing process. This is due to their ability to react with the PN groups and generate reactive species that promote cross-linking and network formation. As a result, the curing time and temperature required for PN resin can be reduced, which improves the efficiency and cost-effectiveness of the process. S atoms can also form strong covalent bonds with the PN groups, which can prevent the molecular chains of the PN resin from unraveling at high temperatures. Therefore, it can be inferred that having a proper proportion of curing agent may improve the thermal stability of the resin. FT-IR spectroscopy was employed to further examine the curing reaction (Figure 4). All samples displayed triazine peaks at 1,520 and 1,360 cm^{-1} . The CN group at 2,230 cm^{-1} weakened after the curing reaction, which is in line with relevant studies [32].

The thermal stability of a polymer is a critical factor in determining its suitability for various industrial

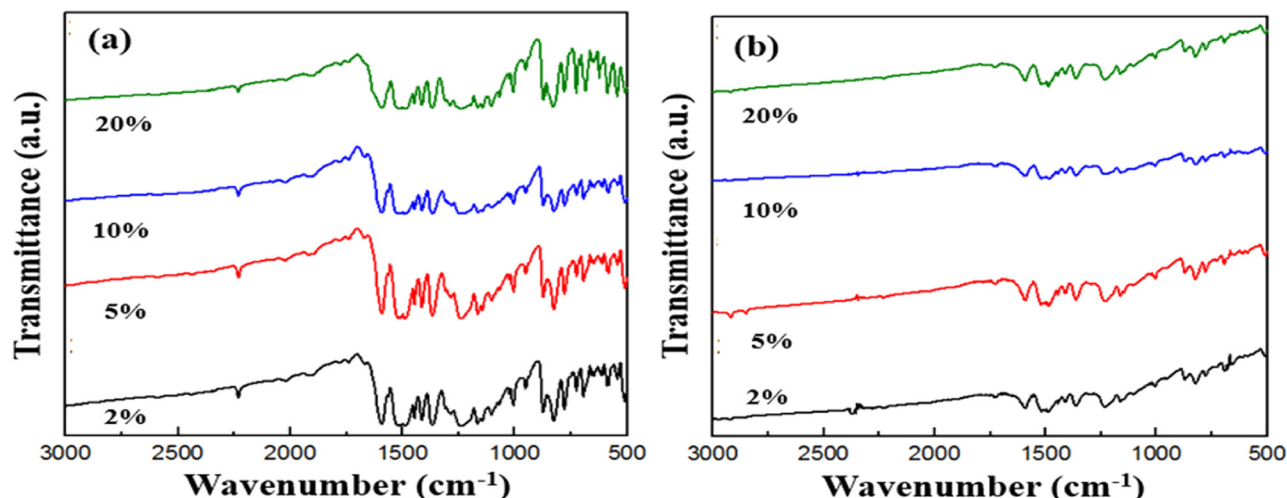


Figure 4: Fourier-transform infrared spectroscopy spectra of samples (a) before and (b) after the curing process with various ratios of curing agents.

applications. The early decomposition peaks that occur before 400°C are mainly attributed to the moisture and the breakdown of impurities present in the resin [33,34]. However, the major decomposition process commences at 500°C, indicating the presence of strong intermolecular forces after the curing process (Figure 5). Table 2 shows that the samples have high thermal stability and are capable of withstanding high temperatures due to their strong intermolecular forces. Furthermore, the thermal decomposition of 5 wt% samples was observed to occur in a specific order, with 10-PN exhibiting the highest thermal stability and 2-PN the lowest. This suggests that the utilization of a 2–5% ratio of a curing agent is insufficient for an efficacious interaction

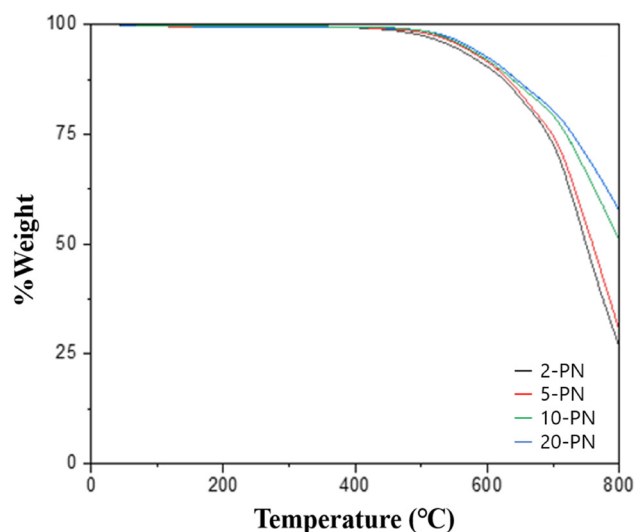


Figure 5: Thermogravimetric analyses of samples with various ratios of curing agents in an air atmosphere.

with the PN resin during the curing process. It is essential to note that the curing process is crucial in enhancing the thermal properties of the polymer, and an inefficient curing process may result in reduced thermal stability [35,36]. However, the utilization of a curing agent in excess of 10% was observed not to be as effective in enhancing the thermal properties, possibly due to surpassing the permissible curing capacity of the PN resin utilized in this study. This could lead to the formation of residual chains, subsequent to the primary decomposition of the curing agent, which may not be adequately linked to the moiety chain of the PN resin, thereby diminishing the overall efficacy of the curing process. The utilization of an excess curing agent may also result in the formation of voids and defects in the resin, which can further compromise the thermal stability of the polymer. Further research is currently underway to elucidate the intricacies of the decomposition mechanism under consideration.

There are several early decomposition peaks that take place prior to 400°C, caused by the breakdown of impurities as depicted in Figure 5. The major decomposition process starts at 500°C, which suggests the presence of

Table 2: Thermal decomposition (Td5%) of samples with various ratios of curing agents

%Curing ratio	Td5% (°C)
2	548.1
5	558.8
10	567.3
20	573.1

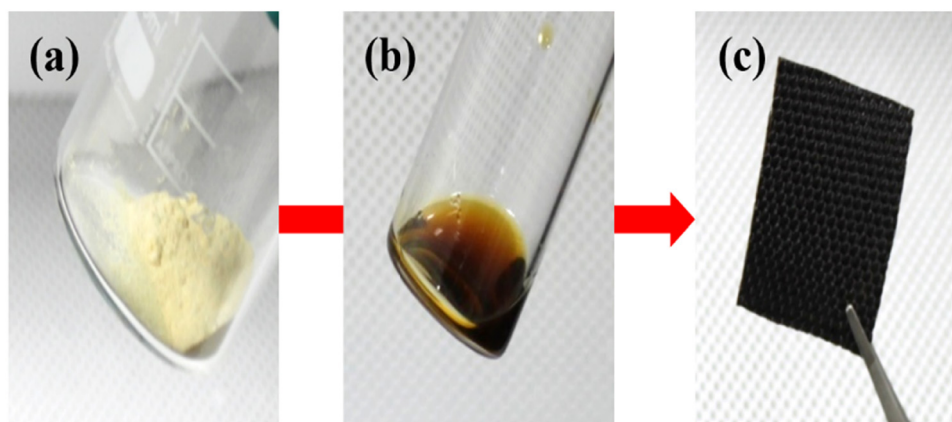


Figure 6: 20-PN in (a) powder form was heated to create (b) a liquified prepolymer and then introduced to (c) glass fiber.

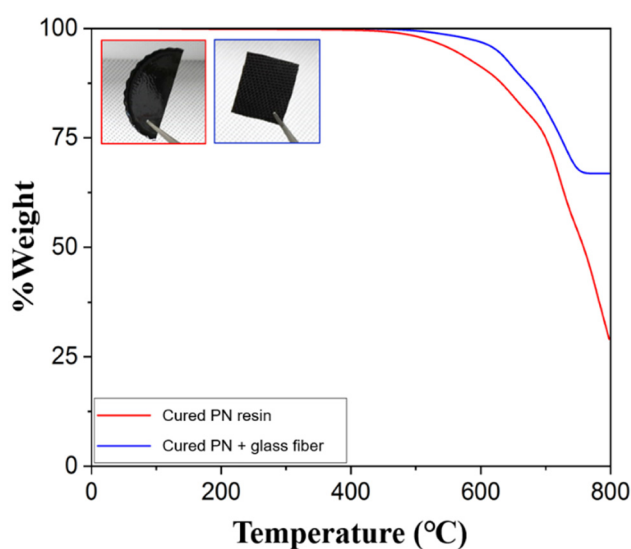


Figure 7: Thermogravimetric analyses of samples with various syntheses in an air atmosphere.

strong intermolecular forces after the curing process as shown in Table 2. The thermal decomposition of a 5 wt% sample was observed to occur in the following order: 10-PN > 20-PN > 5-PN > 2-PN. The present findings suggest that the utilization of a 2–5% ratio of a curing agent is insufficient for an efficacious interaction with the PN resin during the curing process. Moreover, it was observed that utilizing a curing agent in excess of 10% was not as effective in enhancing the thermal properties. This could be attributed to the fact that the use of a curing agent in excess of 10% may surpass the permissible curing capacity of the PN resin utilized in this study. It is plausible that the residual chains, subsequent to the primary decomposition of the curing agent, may not be adequately linked to the

moiety chain of the PN resin, thereby diminishing the overall efficacy of the curing process. Further research is currently underway to elucidate the intricacies of the decomposition mechanism under consideration.

The incorporation of reinforcing fillers such as glass fibers has become a prevalent approach in enhancing the thermal properties of polymer composites. In recent years, it has gained considerable attention as a promising method to improve the stability and durability of polymer-based materials [37–39]. The highest thermal property sample (20-PN) in the current study was fabricated by affixing the 20-PN resin to the glass fiber. The process involved heating the 20-PN resin to 200°C, followed by adding the curing agent and stirring the mixture until the resin liquefied. The resulting blend was then applied to the glass fibers and dried for 24 h at 90°C in a vacuum oven, as shown in Figure 6. It is worth noting that the observed 9% increase in thermal decomposition achieved through glass fiber reinforcement, as indicated by the comparison between 20-PN alone and 20-PN-glass fiber in Figure 7, can be attributed to several underlying factors. First, glass fibers are known for their high thermal stability, which can protect the underlying resin matrix from degradation at elevated temperatures. Second, the incorporation of glass fibers can lead to the creation of a thermally stable interphase region at the interface between the fiber and resin matrix. This interphase region can improve the overall thermal stability of 20-PN by preventing degradation in the polymer matrix. Moreover, glass fibers can act as a physical barrier, blocking the diffusion of oxygen and other volatile products during the degradation process. As a result, the likelihood of thermal oxidation and mass loss is reduced. In addition to these mechanisms, the high aspect ratio of glass fibers can also play a crucial role in enhancing the thermal properties of

polymer composites. The elongated shape of the fibers can help distribute stress and improve the mechanical properties of the composite, leading to a more uniform degradation behavior. This enhanced mechanical performance can also contribute to the improved thermal stability of the composite. By increasing the mechanical strength and stiffness of the composite, thermal stability can be enhanced through a reduction in the formation of microcracks and other defects in the composite.

It is important to emphasize that the observed improvement in the thermal properties of PN through glass fiber application is a result of the combined effect of the various underlying mechanisms mentioned above. It is also worth noting that the optimal level of reinforcement required to achieve the desired thermal properties depends on the specific application requirements and the method of manufacture. In summary, the results of the current study suggest that the thermal properties of PN resin can be readily enhanced to reach temperatures as high as 600°C or beyond, contingent on the specific method of reinforcement employed. The use of glass fibers as a reinforcing filler is an effective approach to improve the thermal stability of PN composites, and this could have significant implications for various high-temperature applications.

4 Conclusions

Proper use of curing agents is essential for optimal thermal stability in high-temperature polymers like PN resin. Here, a 20% concentration showed the best physiochemical characteristics. Combining 20-PN with a glass fiber matrix further enhances thermal stability. Upcoming research should focus on refining the curing agent selection and optimizing manufacturing processes. By optimizing the curing process, as well as other manufacturing processes, the PN resin may exhibit extraordinary thermal resistance up to temperatures as high as 600°C. Such remarkable thermal stability makes PN resin an extremely promising material for applications that require withstanding high-temperature conditions.

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