MOLEKUL
eISSN: 2503-0310
Articles
https://doi.org/10.20884/1.jm.2025.20.1.13317

Study on Properties Influence of Carbon Fiber-reinforced Polyimide Composites using Melamine as a Crosslinking Agent

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Received October 07, 2024; **Accepted** January 14, 2025; **Available online** March 20, 2025

ABSTRACT: Advances in carbon fiber reinforced polymer (CFRP) technology remain critical, particularly in meeting the demand for lightweight and durable materials in the transportation industry. With the advent of electric vehicles (EVs), there is a pressing need for composite materials that offer not only exceptional mechanical strength but also high-temperature stability and heat resistance. Polyimide, known for its excellent heat resistance and flame retardancy properties, is an optimal choice for developing such composites. Furthermore, the incorporation of melamine as a crosslinker in polyimide has been shown to significantly enhance its performance. Our study involved the production of a carbon fiber reinforced composite with a melamine crosslinked polyimide matrix (CFMPI), to meet these critical requirements. The composite showed a tensile strength of 84.17 MPa, a tensile modulus of 1899.14 MPa at 1.5% mole substitution of 4,4′-oxydianiline by melamine as a crosslinker for polyimide with thermal stability up to 562 °C. These results indicated that this composite material is highly suitable for use in EVs.

Keywords: advanced composites, carbon fiber reinforced polymer, lightweight materials, melamine-crosslinker, polyimide composites.

INTRODUCTION

The carbon-reinforced polymer has been a subject of increasing interest in recent years, driven by their enviromental sustainability, advancements in manufacturing, increasing demand in aerospace, defence, and sport automotives (Butenegro et al., 2021; Nagendra et al., 2023; Yang & Ji, 2018). Despite significant progress, carbon fiber-reinforced polymer (CFRP) composites with an epoxy matrix, a thermosetting resin, are known to have only heat stability to 150 °C. In addition, the composite is prone to brittle failure behavior, delamination, weak interface, low damage resistance to impact, poor wettability, and fatigue resistance (Zhao et al., 2022). This gap has significant implications for the performance of CFRP, which is starting to be considered a material for engine components, heat shields, and electronic components (Almushaikeh et al., 2023).

Recent studies have made notable contributions to our understanding of carbon fiber-reinforced polymer using polyimide (CFRPI) as their matrics. For instance, Wang et al. reported their research on the impact properties enhancement of hybrid composites using carbon fiber and polyimide fiber as reinforcement. They found that the use of hybrid fibers reduced the density of the composite material by up to 20% and increased the impact properties by up to 22% (Wang et al., 2021). Liu et al. showed that surface modification using metal mesh can reduce the resistivity of the composite so that it is suitable for application as a high-temperature resistant composite and requires low electrical resistance (H. Liu et al., 2023). However, these studies have also revealed limitations and uncertainties that warrant further investigation. Specifically, the current carbon fiber-reinforced polymer (CFRP) with an epoxy resin matrix is unable to withstand temperatures above 150 °C. Additionally, the use of polyimide and carbon fiber hybrids fails to enhance tensile strength. This highlights the pressing need for advancements in polyimide resin to overcome the limitations in tensile strength of carbon fiber-reinforced polyimide composites. A comprehensive review of the literature reveals that the use of melamine as a crosslinker can increase the tensile strength and reduce the surface hydrophobicity of carbon fiber-reinforced polyimide composite materials (Chen et al., 2022; Dayarian et al., 2023; S. Liu et al., 2021).

This research aims to investigate the relationship between melamine content and their impact on tensile, thermal stability, and hydrophilic properties. Based on a thorough analysis of the existing literature and preliminary findings, we hypothesize that partial replacement of ODA with melamine will form a cross-linked polyimide with melamine as the cross-linking agent. The use of melamine cross-linked polyimide as a carbon fiber composite matrix (CFMPI) will produce CFRPI that is stable at temperatures above 350 °C, has high tensile strength and is hydrophilic. Our study seeks to contribute to the existing body of knowledge through the use of melamine-crosslinked polyimide as a matrix for CFRP.

EXPERIMENTAL SECTION

Materials

The carbon sheet used was commercial 2×2 twill 3K 220 gsm carbon fiber. Pyromellitic dianhydride (PMDA) 97%, 4,4'-oxydianhydride (ODA) 97%, melamine (mel) 99%, and dimethyl formamide (DMF) 99.8% were obtained from SigmaAldrich through local Indonesian distribution.

Procedure

Cross-linked polyimide resin was prepared by adding ODA, PMDA, and mel sequentially into DMF under inert gas flow with the composition in **Table 1**. Each addition of material was made after the previous material had completely dissolved. The polyimide resin was cast on a clean glass surface, left for five minutes at room condition, and then soaked in water until the film sheet was released. The obtained film sheet was then dried in a 65 °C oven. The cross-linking agent membrane was made by using phase inversion method (Ahmad et al., 2012). Membrane printing solutions consist of cross-linking agent membranes withvarying concentrations of 10, 12, 14, 16, and 18 wt% with cross-linking agent mass needed are 1.1, 1.4, 1.6, 1.9, and 2.2 g, respectively. They were dissolved in 6.8 mL of DMSO, 2.3 mL of acetone, 0.5 mL of DMP in stirring condition(400 rpm) until the solution was homogeneous. The printing solution was allowed to settle and remove airbubbles, then poured into a glass plate mold and dipped immediately in a coagulation bath. The obtained membrane was washed with water to remove any remaining solvents and additives.

Characterization

To obtain the characteristics of the carbon fiber reinforced melamine cross-linked polyimide composite material, analysis using infrared absorption spectroscopy (FTIR, FT/IR-4600, Jasco, Japan) from 450 cm^{-1} to 4000 cm^{-1} of wave number. The tensile test, was done with a universal testing machine (UTM, Toyoseiki Strograph VGS 5-E, Japan) followed ASTM D3039 Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials based on this standard, the length of the test specimen is 175 mm, the grip length is 25 mm, as shown in **Figure 2** (ASTM D3039, 2017). Thermal gravimetry (TG-DTA, TG-DTA 8120, Rigaku, Japan) from room temperature to 900 °C, and determination of the contact angle with a drop of water (digital microscope, Keyence VHX-500, United State of America).

Table 1. The composition of polyimide (PI) and melamine-crosslinked PI (MPI) precursors

	PMDA (g)	ODA (g)	Melamine (g)	DMF (g)
PI	1.454	1.335	0.000	20.494
0.5% MPI	1.454	1.325	0.004	20.451
1.0% MPI	1.454	1.315	0.008	20.409
1.5% MPI	1.454	1.305	0.013	20.366

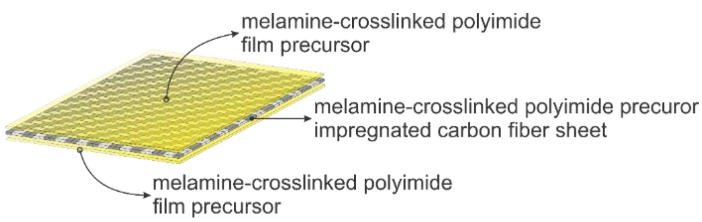

Figure 1. Illustration of MPI-CF-MPI sandwich arrangement in the manufacturing process of carbon fiber reinforced melamine crosslinked polyimide composite material (CFMPI).

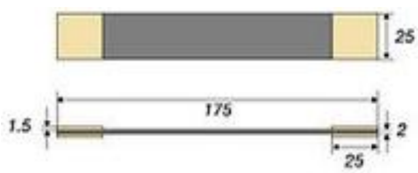

Figure 2. Dimension of the specimen based on ASTM D3039 (ASTM D3039, 2017)

RESULTS AND DISCUSSION

In the initial process, namely the synthesis of polyimide precursors and melamine-crosslinked polyimide, each addition of 1 molecule of melamine will reduce 1.5 molecules of ODA. This was determined to ensure that all PMDAs will bind to ODA and melamine. It is known that the polyimide chain is formed from the cleavage of the anhydride bond in PMDA by an amine group followed by the release of an ─OH group from the amide group and an H from the amine when the imidization process is carried out until a water molecule is released. Furthermore, because ODA has two amine groups and three amine groups in melamine, each addition of one molecule of melamine must be followed by a reduction of one and a half molecules of ODA (**Figure 3**).

Before coating the carbon fiber sheet, analysis was carried out on the polyimide film precursor (PAA) and melamine cross-linked polyimide film precursor (MPAA). In addition, it was also carried out on the polyimide film (PI) and melamine cross-linked polyimide film (MPI). This was done to ensure that the precursors had been synthesized and then, to ensure that all precursors had been imidized into polyimide. In the FTIR spectrum analysis, in addition to observing the presence of each infrared absorption peak formed, attention was focused on the disappearance of the -OH, C=O, and C-N functional groups from amides in the FTIR spectra of MPAA, and the appearance of C=O and imide ring absorption peaks in the FTIR spectra of MPI (**Table 2**). The imine functional group from melamine is not visible in the spectrum, this could be due to its very small amount. The triazine ring which should appear at wave numbers 813, 1550, and 1654 cm^{-1} overlaps with the absorption peaks of ether and C=O as well as C-N amide, therefore the FTIR spectrum of MPI and MPAA is the same as the FTIR spectrum of PI and PAA (**Figure 4**) (Zhu & Xu, 2018).

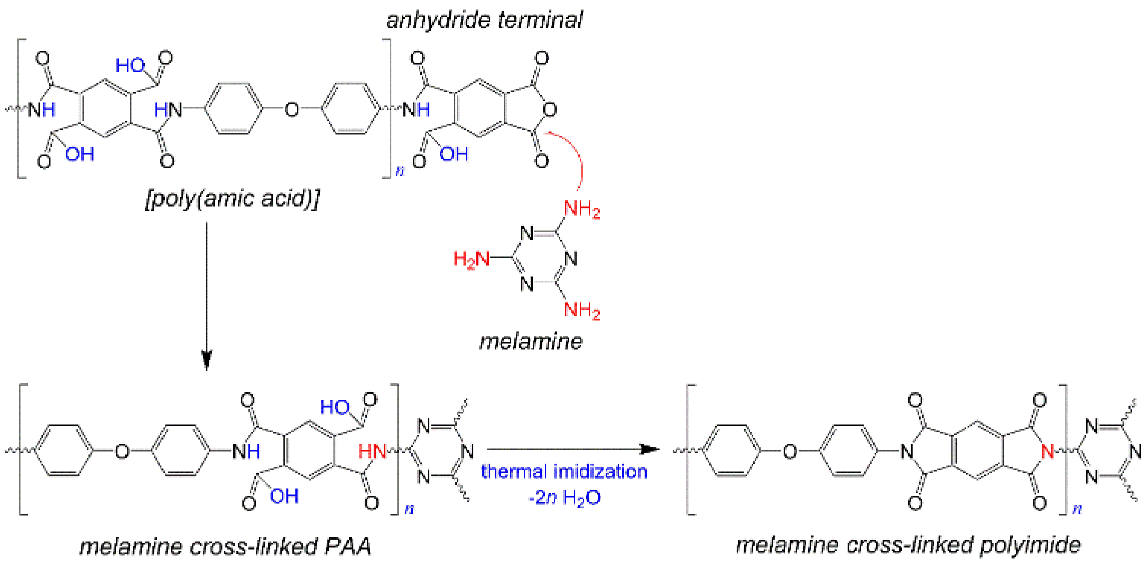

Figure 3. A plausible melamine-crosslinked polyimide reaction.

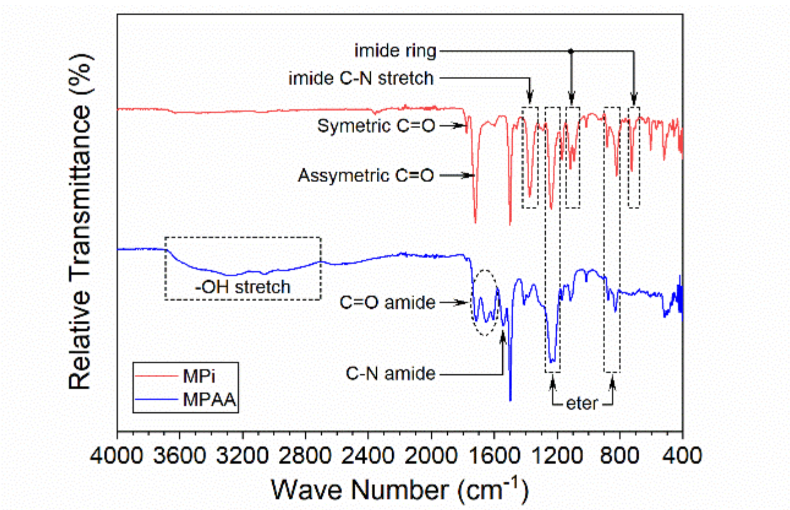

Figure 4. FTIR spectrum of melamine-crosslinked polyimide precursor (MPAA) and melamine-crosslinked polyimide (MPI).

One of the problems that arise in using PI as a matrix for carbon fiber-reinforced polymer composites is the hydrophobic nature of PI which will result in weak interactions between the matrix and the reinforcing material (Soon et al., 2013; Yang & Ji, 2018). By using melamine as a cross-linking agent that is rich in lone pair electrons, it was found in this study that the hydrophobicity of PI decreased with the increasing addition of melamine (**Figure 5**). The composite with a melamine content of 1.5% showed the smallest contact angle with an average value of 65.4 ° (more complete data are in the supplementary file).

One of the main purposes of using melamine-crosslinked PI as a matrix for CFRPI is to increase the thermal stability higher than epoxy resin. Through observation of TG-DTA thermograms, it was found that PI degraded at a temperature of 513 °C. Adding melamine at 0.5, 1.0, and 1.5% increased the thermal stability to 518, 532, and 562 °C, respectively, according to the equation $y = 25x^2 - 53x + 513.35$, where y is the degradation temperature (°C) and x is the mole percentage of melamine added (**Figure 6**).

Table 2. Peak list of FTIR spectrum of MPI and MPAA

Sample	Wave Number (cm^{-1})	Vibration	Ref.
Poly(amic acid)	2750-3680	—OH stretching	(Rasheed & Kareem, 2020)
	1600, 1650, 1715	C=O amide	(Rasheed & Kareem, 2020)
	1545	C—N amide	(Rasheed & Kareem, 2020)
	830, 875 and 1220, 1240	Eter	(Rasheed & Kareem, 2020)
Polyimide	1775	Symetric C=O	(Kizil et al., 2014; Van De Velde & Kiekens, 2002)
	1720	Assymetric C=O	(Cai & Neyer, 2010; Van De Velde & Kiekens, 2002)
	1375	Imide C-N amide	(Kizil et al., 2014; Van De Velde & Kiekens, 2002)
	820, 880 and 1239	Eter	(Kizil et al., 2014)
	725, and 1090, 1115	Imide Ring	(Cai & Neyer, 2010)

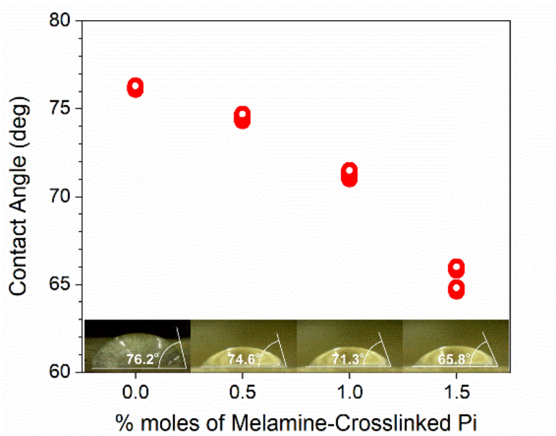

Figure 5. Contact angle of water and melamine-crosslinked polyimide films.

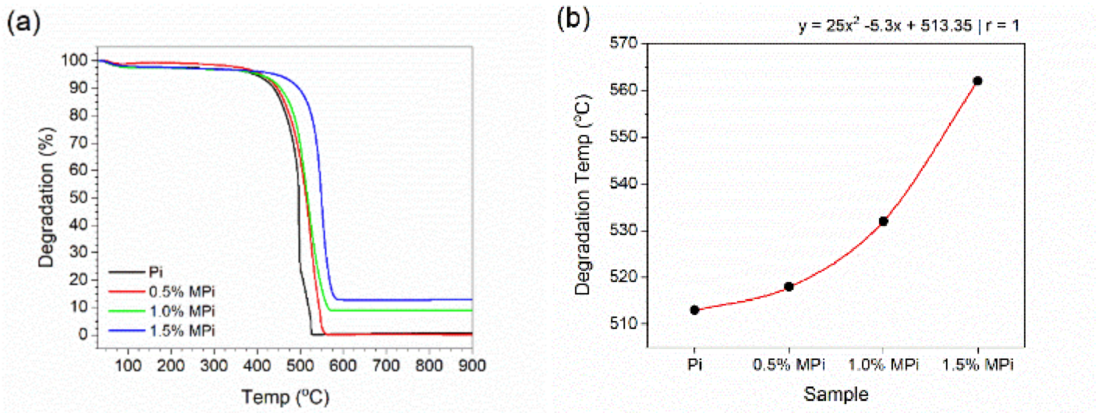

Figure 6. (a) TGA thermogram of polyimide film (PI) and melamine-crosslinked polyimide films (MPI) and (b) relationship curve of degradation temperature to the percentage of moles of melamine used as a cross-linking agent.

Tensile properties of carbon fiber reinforced polyimide (CFPI) and carbon fiber reinforced melamine-crosslinked polyimide (CFMPI) composites was determined using the technique as per ASTM D3039 standard. The tensile properties of all samples were tested in different CFPI and CFMPI plates using five experimental specimens from each series. The results of the tensile strength test are shown in **Figure 7**. From the plot, it can be seen that the use of melamine as a crosslinker can increase the tensile strain. Using equations 1-3 shows that the replacement of ODA by melamine as much as 0.5% mol decreases the tensile strength and tensile modulus. Furthermore, adding more melamine can increase it, and is better than pristine PI.

$$\text{Tensile Strain } (\%) = \frac{\Delta L}{L_0} \times 100\% \quad \text{(Equation 1)}$$

$$\text{Tensile Strength}, \sigma = \frac{\text{Load}}{A} \quad \text{(Equation 2)}$$

$$\text{Tensile Modulus}, \varepsilon = \frac{\sigma}{(\Delta L/L_0)} \quad \text{(Equation 3)}$$

where ΔL is the stroke (m), L_o is initial length of sample (m), and A is testing area (m^2). The results of the detailed calculations can be obtained in the supplementary file. The average values of the test results are presented in **Table 3** and **Figure 8**.

By plotting the tensile properties, it is shown that the tensile strength of the composite increases with the increase of melamine mole percentage as crosslinker of polyimide more than 1.0%, but the modulus strength becomes higher than pristine polyimide after the melamine percentage is above 1.5%. However, the use of melamine as crosslinking agent for polyimide shows improvement in tensile properties though tensile properties decreases At percentage of melamine 0.5%, this occurred because melamine may not form strong chemical bonds with the composite matrix, leading to weak interfaces that can initiate micro-cracks under tensile stress (Voigt et al., 2003).

The composite mechanical and thermal characteristics were compared with the standard specifications for automotive applications. According to the findings, this composite modulus and tensile strength are suitable for non-structural automotive components like dashboards and interior parts. Still, they are insufficient for structural components which require much higher values (Fitri et al., 2021). In particular, the composite tensile strength (84.17 MPa) and tensile modulus (1.899 GPa) fulfill the rigidity and strength requirements for structural applications but it does not meet the requirements for interior and non-load-bearing components (Fitri et al., 2021). On the other hand, the composite thermal stability (562 °C) significantly surpasses the usual automotive standards indicating its potential for application in high-temperature settings like engine parts (Alshammari et al., 2021). According to these results, the composite material is better suited for uses where heat resistance is crucial but additional mechanical property improvement would be required to satisfy the requirements of structural elements in automotive design (Alshammari et al., 2021). The comparison for automotive applications is shown at the **Table 4**.

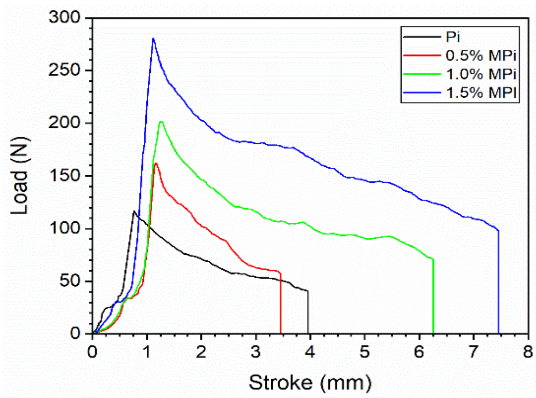

Figure 7. Tensile strength plot of carbon fiber reinforced polyimide (PI, black line), carbon fiber reinforced 0.5% melamine-crosslinked polyimide (0.5% MPI, red line), carbon fiber reinforced 1.0% melamine-crosslinked polyimide (1.0% MPI, green line), and carbon fiber reinforced 1.5% melamine-crosslinked polyimide (1.5% MPI, blue line).

Table 3. Average tensile properties of CFPI and CFMPI samples

Sample	Width, *w* (mm)	Gauge, L_0 (mm)	Stroke, ΔL (mm)	Load, *F* (N)	Tensile Strain (%)	Tensile Strength, σ (MPa)	Tensile Modulus, *ε* (MPa)
PI	3.00	25.0	0.76	116.28	2.98	51.27	1695.43
0.5% MPI	3.00	25.0	1.17	162.44	4.61	46.20	985.50
1.0% MPI	3.00	25.0	1.26	202.82	4.97	53.75	1061.23
1.5% MPI	3.00	25.0	1.11	279.78	4.36	84.17	1899.14

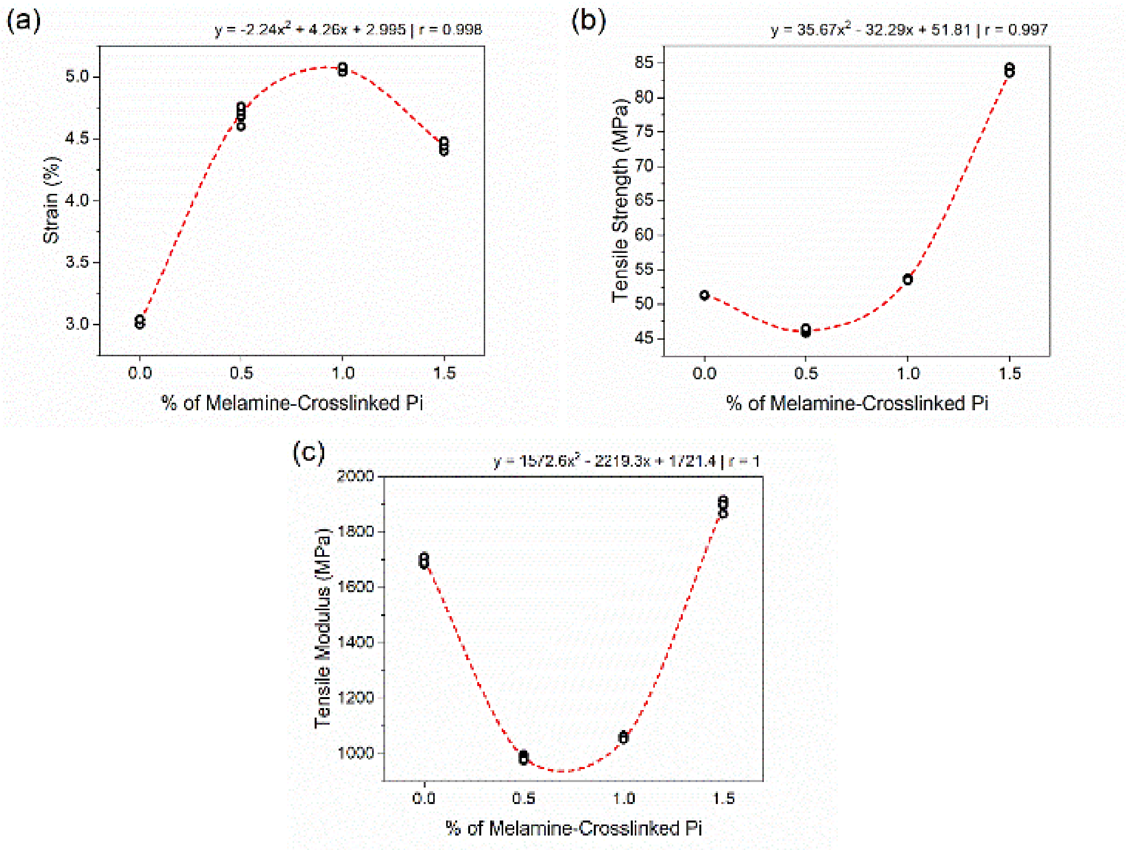

Figure 8. Plot of average strain, where *y* was strain (%) and *x* was the percentage of moles of melamine used as a crosslinking agent (**a**), tensile strength, where *y* was tensile strength (MPa) and *x* was the percentage of moles of melamine used as a crosslinking agent (**b**), and tensile modulus, where *y* was tensile modulus (MPa) and *x* was the percentage of moles of melamine used as a crosslinking agent (**c**) of carbon fiber-reinforced melamine cross-linked polyimide. Each sample was tested five times for different specimens.

Table 4. The comparison the findings and requirements for automotive application

Property	Your Composite	Automotive Requirements
Tensile Strength	84.17 MPa	Interior Parts: 20–40 MPa (Fitri et al., 2021) Dashboard: 30–110 MPa Structural Components: 400–800 MPa (Fitri et al., 2021)
Tensile Modulus	1.899 GPa (1899.14 MPa)	Interior Parts: 1.0–2.5 GPa (Fitri et al., 2021) Structural Components: 50–150 GPa (Fitri et al., 2021)
Thermal Stability	562 °C	General Applications: 200–300 °C (Alshammari et al., 2021) High-Temperature Applications: Up to 400 °C (Alshammari et al., 2021)

CONCLUSIONS

The composite of melamine crosslinked polyimide reinforced with carbon fiber (CFMPI) with a content of 1.5% melamine showed the advantages of carbon fiber-reinforced polymer composites. This composite had a water contact angle of 65.4 °, indicating a decrease in hydrophobicity, which allowed it to interact well with carbon fiber. In addition to having thermal stability up to 562 °C, this composite has a tensile strength of up to 84.17 MPa with a strain of 4.36% and a modulus of 1899.14 MPa. Thus, this study shows that the use of melamine crosslinked polyimide with an amount of 1.5% mol and more can be used as a CFRP matrix for body and automotive components materials.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Education, Culture, Research, and Technology of the Republic of Indonesia for funding this research with contract No. 778/PP/STT-WKN/PWK/VI/2024 and the Research Center of Polymer Technology of the

National Research and Innovation Agency of Republic of Indonesia (*BRIN*) for its facilities for guidance, as well as measurement and characterization of research results.

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