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THERMAL ANALYSIS AND MICROSTRUCTURAL STUDY ON PHENOL COATED CFRP LAMINATES WITH ZrO_2- GRAPHENE FILLERS

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Abstract: This study focuses on the microstructural investigation of phenol-coated Carbon Fiber Reinforced Polymer (CFRP) laminates incorporated with Zirconium Oxide (ZrO2) and graphene fillers, fabricated using the Vacuum Resin Transfer Molding (VRTM) process. The objective is to explore the effects of these fillers on the laminate's mechanical, thermal, and chemical properties. The study utilizes various characterization techniques such as Scanning Electron Microscopy (SEM). The laminates were fabricated using a vacuum-assisted resin transfer molding (VARTM) process, incorporating varying concentrations of ZrO_2 (0.5–2 wt%) and graphene (0.5–2 wt%) fillers. The results revealed that a synergistic combination of ZrO_2 and graphene fillers significantly improved the dispersion uniformity and interfacial bonding, resulting in enhanced mechanical properties such as tensile strength, modulus, and fracture toughness. Furthermore, thermal analysis indicated improved thermal stability and resistance to degradation at elevated temperatures. This study demonstrates the potential of hybrid ZrO_2-graphene fillers to optimize the performance of phenol-coated CFRP laminates for advanced structural applications, including aerospace and automotive industries.

Keywords: CFRP laminates, Phenol, SEM, ZrO2, graphene fillers.

1.Introduction

Carbon-fiber-reinforced composite materials have been known to be useful for the purpose of ablation resistance Specially, in moderate ablation environments, the carbon–phenolic (C–Ph) composites are considered extensively to be efficient ablative thermal protection materials [1]. For C-Ph composites to endure air ablative conditions as long as feasible, it is desirable if the matrix and fiber reinforcement can keep their original structure, properties, and shape. Thus, enhancing the ablative characteristics and high-temperature mechanical capabilities of C-Ph composites is an immediate necessity [2]. Facil impregnation with natural rubber solution changes the carbon-fiber surface. Lightweight and pliable, these composites are made of modified carbon fiber and phenolic resin. In addition to thermal insulation and flexural strength, the study looked into ablation and thermal characteristics [3]. The optimized carbon-fiber/phenolic-resin composites showed more strain during fracture and less flexural modulus after the modifications. Furthermore, they displayed remarkable ablation, thermal insulation, and low-density qualities. New carbon-phenolic ablative age ushered forth by these innovations [4]. When coming to Earth, decomposition gas mixtures consist of air are formed, whereas when returning to Mars, CO2 gas combinations are made. A passive thermal-protection system including layers of carbon-phenolic ablative material was evaluated for its thermal-insulation qualities using a model of transient heat conduction. By analyzing the mass loss and gas components produced during pyrolysis, this work delves into the pyrolysis properties of carbon-phenolic composites [5].To improve these drawbacks, fillers with ZrO2 and graphene have been used. These fillers are said to improve thermal conductivity, strengthen mechanical properties, and resist environmental attack. Flame-retardant, chemically-stable and thermally-resistant phenolic resins are applied to the surface of the CFRP laminate. Nevertheless, the performance of phenolic-coated CFRP laminates is improved with advanced fillers like ZrO2 and graphene in demanding environments.

1.1 Advantages of Phenol Coated CFRP Laminates with VRTM Process:

Phenol coatings improve the CFRP's resistance to high temperatures, making it suitable for use in extreme environments. The phenolic coating ensures that the CFRP laminates perform well in chemically aggressive environments, extending their lifetime. The VRTM process allows for complex shapes and sizes, making it ideal for custom applications in industries such as aerospace, automotive, and energy. VRTM typically results in smooth surfaces with fewer defects, which is important for aesthetic and functional purposes.

2. Literature Review

Phenol-coated Carbon Fiber Reinforced Polymer (CFRP) laminates have attracted interest because of their excellent fire resistance, thermal stability, and chemical durability. To increase the service life and efficiency of these materials, the microstructural characteristics need to be understood. This review focuses on the microstructure of phenol-coated CFRP laminates and how it affects their performance. Kumar, A.; Ranjan **[6]** This study focuses on recent advancements in carbon-and-phenolic and carbon-and-elastomeric composites, considering factors such as erosion speed; high-temperature resistance; tensile, bending, and compressive strength; fiber–matrix interaction; and char formation.Yafeng Li, Jinru Sun **[7]** In their study on the damage behaviour of CFRP laminates exposed to impulse lightning current. Measurement of near-field lightning mechanical impact on the CFRP laminates was achieved by a self-established device that effectively overcome the strong electromagnetic inference.Sayam, A., Rahman **[8]** This study has thoroughly reviewed the contemporary progress in the field of carbonaceous fillers reinforced polymer matrix composites' mechanical properties, their structural applications and critically analyzed some widely used manufacturing methods. At first, the mechanical performance of carbon fiber-reinforced polymer composites was analyzed. Abdulganiyu, I.A et al **[9]** The present study investigated the dynamic impact properties of carbon-fiber-reinforced phenolic composites (CFRPCs) modified with microfillers. The CFRPCs were fabricated using 2D woven carbon fibers, two phenolic resole resins and two microfillers. Li et al.**[10]** have been carried out on the dynamic mechanical properties of plain CF-reinforced polymer composites, there is little information on the dynamic impact behaviour of microfiller-modified CFRPCs Tayyab Subhani**[11]** In their study to Carbon fiber phenolic matrix composites were manufactured with nanometer and micrometer sized particulate reinforcements, i.e. carbon nanotubes and silicon carbide particles, so as to investigate the individual and combined effect of the reinforcements on the microstructural evolution and mechanical performance of the composites.Sakthi Balan, G et al **[12]** This study focuses on Carbon Fiber Reinforced Polymers (CFRPs) have revolutionized material science due to their exceptional strength-to-weight ratio, stiffness, and durability. However, the continuous pursuit of enhanced performance has led researchers to explore innovative techniques to further optimize the microstructure of these materials. Ding et al. **[13]** reported that the zirconium silicide modified C/Ph composites formed a mixed layer of solid phase zirconia (ZrO2) and liquid phase silica on the ablative surface, preventing the oxygen component from diffusing into the interior of materials. Amirsardari et al. **[14]** investigated the effects of GO and zirconium boride (ZrB2) on thermal stabilities of C/Ph composites. The presence of ZrB2 with formation ZrO2 in C/Ph composites could decrease the ablation rate, and protect the underlying unoxidized material from the structural damage caused by ablation.Subha, S., Singh, D **[15]** In this study is to investigate the ablation, mechanical properties of carbon-phenolic/Zirconia (Zr) based nanocomposites. The multi walled carbon nano tubes (CNT) tubes and Graphene nanoplatelets (GNP) fillers were synthesis with Zr using Sol-gel process. Composite samples with varying the nano-fillers loading (0.05 wt.% to 0.1 wt.%) were prepared by hand-layup method. Srikanth et al. **[16]** manufactured the high ablation resistance rayon-based carbon–fabric/phenolic composites using nanosilica powder as a filler material. Nanosilica filled carbon–phenolic composite exhibited higher ablation resistance compared to the unfilled composite.Aidin Mirzapour et al. [17] studied the effect of nanosilica on the mechanical, thermal and ablation properties of chopped carbon fibre/phenolic composites. They observed better thermal stability and ablation response in nano-modified samples. Joung-Man Park et al. [18] evaluated the effects of carbon nanotubes and carbon fiber reinforcements on thermal conductivity and ablation properties of carbon/phenolic composites. Both carbon fiber mat and CNT/phenolic composites exhibited much better thermal conductivity and ablation properties than that of neat phenolic resin. Zuo-Jia Wang et al. **[19]** indicated that the uniformity of the CNT dispersion played an important role in the ablation resistance of CNT filled phenolic composites. Zahra Eslami et al. **[20]** investigated the thermal, mechanical and ablation properties of carbon fibre/phenolic composites filled with multiwall carbon nanotubes (MWCNTs). The linear and mass ablation rates of the nanocomposites were distinctly decreased after modified with small amount of MWCNTs. To address these issues, the incorporation of fillers such as Zirconium Oxide (ZrO2) and graphene has been explored. These fillers are known to enhance thermal conductivity, improve mechanical properties, and provide better resistance to environmental degradation. Phenolic resins are often used as coatings for CFRP laminates to improve their fire resistance, chemical stability, and thermal resistance. When combined with advanced fillers like ZrO2 and graphene, phenolic-coated CFRP laminates exhibit enhanced performance in demanding environments.

3.Methodology

The VRTM process was utilized to fabricate the composite laminates. In this process, the carbon fiber preforms are placed inside a closed mold, and a vacuum is applied to remove air from the mold. Then, the phenolic resin containing varying concentrations of ZrO2 and graphene fillers is injected into the mold. The resin is allowed to cure, forming the final composite laminate

Materials: The material preparation step ensures that all components, including phenolic resin, ZrO_2 nanoparticles, graphene nanoplatelets, and CFRP laminates, are in an optimal state for effective coating

1. **Phenolic Resin:** Resol (liquid) or novolac (powder or pre-polymerized liquid, requiring a hardener like hexamethylenetetramine).
2. **ZrO_2 Nanoparticles:** Particle size 50–200 nm.
3. **Graphene Nanoplatelets:** High aspect ratio flakes (e.g., 1–5 µm lateral size and <10 nm thickness).

3.1 Preparation of Filler-Resin Composite

The preparation of a filler-resin composite involves steps to ensure a homogeneous mixture of fillers (ZrO_2 nanoparticles and graphene) within the phenolic resin matrix. Phenolic resin is mixed with varying concentrations of ZrO2 nanoparticles and graphene sheets. The fillers are dispersed in the resin through mechanical stirring, ultrasonic treatment, or other dispersion techniques to ensure a uniform distribution. The concentration of fillers can vary depending on the desired properties of the final composite. For instance, a higher concentration of ZrO2 may improve thermal stability, while increased graphene content could enhance mechanical strength This is critical for achieving optimal dispersion and ensuring the final composite exhibits the properties

- Weigh ZrO_2 and graphene fillers in the desired proportions (e.g., 0.5–5 wt% each).
- Use a solvent like acetone, ethanol, or toluene to assist in dispersion.
- Employ ultrasonication for 30–60 minutes to achieve homogenous dispersion of ZrO_2 and graphene in the solvent.

- Add the dispersed fillers to the phenolic resin gradually while stirring.
- Continue mixing using a high-shear mixer to ensure uniform filler distribution in the resin.
- Degas the resin mixture under vacuum to remove trapped air bubbles.

3.2 Vacuum Resin Transfer Molding (VRTM) Process

Vacuum Resin Transfer Molding (VRTM) is a composite manufacturing technique used to produce high-performance fiber-reinforced polymer composites. It is a closed-mold process where resin is drawn into a dry fiber preform using a vacuum

1. **Mold Setup:** The setup for fabricating Vacuum Resin Transfer Molding (VRTM) composites with Zirconium Oxide (ZrO2) and Graphene Fillers involves careful preparation of materials, equipment, and the infusion process. Below is a step-by-step guide to setting up a VRTM process for fabricating these advanced composite materials.
2. **Resin Injection:** A vacuum is applied to remove air from the mold, and then a resin (in this case, phenolic resin) is injected into the mold, impregnating the fiber preform.
3. **Curing:** Once the resin is injected, the composite material is allowed to cure, either at room temperature or with additional heat, depending on the resin used. The process creates a fully consolidated, high-strength laminate.

4. Results And Discussions

SEM images reveal the distribution of ZrO2 and graphene within the phenolic resin matrix. The ZrO2 particles appear as uniformly dispersed nanoparticles within the resin, forming a reinforcing phase that enhances the thermal stability of the composite. Graphene sheets are well integrated into the resin matrix, providing enhanced interfacial bonding between the carbon fibers and the matrix. At higher graphene concentrations, agglomeration tends to occur, but the overall distribution remains relatively uniform, ensuring that the graphene sheets are effectively integrated to improve the mechanical properties of the CFRP laminate

Microstructure analysis

SEM analysis revealed uniform dispersion of ZrO_2 and graphene within the phenolic matrix, contributing to the improved material properties. The phenol coating enhanced the adhesion between the CFRP and fillers, minimizing delamination

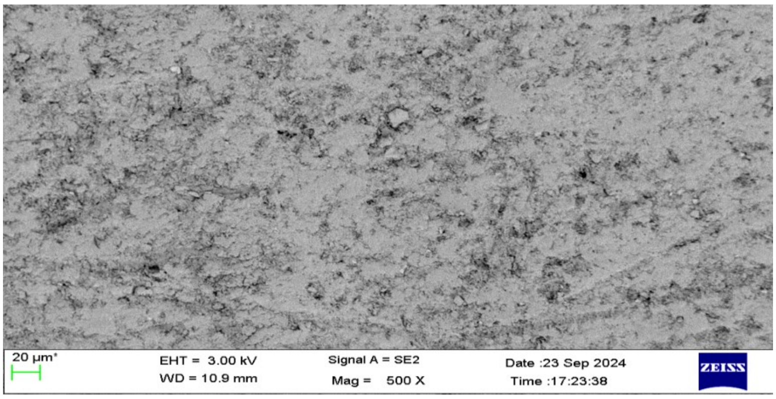

Fig1: phenol coating CFRP Laminate-1

The micrograph shows distinct phases or regions that might correspond to ZrO_2 or graphene fillers. At 500× magnification, filler clumping is not overtly evident, but finer magnifications might reveal agglomeration. Examine regions at higher magnifications (e.g., 1,000×–5,000×) for detailed filler-matrix interaction, filler morphology, and any nanoscale defects.

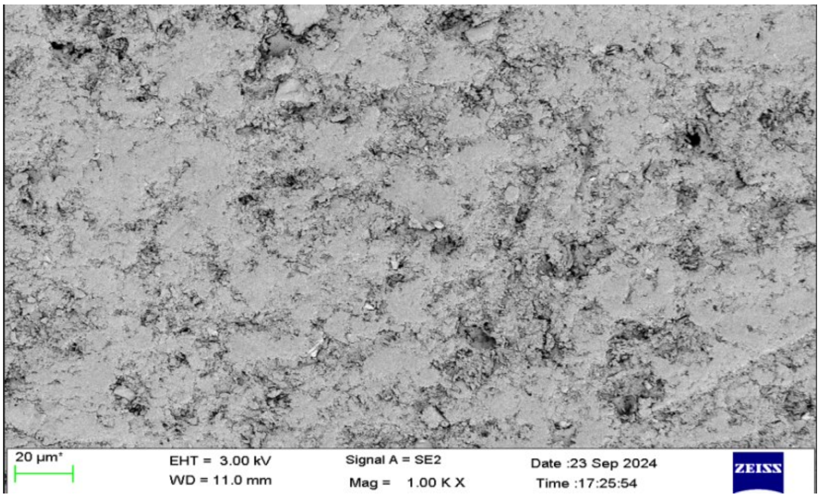

Fig 2: phenol coating CFRP Laminate-1.5

The image you provided is a scanning electron microscope (SEM) image of a carbon fiber reinforced polymer (CFRP) laminate with a phenol coating. The magnification is 1,000 times (1.00 K X). The matrix of the CFRP laminate appears as a darker, more porous material. This matrix is likely made of a polymer resin, such as epoxy.

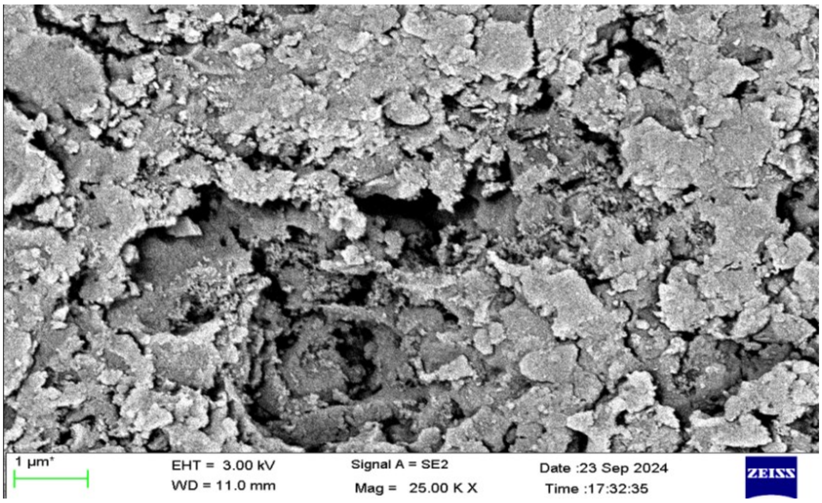

Fig3: phenol coating CFRP Laminate-3

To analyze the SEM image you provided, which appears to be a closer look at a phenol-coated CFRP laminate interface between the phenol coating and the CFRP matrix is not clearly distinguishable at this magnification. This suggests that the coating may have good adhesion to the underlying material.

TGA AND DTA Analysis with phenolic

TGA can be used to compare phenolic resin with other resins, such as polyimide and CE. TGA results can show that phenolic resin has a low char yield and decomposition onset temperature. TGA is a combination of gravimetric analysis and oven drying. It records the weight of a specimen and the temperature of an oven until the specimen reaches a constant weight. TGA can be connected to a computer for data processing and analysis. DTA can be used to study the thermal degradation of a phenolic polymer, including the weight loss and the gases evolved at different temperatures

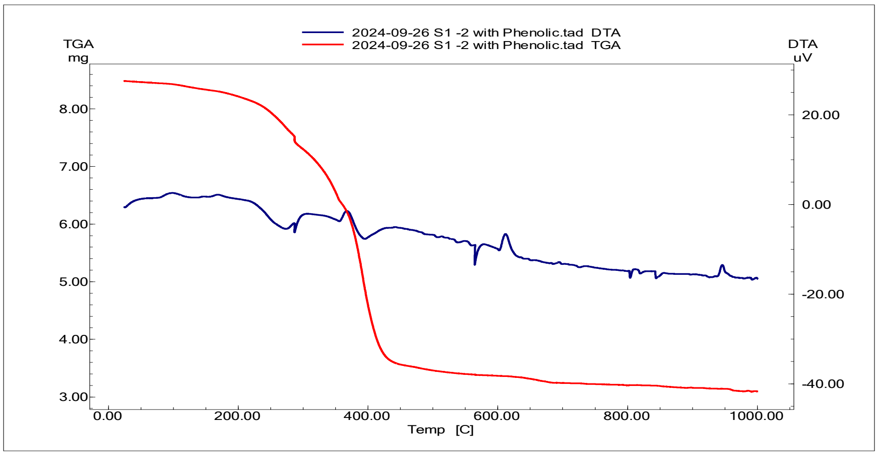

Fig 4: Validation sample-1 TGA & DTA

The DTA curve shows the difference in temperature between the sample and a reference material as a function of temperature. In this case, the temperature difference is plotted against temperature in degrees Celsius

Major Weight Loss (Around 200-500°C): This significant weight loss indicates the decomposition or degradation of the sample's components. The rate of weight loss increases rapidly, suggesting a thermal event like melting or decomposition.

Exothermic Peak (Around 200-500°C): This peak corresponds to the major weight loss observed in the TGA, indicating an exothermic process like decomposition or oxidation.

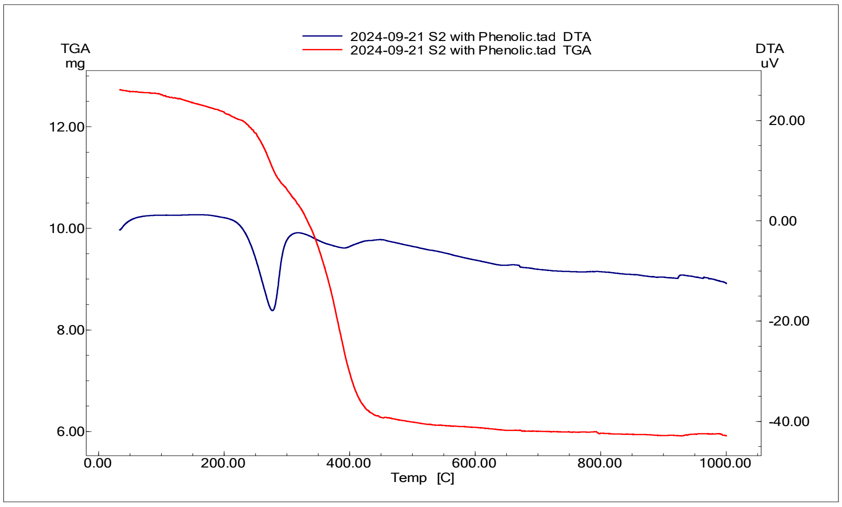

Fig 5: Validation sample-2 TGA & DTA

The combination of the TGA and DTA curves shows that there are numerous stages of heat deterioration in the sample. Decomposition occurs at temperatures between 200 and 500 °C, after which the initial weight loss occurs as a result of moisture evaporation. The sample has apparently stabilized after the decomposition process, as indicated by the last plateau region.

The Major Weight Loss (Around 200-500°C) The significant weight loss indicates the decomposition or degradation of the sample's components. The rate of weight loss increases rapidly, suggesting a thermal event like melting or decomposition.

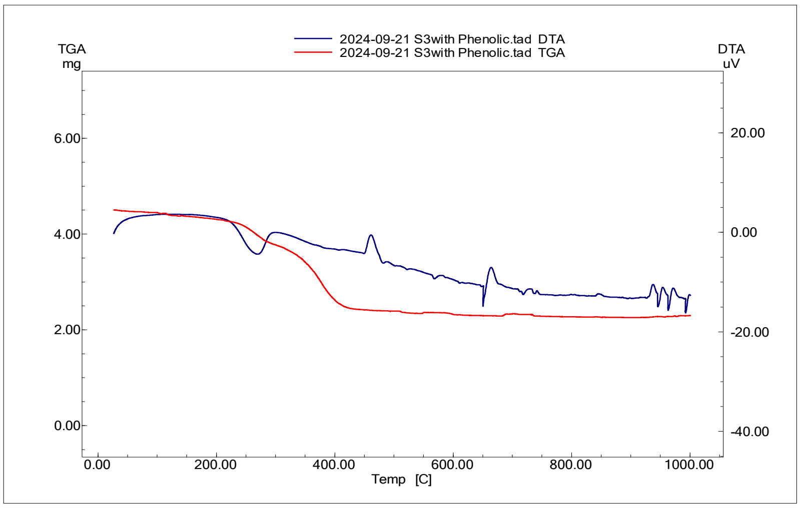

Fig 6: Validation sample-3 TGA & DTA

The differential thermal analysis (DTA) curve plots the temperature difference between a sample and a reference material against time. Several steps of heat deterioration are shown by the combined TGA and DTA curves for the sample. Evaporation of water causes the first loss of mass, and then, between 200 and 500 degrees Celsius, there is substantial breakdown. The sample has apparently stabilized after the decomposition process, as indicated by the last plateau region.

DSC Analysis:

Differential Scanning Calorimetry) analysis is a thermal analysis technique used to study the thermal properties of materials. DSC measures the heat flow into or out of a sample as it is heated or cooled. This heat flow is related to the thermal properties of the material, such as melting points, glass transition temperatures, and heat capacities

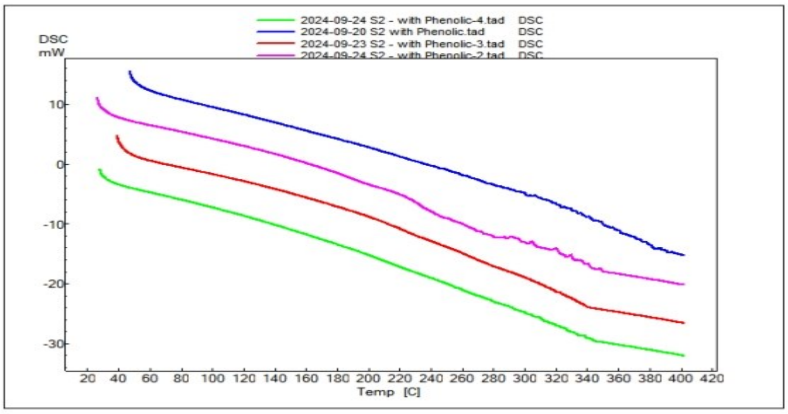

Fig 7: Validation of with phenolic - DSC

This figure appears to represent a Differential Scanning Calorimetry (DSC) thermogram. DSC is commonly used to study thermal transitions of materials, such as melting points, glass transition temperatures, and thermal stability

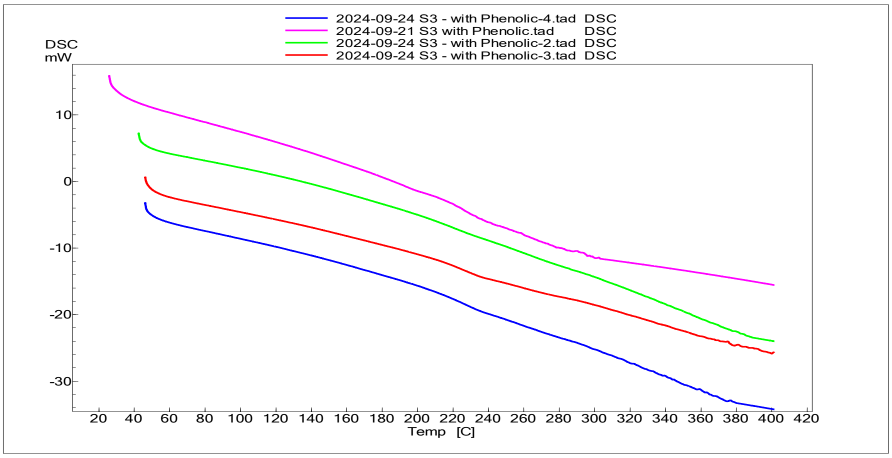

Fig8: Validation of with phenolic - DSC

Above figure The DSC thermogram compares the thermal behavior of four different samples, each labeled with specific phenolic modifications (Phenolic:4, Phenolic:1, Phenolic:2, Phenolic:3)

- Phenolic:1 is the most thermally stable sample, maintaining integrity at higher temperatures.
- Phenolic:4 shows the least thermal stability, with earlier degradation.
- Phenolic:2 and Phenolic:3are intermediate, with slight variations likely due to chemical structure or composition.

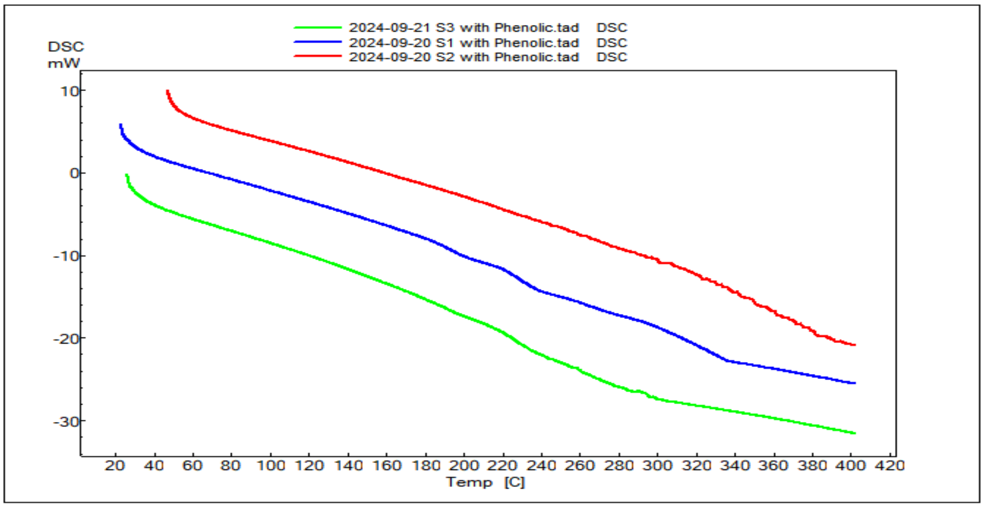

Fig 9: Validation of with phenolic - DSC3S

Above figure The DSC3S curves reveal that the three samples have some similarities in their thermal behavior, but there are also distinct differences It's particularly useful in studying the thermal properties of materials, such as their melting point, glass transition temperature, and crystallization behavior.

5.Conclusion

This comprehensive microstructural investigation highlights the potential of ZrO_2 and graphene fillers in phenol-coated CFRP laminates for advanced applications requiring superior thermal, mechanical, and structural properties, Synergistic effects of ZrO_2 and graphene led to a substantial increase in thermal stability, with an optimal combination (1 wt% ZrO_2 + 1 wt% graphene) showing the highest onset degradation temperature and reduced weight loss.

- Microstructural improvements directly correlated with enhanced mechanical properties (e.g., tensile strength, modulus, and toughness) due to better fiber-matrix-filler interactions.
- ZrO_2 nanoparticles contributed to toughness enhancement by absorbing energy and deflecting cracks.
- Graphene improved stiffness and strength due to its exceptional load transfer capabilities
- Improved interfacial adhesion due to complementary filler characteristics (toughness from ZrO_2 and strength/stiffness from graphene).
- Laminates exhibited sharper exothermic peaks in the DSC analysis, indicating improved cross-linking density in the resin due to filler interaction.

Future Recommendations

1. Investigate the long-term durability of ZrO_2 and graphene-reinforced CFRP laminates under fatigue and environmental exposure.
2. Explore alternative coating techniques for improved filler dispersion at higher concentrations.
3. Study the effects of filler functionalization (e.g., surface modification of ZrO_2 and graphene) on interfacial bonding and overall performance.

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