

Poly(imide-melamide-formaldehyde-phenol) Copolymer for Heat Shield Coatings

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Abstract

Poly(trimellitimide-melamide-phenol-formaldehyde) (PTMIMPF) copolymers were synthesized through the condensation of the prepolymer N, N'-(4, 4'-diaminodiphenyl ether) bis trimellitimide diacid chloride with melamine in pyridine and aqueous media, followed by reaction with formaldehyde and phenol using microwave irradiation. The pyromellitimide polymer was synthesized by reacting pyromellitic anhydride with 4,4'-oxydianiline, and subsequently, copolymers of pyromellitimide and trimellitimide-melamine were prepared by in situ polymerization. The molecular structure and thermal properties of the copolymerized polyimides were characterized through various spectroscopic and thermal analysis techniques. Differential scanning calorimetry analysis indicated endothermic melting peaks at 325°C and 570°C for polytrimellitimide-melamine (PTMIM), suggesting its suitability for heat shielding applications. Liquid chromatography-mass spectrometry confirmed the presence of melamine, diaminodiphenyl ether, trimellitic anhydride, and pyromellitic anhydride groups, indicative of the cleavage of bonds within the copolymers. The ¹H nuclear magnetic resonance spectrum of PTMIMPF revealed aromatic -CH₂-N linkages, confirming the condensation polymerization of melamine with formaldehyde-phenol. Aromatic hydrogen peaks for alkyl-substituted benzene rings appeared as multiplets in 6.683-8.275 ppm range. Peaks at 7-7.5 ppm showed unsymmetrical delta H due to aromatic protons, while peaks at 3.695-4.604 ppm indicated the presence of an amide linkage between benzene and melamine. Microstructure and elemental composition analyses of PTMIM, poly(pyromellitimide-melamine), and PTMIMPF copolymers were conducted using energy dispersive X-ray (EDX) spectroscopy and scanning electron microscopy (SEM). To mitigate high heat conduction and erosion, a 2 mm thick coating of thermal insulation polyimide composite (TIPC) of PTMIMPF-SiC-epoxy resin was applied on tungsten pieces layered onto aluminum plates and subjected to infrared heat flux (IR-HF) exposure. The back wall temperature of the TIPC-coated aluminum plate remained at 69°C after 150 seconds of exposure to 10 W/cm² of IR-HF. SEM and EDX analyses before and after the IR-HF exposure revealed larger solid aggregates of trimellitimide connected with phenol formaldehyde and thinner molecules of biphenyl ether, forming a smooth, homogeneous polymer char surface post-exposure that reduced heat conduction to the metallic substrate. This study demonstrates the potential of PTMIMPF copolymers for effective heat shielding applications, validated by comprehensive spectroscopic and thermal analyses, highlighting their promising thermal and structural properties.

Categories: Advanced Materials, Chemical Process Optimization, Polymer Science and Engineering

Keywords: coefficient of thermal expansion, differential scanning calorimetric analysis, differential thermal analysis, energy dispersive x-ray spectrometry, fourier transform infra- red spectroscopy, laser flash thermal analysis, liquid chromatography-mass spectrometry, poly(trimellitimide-melamide-phenol formaldehyde) copolymer, x-ray diffractogram, infrared heat flux

Introduction

Aerospace technology faces significant challenges due to extreme climatic conditions and kinetic heating of metallic substrates. The rapid increase in back wall temperature of aerial vehicle casings, caused by high thermal conductivity, adversely affects their internal structures. To mitigate this, ablative polymer composites are applied to metallic surfaces, protecting aerodynamic surfaces, propulsion systems, and internal structures from high kinetic heating. These composites regulate heat and mass transfer by sacrificing material during kinetic heating. Under typical conditions, ablative polymer composite coatings are designed to withstand multiple high-heat cycles before significant degradation occurs. However, for aerial vehicles subjected to extreme thermal environments, periodic inspection and reapplication may be necessary to maintain optimal performance. Based on current data, reapplication might be required after approximately five high-heat exposure cycles, but this can vary depending on specific use cases and environmental factors. It is crucial for the thermal conductivity of these polymer composites to be very low, while their specific heat must be higher than that of the metallic structures. During exposure to high heat, thermal energy from kinetic heating is absorbed, dissipated, and blocked by the ablative composite polymeric coating layers. This results in charring and cross-linking of the outer composite material, forming a heat-insulating structure that prevents heat transfer to the inner structure.

For structural applications, ablative composites mainly consist of reinforcements and matrix materials. Polyimides are particularly suitable as matrix materials in high-performance composites due to their exceptional thermo-oxidative stability [1,2], good mechanical properties, high glass transition temperature, modulus, and mechanical strength [5,4]. The generic repeat unit in polyimides consists of heterocyclic imide and aromatic groups linked sequentially by oxygen or a group of atoms, resulting in a rigid structure [5,6]. Consequently, polyimides exhibit lower coefficients of thermal expansion (CTE) compared to thermoplastic polymers with coiled, flexible chains [7,8]. The morphology of long, linear ordered chains provides solvent resistance to aromatic polyimides. Due to their excellent thermal and chemical resistance, low thermal and electrical conductivity, polyimides are widely used as thin film insulators in the electronics industry [9]. High-performance polyimides, with their high-temperature stability, solvent resistance, and high strength, are applicable in high-tech aerospace, aviation, and electronics industries [10].

Phenol formaldehyde (PF) thermoset polymer has a polar surface with 1H bond donor and 1H bond acceptor. PF resin, with a flash point of 72.5°C and a melting point of 181.8°C, is hard and brittle, resulting in debonding from surfaces. Phenolic and epoxy resins (ERs), with their cross-linked networks, are prominently used as thermosetting high-temperature insulation materials. The curing process of ER with PF resin has been optimized using ¹H-NMR and differential scanning calorimetry (DSC) methods [11]. Intumescent coatings based on melamine-polyimide composites have been developed through microwave irradiation by Gupta et al. [12]. The oxidative stability of carbon fiber reinforced fluorinated polyimides has been studied using thermogravimetric analysis (TGA) techniques [13]. Melamine-epoxy-based thermosetting resin and its silane derivative have been prepared and analyzed using DSC and TGA [14]. CO₂-induced plasticization of polyimide membranes for gas separation was studied by Zhang et al. [15].

In the present investigation, the composition of the thermal insulation coating has been enhanced with a matrix of poly(trimellitimide-melamide-phenol-formaldehyde) (PTMIMPF)-ER and glass fibers reinforced with a siloxane coupling agent to bind the ablative coating on metals. The synthesis conditions and performance parameters were carefully adjusted to achieve optimal thermal insulation properties. Emphasizing the improved capabilities of the PTMIMPF-based thermal insulation polyimide composite (TIPC) material, we have added a detailed comparison of the thermal performance parameters of our PTMIMPF composite against the current gold standard in thermal insulation materials in the Discussion section.

The PTMIMPF copolymer was synthesized through in situ polymerization of prepolymer N, N'-(4,4'-diaminodiphenyl ether) bis trimellitimide diacid chloride with melamine, followed by a reaction with formaldehyde and phenol under microwave irradiation. The molecular structure-property elucidation of aromatic polyimide-amide and its ER composites was conducted using various spectroscopic techniques. Their crystalline structure was evaluated by X-ray diffraction (XRD) and thermal properties were evaluated using DSC, TGA, and differential thermal analysis (DTA) techniques. Thermal conductivity,

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diffusivity, specific heat, and CTE of the synthesized polyimide copolymers were determined using laser flash thermal analysis (LFTA) and dilatometry. Surface morphology and elemental analysis of poly(trimellitimide-melamine) (PTMIM), PPMIM, and PTMIMPF copolymers were studied using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy.

The PTMIMPF composite coatings with ER were applied to tungsten alloy pieces layered on an aluminum plate substrate. Both coated and uncoated samples were subjected to infrared heat flux thermal exposure of 10 W/cm² for 150 seconds. The effectiveness of the coating in preventing heating, heat conduction to the metal substrate, erosion of the coating, and changes in morphology and microstructure of the coatings were studied using thermocouples, a thermal data acquisition system, and SEM-EDX spectroscopy.

Materials And Methods

Materials

Reagents trimellitic anhydride, pyromellitic anhydride, diaminodiphenyl ether, and thionyl chloride were Aldrich make; Acetic acid and pyridine, m-cresol, methanol, and n-hexane were obtained from Merck Chemicals Co. All reagents were of GR grade.

Synthesis procedure

Synthesis of poly(trimellitimide-melamine-phenol formaldehyde) resin was done through microwave assisted poly-condensation reaction of the prepolymer N, N'-(4,4'-diaminodiphenyl ether) bis trimellitimide diacid chloride with melamine followed by reaction with formaldehyde and phenol subsequently (Figures 1, 2, and 3). LG Microwave Oven, Model MH 4048GW, with a power of 1200 watt was used for polycondensation reaction of prepolymer with melamine and PF. Procedure for synthesis is given below.

Synthesis of Poly(trimellitimide-melamine) (PTMIM)

In a 500 mL round-bottom flask, 19.5 g of trimellitic anhydride carbonyl chloride and 10 g of 4,4'-oxydianiline were stirred for 24 hours at room temperature in a solution of 100 mL glacial acetic acid and 75 mL pyridine. Subsequently, 20 mL of 1M hydrochloric acid was added dropwise with constant stirring to facilitate the formation of imide linkages from the anhydride. During the initial 8-hour reaction period, the anhydride reacts with the amine groups of diamino-diphenyl ether, forming amide and carboxylic acid groups. The primary purpose of adding HCl is to convert these groups into imide bonds.

A mixture of toluene and isopropanol was used as the solvent system to dissolve 5 g of melamine powder, which was then added to the reaction mixture to facilitate the condensation of bismellitimide carbonyl chloride biphenyl ether with melamine. The mixture was stirred overnight. Afterward, 50 mL of m-cresol was added, and the reaction mixture was stirred for 1 hour to form a homogeneous solution, which was then subjected to microwave irradiation.

Microwave irradiation was conducted at 80% power of a 1200 watt microwave oven operating at 2450 MHz, translating to an effective power output of 960 watts. The use of toluene and isopropanol as co-solvents, combined with the specified microwave irradiation conditions, ensured the complete dissolution and efficient reaction of melamine. The irradiated mixture was poured into 150 mL of methanol and stirred for 15 minutes. The resulting precipitated powder was filtered under vacuum, washed several times with methanol, and dried at 120°C for 12 hours under reduced pressure.

The yield of the yellow polymer, poly(bismellitimide-melamine), was 25.5 grams, corresponding to a yield of 99.7%. Complete reaction schemes for the synthesis of bismellitimide carbonyl chloride biphenyl ether and its melamine adduct are shown in Figures 1 and 2, respectively.

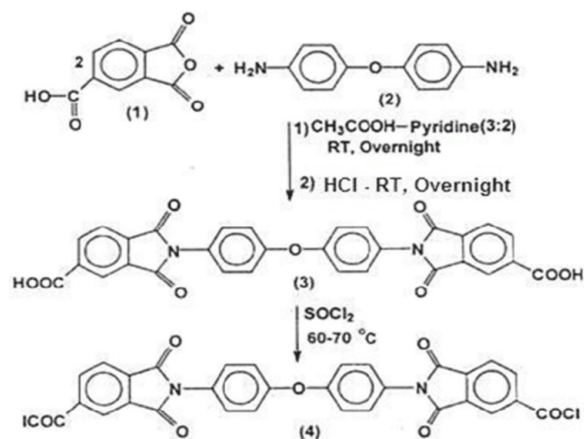


FIGURE 1: Synthesis of bismellitimide carbonyl chloride biphenyl ether (1), trimellitic anhydride (2), diamino biphenyl ether (3), bismellitimide carboxylic acid biphenyl ether (4), and bismellitimide carbonyl chloride biphenyl ether

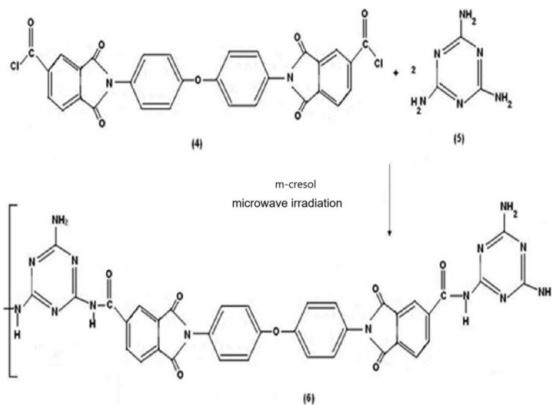


FIGURE 2: Poly(bismellitimide-melamide) (6) synthesis : condensation of bismellitimide carbonyl chloride biphenyl ether (4) with melamine (5)

Synthesis of Poly(Trimellitimide-Melamide-Phenol Formaldehyde) Copolymer

Poly(bismellitimide-melamine) was synthesized using the procedure described in Materials and Methods section. To this, 9.5 g of phenol and 10 mL of a 53% formaldehyde aqueous solution were added, and the mixture was stirred for 15 minutes. The reaction mixture was then placed in a microwave oven at 960 watts for 90 seconds. The irradiated mixture was poured into 150 mL of methanol and stirred for 15 minutes. The resulting precipitated polymer was filtered under vacuum. The yield was 25.87 g, corresponding to 99.6% of a brown powder of poly(bismellitimide-melamide-phenol formaldehyde) (PTMIMPF-1) copolymer. The reaction schemes for synthesizing the poly(trimellitimide-melamide-phenol-formaldehyde) adduct are shown in Figure 3.

Preparation of Poly(Trimellitimide-Melamide-Phenol Formaldehyde) Copolymer: Aqueous

The copolymer of trimellitimide-melamide-phenol formaldehyde was prepared using the same procedure as described above, except that 75 mL of distilled water was used instead of pyridine as the solvent. The yield of the brown polymer, poly(trimellitimide-melamine-phenol formaldehyde) (PTMIMPF-2), was 30 grams, corresponding to a yield of 99.85%.

Synthesis of N,N'-(4,4'-Diphenyl Ether) Pyro-Bis-Mellitimide Prepolymer

In a 500 mL round-bottom flask, 19.5 g of pyromellitic anhydride and 10 g of 4,4'-oxydianiline were stirred for 24 hours at room temperature in a solution of 100 mL glacial acetic acid and 75 mL distilled water. Subsequently, 20 mL of 1M hydrochloric acid was added dropwise with constant stirring. The mixture was stirred overnight, filtered, and dried in an oven at 60°C. The yield was 22 grams of a lemon-yellow solid powder of the prepolymer N,N'-(4,4'-pyro bis-mellitimide), corresponding to a yield of 99.8%. The reaction scheme is shown in Figure 4.

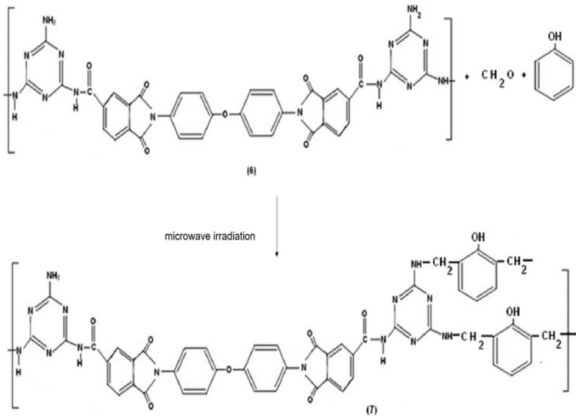


FIGURE 3: Cross-linking polymerization of bis trimellitimide-melamide (6) with phenol and formaldehyde to form poly(trimellitimide-melamide-phenol formaldehyde phenol) copolymer (7)

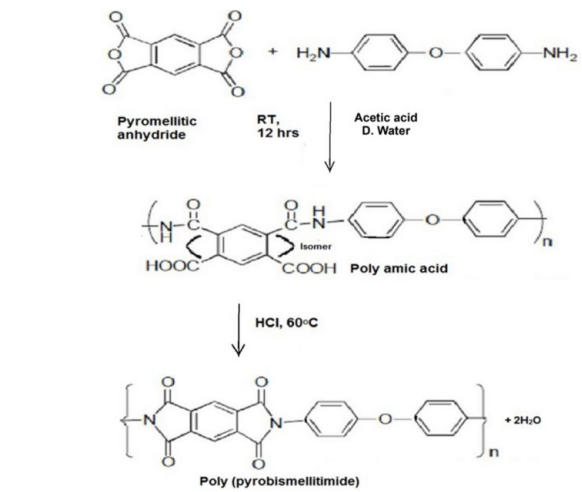


FIGURE 4: Synthesis of poly(pyro bismellitimide) prepolymer

Instrumentation techniques for characterization of polyimide copolymers

Fourier transform infrared (FTIR) spectroscopy: FTIR spectra of polyimide-amide copolymer pellets with KBr were recorded in the wave number range of 400–4000 cm^{−1} using a Bruker FTIR spectrophotometer.

Wide-angle powder XRD: XRD analysis was conducted to identify the crystalline phases present in the polyimide composite materials using a PANalytical High-End X-Ray Diffractometer, with a scanning rate of 4° per minute.

Nuclear magnetic resonance (NMR) spectroscopy: ¹H and ¹³C NMR spectra were recorded to determine the chemical structure of polyimides in deuterated dimethyl sulfoxide (DMSO) and ¹³C-DMSO solutions, using a Bruker-500 400 MHz instrument, with tetramethylsilane as the internal standard.

Liquid chromatography-mass spectrometry (LC-MS): LC-MS spectra were used to determine the molecular masses of fragment groups for the structural elucidation of polyimides and to identify the products formed during the ablation of the polyimide composite.

Gas chromatography-mass spectrometry (GC-MS): GC-MS analysis of polyimide copolymers was conducted in DMSO solvent to determine their molecular weights.

Differential thermal analysis (DTA): DTA was employed to measure the enthalpy changes in samples as they were heated or cooled under fixed conditions, using a reference material of known specific heat.

Thermogravimetric analysis (TGA): TGA was used to measure weight changes, and DSC was utilized to explore the thermal behavior of polyimides, specifically the changes that occur upon heating, such as the melting of a crystalline polymer. DSC and TGA analyses of trimellitimide carbonyl chloride, PTMIM copolymer, PTMIM-montmorillonite composite, and PTMIMPF resin were conducted using a Shimadzu DSC-60 and TGA-51 under a nitrogen atmosphere. TGA was performed at a heating rate of 10°C per minute under a nitrogen flow rate of 50 mL per minute, using a Setaram MTB 10-B microbalance. Polyimide samples, in the form of powder, were placed in open vitreous silica pans. The precision of temperature measurements was ±1.5°C in the temperature range of 20–1000°C.

Thermal properties determination of polyimide copolymers

The LFTA technique was utilized to determine the thermal diffusivity (D or α) of PTMIM and PPMIM copolymers. Circular pellets with a diameter of 12.6 mm and a thickness of 2 mm were prepared from PTMIM, pyromellitimide, and PTMIM-pyromellitimide (PTMIM-PMIM) copolymers through hydraulic compression at a pressure of 14 kbar. These samples were then used to measure their density (ρ), thermal conductivity (k), thermal diffusivity, and specific heat (Cp). The thermal diffusivity (α) is related to thermal conductivity (λ or k), specific heat (Cp), and density (ρ) by the equation:

$$\alpha = \lambda / (\rho \times Cp).$$

In heat transfer analysis, thermal diffusivity is defined as the thermal conductivity divided by the density and specific heat capacity at constant pressure, indicating a material's ability to conduct thermal energy relative to its capacity to store thermal energy. For a one-dimensional, adiabatic scenario, thermal diffusivity (α) can be calculated from the temperature rise using the equation: $\alpha = d^2 / (\pi^2 t_{1/2})$, where t_{1/2} is the half-rise time or the time required to reach 50% of the maximum temperature on the back face. Term 'd' represents the thickness of the sample. Specifically, it is the distance through which the heat pulse travels from the front face, where the laser pulse is applied, to the back face of the sample, where the temperature rise is measured. This thickness d is a crucial parameter in determining the thermal diffusivity as it relates the spatial dimension of the sample to the time it takes for the heat to diffuse through it.

$$Q = \text{absorbed energy} = (m \text{ Cp } \Delta T)_{\text{ref}} = (m \text{ Cp } \Delta T)_{\text{sample}}$$

$$Cp_{\text{sample}} = (m \text{ Cp } \Delta T)_{\text{ref}} / (m \Delta T)_{\text{sample}}$$

For calibration of the IR detector output voltage (ΔV), we used sapphire (Al₂O₃) as the reference material. Sapphire was chosen due to its well-documented thermal properties, which are essential for accurate calibration. The specific heat (Cp) of sapphire is 0.77 J/g·K, and its density (ρ) is 3.98 g/cm³. These properties were used to calibrate the IR detector by measuring the change in output voltage (ΔV) resulting from the absorbed laser energy at each temperature rise. The calibration process involved the following steps: Preparation of Reference Material: Circular pellets of sapphire with a diameter of 12.6 mm and a thickness of 2 mm were prepared. Measurement of ΔV: The change in output voltage (ΔV) of the IR detector was measured at each temperature rise induced by the absorbed laser energy. Calculation of Absorbed Energy: The absorbed energy (Q) was calculated using the known mass (m), specific heat (Cp), and temperature rise (ΔT) of the sapphire reference material. For determination of Specific Heat (Cp) of Polyimide Samples, their absorbed energy was divided by the product of mass and ΔV of the test sample. Thermal conductivity k of polyimide samples was calculated from equation $k = \alpha \rho \text{ Cp}$.

Surface morphology of polyimide composites

The surface morphology of polyimide composites was examined using lower secondary electron imaging with a field emission SEM-EDX instrument (FEI, USA). The SEM utilized a focused beam of high-energy electrons to generate various signals at the surface of solid specimens. These signals, resulting from electron-sample interactions, provided detailed information about the sample's external morphology (texture), chemical composition, crystalline structure, and material orientation. To prepare the samples, an ultrathin gold layer was sputtered onto the surfaces of polyimide copolymers to prevent electrostatic charging. The cross-sections of the coatings were polished to a micron finish and examined using optical microscopy. SEM, combined with EDX spectroscopy, was employed to analyze the chemical compositions at specific points on the polyimide composite samples.

Thermal insulation tests (heat flux exposure tests) of polyimide composite coating (TIPC) on metal substrates

Thermal insulation tests were performed on both uncoated and polyimide-composite (TIPC) coated tungsten alloy (TA) samples placed on aluminum plates. An IR irradiator was used to expose the samples to heat flux. The back wall temperature of the aluminum structures was monitored using a thermocouple connected to a digital temperature recorder. Detailed experimental procedures and results of the thermal insulation tests for the TIPC-coated metallic substrates are provided in Results section.

Results

Synthesis of polyimide-melamide-phenol formaldehyde copolymers

The synthesis of polyimide involves a two-step process. First, polyamic acid is formed by condensing trimellitic anhydride carbonyl chloride with 4,4'-diaminobiphenyl ether in the presence of acetic acid as a catalyst and pyridine as a solvent. This reaction is followed by the addition of hydrochloric acid, resulting in the formation of bismellitimide carbonyl chloride biphenyl ether. In our method, we replaced pyridine with distilled water as the solvent and characterized the resulting polyimides using FTIR and NMR spectral studies. The results indicated the formation of similar products with identical functional groups.

This method facilitated the further condensation of bismellitimide carbonyl chloride biphenyl ether with melamine to form a poly(bis(trimellitimide-melamine) copolymer, which was subsequently cross-linked with formaldehyde and phenol. Both cross-linking processes were carried out in a distilled water medium and under microwave irradiation to form the PTMIMPF copolymer network.

Pyro-bis-mellitimide was prepared by reacting pyromellitic anhydride with 4,4'-diaminobiphenyl ether in the presence of acetic acid as a catalyst and either pyridine or distilled water as the solvent, followed by the addition of hydrochloric acid. To enhance the crystalline structure of the polymer composite, in situ polymerization of trimellitimide-melamine and pyromellitimide was developed. This process produced the poly(trimellitimide-melamide-pyromellitimide melamine) (PTMIM-PMIM) composite, aimed at improving thermal insulation properties.

FTIR spectral analysis

The FTIR spectra of PTMIM, pyromellitimide-melamine (PMIM), and PTMIM-PMIM copolymers are presented in Figures 5, 6, and 7, respectively. The spectral data analysis of the polyamide-imide obtained is shown in Table 1. Additionally, the FTIR spectra of PTMIMPF-1 and PTMIMPF-2 copolymers, prepared in aqueous and pyridine media, are displayed in Figure 8, with their spectral data analysis provided in Table 2.

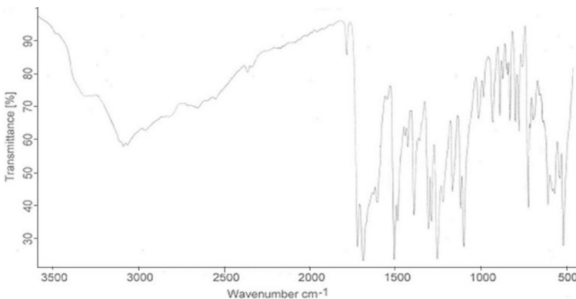


FIGURE 5: FTIR spectra of PTMIM
FTIR, Fourier transform infrared; PTMIM, poly(trimellitimide-melamine)

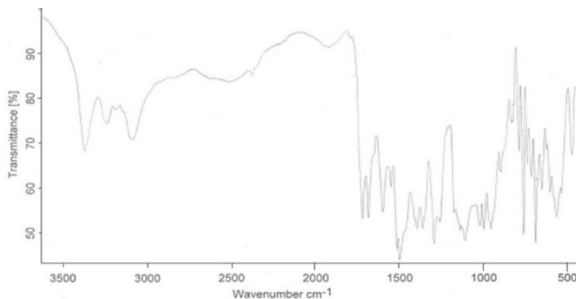


FIGURE 6: FTIR spectra of pyromellitimide-melamine
FTIR, Fourier transform infrared

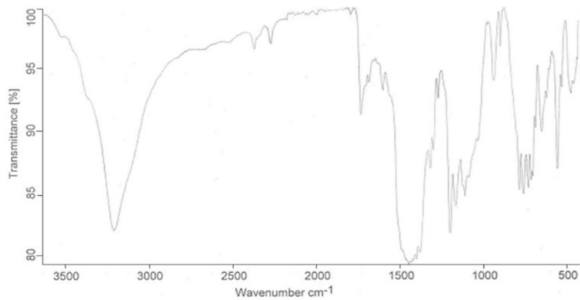


FIGURE 7: FTIR spectra of pyromellitimide-trimellitimide-melamine
FTIR, Fourier transform infrared

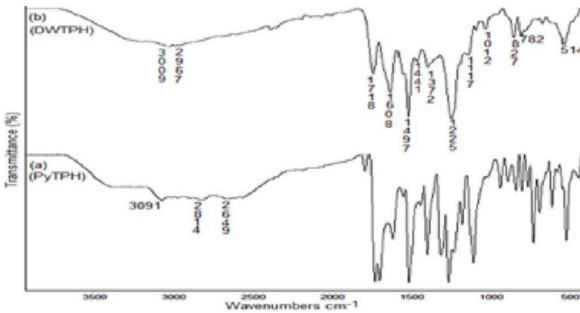


FIGURE 8: FTIR spectra of (a) PTMIMPF-1 (b) PTMIMPF-2 copolymers
FTIR, Fourier transform infrared; PTMIMPF-1, poly(bismellitimide-melamine-phenol formaldehyde); PTMIMPF-2, poly(trimellitimide-melamine-phenol formaldehyde)

Wave number (cm ⁻¹)	Band assignment
3062	-NH- amino stretching
1779.61	C=O stretch overlap with imide bond
1716.82	Five member ring with C=O group
1687.89	Five member ring with C=O group, connected to -N- showing the formation of imide
1604.12	R-NH ₂ primary amine stretching
1502.90	N-H secondary amine aromatic
1430.61	-C-N- stretching
1386.66	Aryl -N- only sharp stretching
1301.36	Aryl-NH ₂ - stretching only observed in polyamide-imide. Not available in polyimides
1117.53	Stretching
1095, 1066, 1012 926.21	Aromatic C-Cl absorptions
1252.31	Aromatic amines displaying strong C-N stretching
757, 717	C-NH-C wagging NH

TABLE 1: FTIR spectral data of poly(trimellitimide-melamine) copolymer
FTIR, Fourier transform infrared

Wave number (cm ⁻¹)	Band assignment
3485.49	-NH- amino stretching
1780.36	C=O stretch overlap with imide bond
1757.21	Five member ring with C=O group
1724.42	Five member ring with C=O group, connected to -N- showing the formation of imide
1604.83	R-NH ₂ primary amine stretching
1508.38	N-H secondary amine aromatic
1425.44	-C-N- stretching
1388.79	Aryl -N- only sharp stretching
1307.78	Aryl -NH ₂ - stretching only observed in polyamide-imide.
1257.63	Aromatic amines displaying strong C-N stretching
1116.82	Stretching
1097.53, 1016.52	Aromatic C-Cl absorptions
723.33	C-NH-C wagging NH
700-600	-NH- out of plane bond
3475.84, 3429.55, 3377.47	-NH- amino stretching
1776.50	C=O stretch overlap with imide bond
1716.70	Five-member ring with C=O group, connected to -N- showing the formation of imide
1633.76	C=O stretching bond amide group
1608.69	R-NH ₂ primary amine stretching
1506.46	N-H secondary amine aromatic
1383.01	Aryl -N- only sharp stretching
1284.63	C-N secondary amine stretching
1246.06	C-O-C stretching
752.26	C-NH-C wagging NH
700-600	-NH- out of plane bond

TABLE 2: FTIR spectral data of PTMIMPF copolymers
FTIR, Fourier transform infrared; PTMIMPF, poly(trimellitimide-melamide-phenol-formaldehyde)

NMR spectrometric analysis of polyimide copolymers

The (¹H) and (¹³C) NMR spectra of the PTMIM copolymer are shown in Figures 9 and 10, respectively. The (¹H) NMR spectra of PTMIMPF-1 and PTMIMPF-2 are presented in Figures 11 and 12, respectively. The (¹H) NMR spectrum of the pyromellitimide prepolymer is shown in Figure 13.

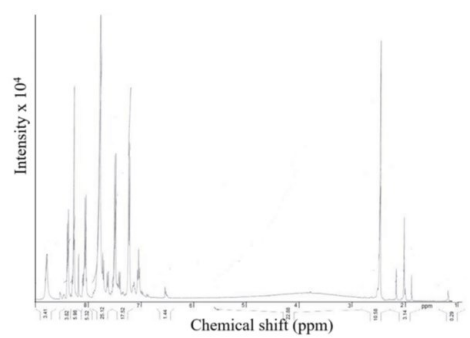


FIGURE 9: 1H NMR spectra of PTMIM-1
NMR, nuclear magnetic resonance; PTMIM-1, poly(trimellitimide-melamine)-1

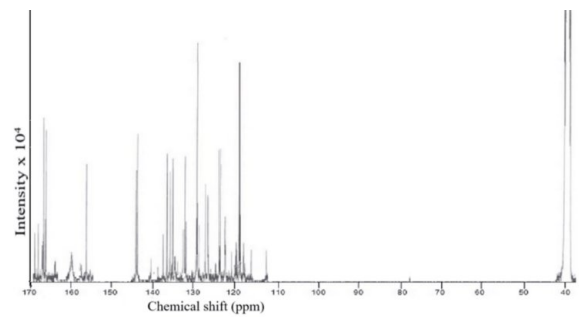


FIGURE 10: ¹³C NMR spectra of PTMIM-1
NMR, nuclear magnetic resonance; PTMIM-1, poly(trimellitimide-melamine)-1

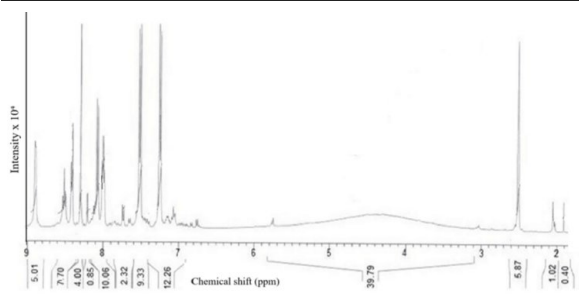


FIGURE 11: ¹H NMR spectra of poly(TMIMPF)-1 copolymer
NMR, nuclear magnetic resonance; poly(TMIMPF)-1, trimellitimide-melamide-phenol-formaldehyde-1

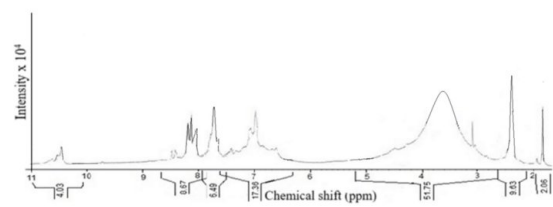


FIGURE 12: ¹H NMR spectra of poly(TMIMPF)-2 copolymer
NMR, nuclear magnetic resonance; poly(TMIMPF)-2, trimellitimide-melamide-phenol-formaldehyde-2

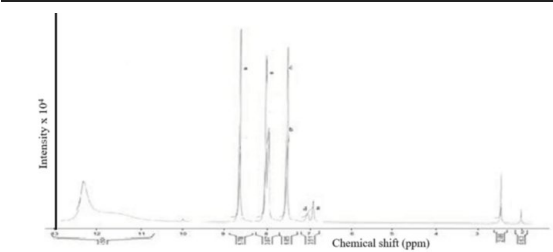


FIGURE 13: ¹H NMR spectra of pyromellitimide prepolymer
NMR, nuclear magnetic resonance

LC-MS analysis of polyimides

The LC-MS spectral results for PTMIM, PTMIMF copolymers, pyromellitimide, and PTMIMPF composite polymers are displayed in Figures 14, 15, 16, and 17, respectively.

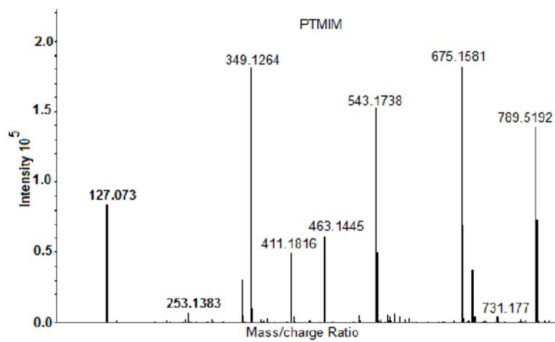


FIGURE 14: LC-MS spectra of PTMIM-1
LC-MS, liquid chromatography-mass spectrometry; PTMIM-1, poly(trimellitimide-melamine-1)

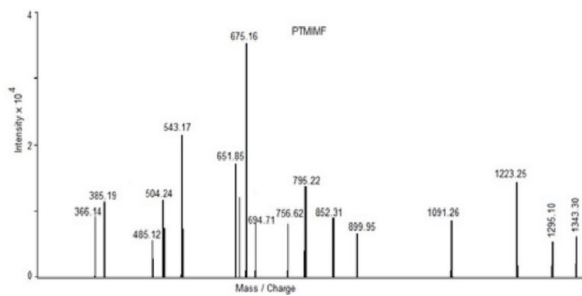


FIGURE 15: LC-MS spectra of PTMIMF-1
LC-MS, liquid chromatography-mass spectrometry; PTMIMF-1, poly(trimellitimide-melamide-formaldehyde)

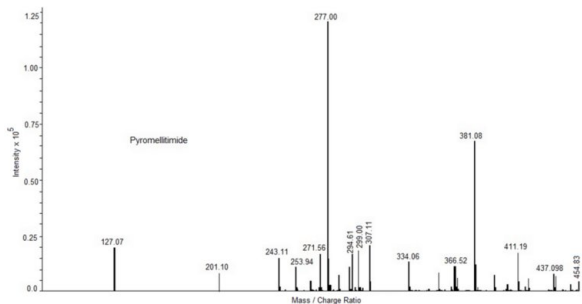


FIGURE 16: LC-MS spectra of pyromellitimide
LC-MS, liquid chromatography-mass spectrometry

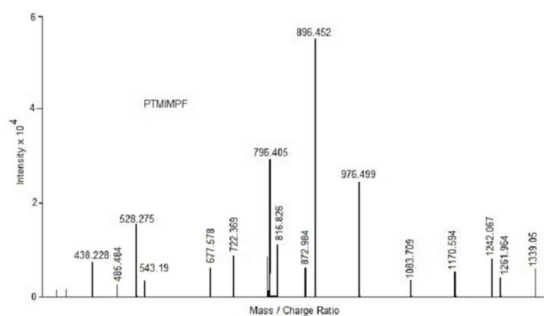


FIGURE 17: LC-MS spectra of poly(trimellitimide-melamide-formaldehyde phenol)
LC-MS, liquid chromatography-mass spectrometry

GC-MS analysis of polyimide copolymers

The molecular weights of PTMIMPF copolymers obtained using the GC-MS technique are as follows:

PTMIMPF before thermal test (prepared in pyridine): 10,911,670

PTMIMPF before thermal test (prepared in distilled water): 10,917,530

PTMIMPF-epoxy composite before thermal test (distilled water): 10,914,211

PTMIMPF-epoxy composite after thermal test (distilled water): 10,728,553

XRD analysis of polyimide-melamide copolymers

XRD analysis was conducted using an X-ray diffractometer with a scanning rate of 4° per minute. The results revealed non-Gaussian distribution patterns, indicating a partially crystalline structure for PTMIM, as depicted in Figure 18, and for pyromellitimide polymers, as shown in Figure 19. The XRD pattern for the

copolymer of poly(trimellitimide-melamide)-pyromellitimide is illustrated in Figure 20.

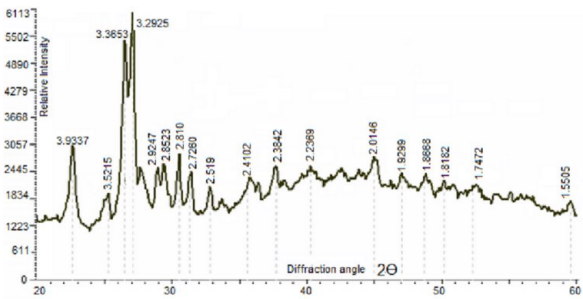


FIGURE 18: XRD diffractogram of poly(trimellitimide-melamine) polymer
XRD, X-ray diffraction

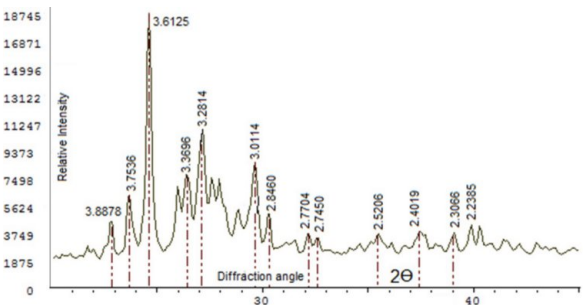


FIGURE 19: XRD diffractogram of pyromellitimide
XRD, X-ray diffraction

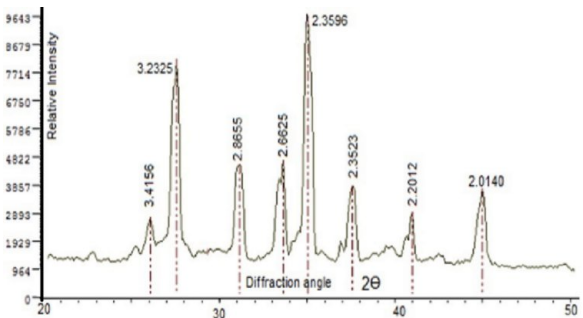


FIGURE 20: XRD spectra of poly(trimellitimide-melamide)-pyromellitimide copolymer
XRD, X-ray diffraction

Thermal properties of polyimides copolymers

Density (ρ) measured and thermal properties like conductivity (k), diffusivity (D) and specific heat (C_p) of PTMIM and PPMIM copolymers as determined by LFTA technique are shown in Tables 3 and 4, respectively.

Name of sample	Dimension, diameter × thickness	Weight (g)	Density (g/cm ³)	Color
PTMIM	12.6mm × 2mm	0.4	1.3	Yellow
PPMIM	12.6mm × 2mm	0.39	1.2	Brown

TABLE 3: Dimension of sample polyimide-melamide copolymers

PTMIM, poly(trimellitimide-melamine); PPMIM, poly(pyromellitimide-melamine)

Name of sample	Temperature (°C)	Specific heat (Cp) J/kg·K	Thermal		CTE (mm/mm·°C)
			Diffusivity (cm ² /s)	Conductivity (k) (W/m.K)	
PTMIM	30	2750.7	0.0014	0.53	57.96
	50	2975.2	0.0013	0.53	50.5
PPMIM	30	2525.6	0.0013	0.48	53.77
	50	2576.2	0.0012	0.43	46.47

TABLE 4: Thermal properties measurement of polyimide-melamide copolymers

CTE, coefficients of thermal expansion; PTMIM, poly(trimellitimide-melamine); PPMIM, poly(pyromellitimide-melamine)

DSC, TGA, and DTA of polyimide copolymers

DSC analysis, with heating and cooling rates of 10°C/min, was used to evaluate the thermal behavior of PTMIM polymer and its silicate composite. The DSC and TGA thermograms of the PTMIM copolymer are shown in Figures 21 and 22. The DSC-TGA thermograms of PTMIM-silicate and PTMIM-silicate-epoxy composites are presented in Figures 23 and 24, respectively. The TGA and DTA of PTMIMPF-1 and PTMIMPF-2 resins are shown in Figures 25 and 26, respectively.

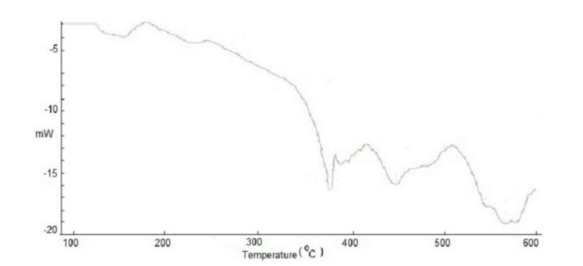


FIGURE 21: DSC thermogram of poly(trimellitimide-melamine) copolymer

DSC, differential scanning calorimetry

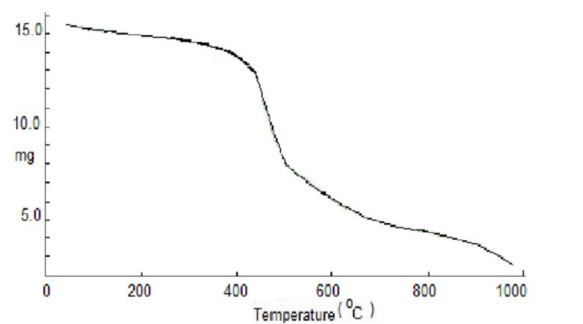


FIGURE 22: TGA thermogram of poly(trimellitimide-melamine) copolymer

TGA, thermogravimetric analysis

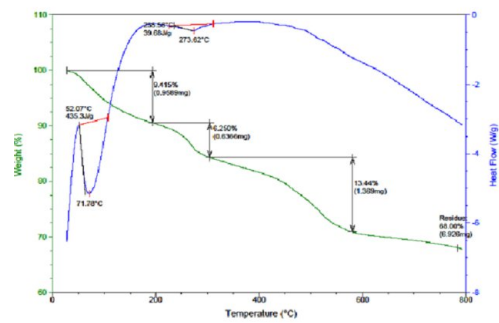


FIGURE 23: DSC-TGA of poly(trimellitimide-melamine)-silicate composite

DSC-TGA, differential scanning calorimetry-thermogravimetric analysis

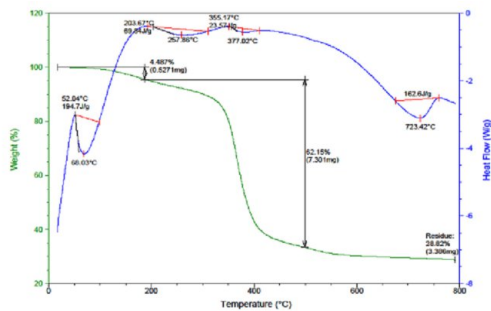


FIGURE 24: DSC and TGA of poly(TMIM)-silicate epoxy composite

DSC, differential scanning calorimetry; TGA, thermogravimetric analysis; poly(TMIM), poly(trimellitimide-melamine)

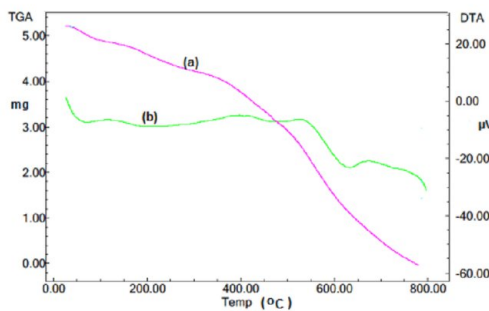


FIGURE 25: (a) TGA, (b) DTA of PTMIMPF-1 resin

TGA, thermogravimetric analysis; DTA, differential thermal analysis

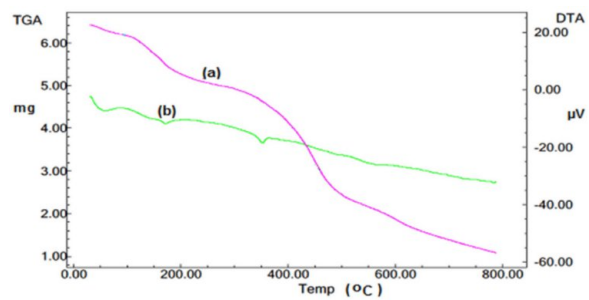


FIGURE 26: (a) TGA, (b) DTA of PTMIMPF-2 resin

TGA, thermogravimetric analysis; DTA, differential thermal analysis; PTMIMPF-2, poly(trimellitimide-melamine-phenol formaldehyde)-2

Composition analysis of PTMIM and pyromellitimide-melamine-silicate composites

Elemental composition analysis of PTMIM and PMIM-silicate composites was carried out using EDX spectral peaks analysis. The results are shown in Figures 27 and 28, with the corresponding data presented in Tables 5 and 6, respectively.

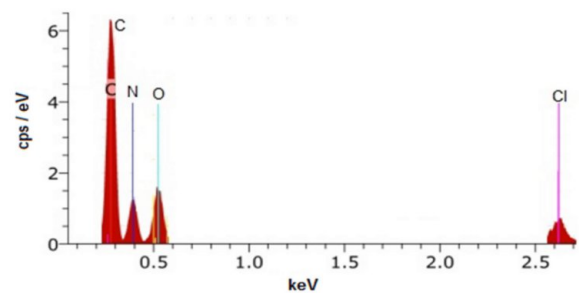


FIGURE 27: EDX spectrum of poly(trimellitimide-melamine) polymer

EDX, energy dispersive X-ray

Element detected	Atomic no.	Concentration in weight percent (wt.%)	Atomic percent (at.%)
C	6	47.10%	47.10%
N	7	26.86%	26.86%
O	8	20.20%	20.20%
Cl	17	5.84%	5.84%
Total		100%	100%

TABLE 5: EDX spectral analysis of poly(trimellitimide-melamine) composition

EDX, energy dispersive X-ray

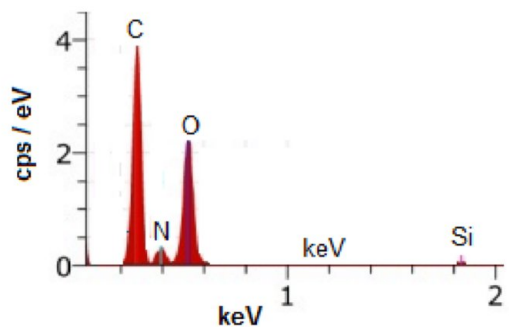


FIGURE 28: EDX spectrum of pyromellitimide-melamine-silicate polymer

EDX, energy dispersive X-ray

Element detected	Atomic no.	Concentration in weight percent (wt.%)	Atomic percent (at.%)
C	6	39.38%	38.85%
N	7	37.86%	49.75%
O	8	17.70%	11.33%
Cl	17	5.06%	0.07%
Total		100%	100%

TABLE 6: EDX analysis of pyromellitimide-melamine copolymer

EDX, energy dispersive X-ray

SEM micrographs of PTMIM, pyromellitimide, and poly(TMIM-PMIM-PF) composites

SEM micrographs of PTMIM, PPMIM, and PTMIM-PPMIM-PF copolymers are shown in Figures 29, 30, and 31, respectively.

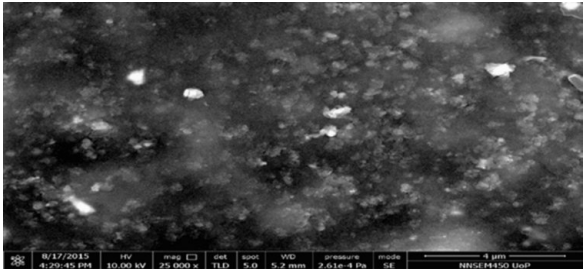


FIGURE 29: SEM micrograph of TMIM polymer

SEM, scanning electron microscopy; TMIM, trimellitimide-melamide

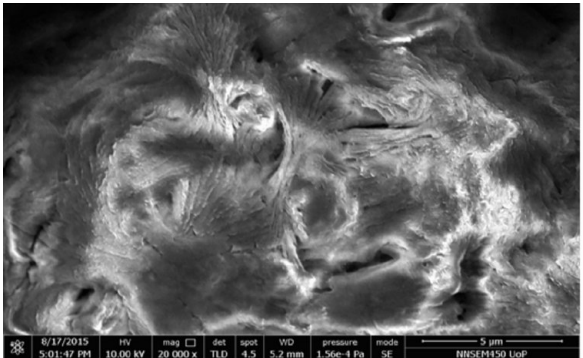


FIGURE 30: SEM micrograph of polypyromellitimide (PPMIM)

SEM, scanning electron microscopy; PPMIM, poly(pyromellitimide-melamine)

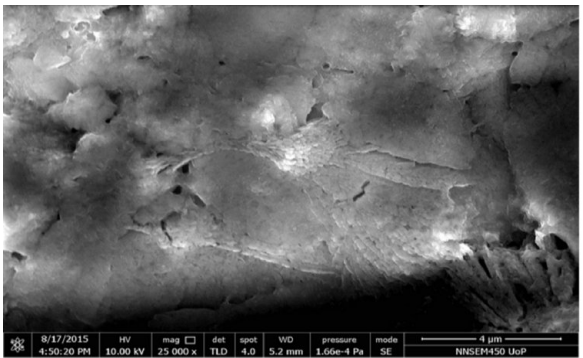


FIGURE 31: SEM micrograph of PTMIM-PMI-PF composite

SEM, scanning electron microscopy; PTMIM-PMI-PF, poly(trimellitimide-melamide-pyromellitimide-phenol formaldehyde)

Thermal insulation polyimide composite (TIPC) coating on metal substrates

Preparation and Application

Composite preparation: A mixture of PTMIMPF, MgO-borax-montmorillonite resin, a coupling agent (3-chloropropyl-trimethoxysilane), and methanol as a solvent was prepared.

Substrate preparation: Aluminum plates (100 mm × 100 mm × 3 mm) were used as substrates. TA pieces were placed

on these aluminum plates with epoxy resin (Figure 32a).

Spraying process: The prepared solution was sprayed onto the tungsten pieces laid on the aluminum plate.

Initial curing: The coated aluminum plate was heated in an oven at 100°C for 10 minutes to ensure proper curing and adhesion of the PTMIMPF coatings.

Cooling: Post-heating, the plate was cooled to room temperature.

Application of TIPC coatings: A second spray of the PTMIMPF mixture with SiC, trimethoxysilane, epoxy resin (Thermal Insulation Polymer Composite, TIPC), and methanol solution was :

Final coating: The PTMIMPF-TIPC coatings were applied to a thickness of 2 mm on the TA pieces laid on the aluminium plate (Figure 32b).

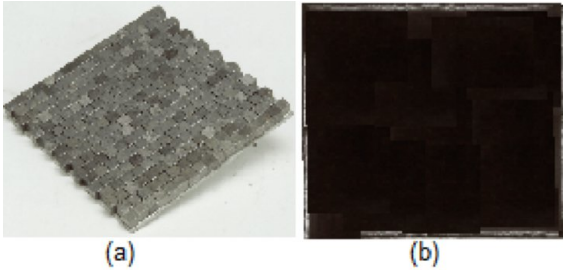


FIGURE 32: TA pieces laid aluminium plates (a) bare (b) with TIPC coating

TA, tungsten alloy; TIPC, thermal insulation polyimide composite

Thermal insulation test of polyimide composite (TIPC)-coated metal substrates

The study evaluated the thermal performance of TIPC coatings, specifically PTMIMPF-SiC and epoxy resin, applied to tungsten pieces laid on the aluminum plates. The analysis focused on heat transfer, thermal diffusivity, and back wall temperature measurements of bothcoated and uncoated aluminum plates us

Procedure

Coating application: The TIPC coatings, consisting of PTMIMPF-SiC and epoxy resin, were sprayed onto tungsten pieces laid on aluminum plates.

Initial curing: The coated aluminum plates were heated in an oven at 100°C for 10 minutes to ensure proper curing and adhesion, then cooled to room temperature.

IR Irradiation Test

Setup: Flat samples were subjected to planar flat-type infrared heating panels.

Calibration: The heating panel was calibrated using a thin foil heat flux gauge to correlate its input power with heat flux output.

The desired heat flux of 10 W/cm² was achieved and verified through this calibration.

Sensor placement: K-type thermocouple sensors were bonded to the test samples using high-temperature bonding material.

Testing: Both PTMIMPF-SiC-epoxy-based TIPC coated and uncoated bare aluminium flat samples were exposed to a constant IR heat flux of 10 W/cm² for 150 seconds using IR heaters. Back temperature data was recorded throughout the test duration.

Post-exposure analysis: Following IR irradiation, the TA pieces on the aluminum plate coated with PTMIMPF TIPC resin

were evaluated for heat transfer and thermal diffusivity (Figure 33).

Temperature profiling: Back wall time-temperature profile curves for both the TIPC-coated and uncoated aluminum plates were plotted and analyzed to determine performance of PTMIMPF coating in thermal insulation of metal substrates (Figure 34).



FIGURE 33: TA pieces laid aluminium plate with TIPC coatings after heat flux tests
TA, tungsten alloy; TIPC, thermal insulation polyimide composite

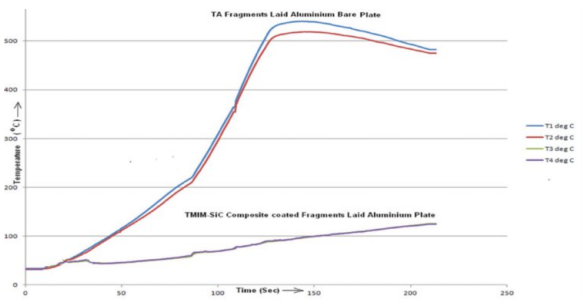


FIGURE 34: Time-temperature profile curves of TIPC-coated tungsten pieces laid on aluminium plate compared with bare TAs laid on aluminium plate
TIPC, thermal insulation polyimide composite; TA, tungsten alloy

Discussion

A novel method for synthesizing the PTMIMPF copolymer has been successfully developed through condensation polymerization, followed by the preparation of its TI

Structural analysis

FTIR spectra: Confirmed the presence of imide groups with characteristic absorption bands at 1780, 1724, and 1383 cm⁻¹ for poly(TMIM) and similar bands for PTMIMPF polymers.

NMR spectral analysis: The ¹H and ¹³C NMR spectra of PTMIM revealed methylene linkages and aromatic hydrogen peaks, confirming successful condensation polymerization. Peaks: 4.2 ppm and 160 ppm, respectively.

LC-MS spectra: Indicated the presence of melamine, diamino-diphenyl ether, trimellitic-anhydride, and pyromellitic anhydride fragment groups. Higher molecular mass peaks suggested cross-linking, resulting in a thermosetting composite.

XRD analysis: Provided valuable information on the crystalline structure of the copolymers, indicating a partially crystalline structure beneficial for achieving desirable mec

Thermal analysis

DSC analysis: Showed distinct melting and glass transition temperatures, indicating good thermal stability.

TGA analysis: Demonstrated high thermal degradation temperatures, confirming robustness under high-temperature conditions.

DTA analysis: Provided additional insights into the thermal transitions and stability of the materials.

LFTA analysis: Showed excellent thermal conductivity and diffusivity, making the copolymers suitable for high-performance thermal insulation and protective coatings.

The PTMIM copolymer's higher specific heat provides better heat insulating properties. Lower thermal diffusivity and expansion coefficients of PPMIM and PTMIM su

EDX-SEM microstructure analysis

EDX spectra: Revealed the presence of nitrogen, oxygen, carbon, and chlorine, aligning with the theoretical molecular structure.

Elemental composition: High carbon content (47.10%), significant nitrogen (26.86%), oxygen (20.20%), and chlorine (5.84%) percentages, consistent with the functional groups in the PTMIMPF copolymer.

SEM micrographs: Showed larger aggregates of trimellitimide with finer granules of melamine and bundles of fibers forming interconnected structures.

Thermal insulation performance

Heat flux tests: The thermal insulation performance of PTMIMPF coatings was evaluated by applying the composite to aluminum plates and subjecting them to an IR heat flux of 10 W/cm². The TIPC-coated metallic plates maintained temperatures below 100°C for 150 seconds and below 150°C for 180 seconds.

Weight loss and degradation: At 375°C, a weight loss of 36% was observed due to degradation and cleavage of carboxyl and hydroxyl groups. At 570°C, the glass transition temperature and an endothermic peak signified the melting of the composite. The stable carbonaceous char formed provided high heat protection.

The back wall temperature of the PTMIMPF-coated aluminium substrate reached 69°C after 150 seconds of HF-IR exposure with no erosion, while an uncoated aluminum plate melted under the same conditions.

Performance comparison with gold standard materials

The GC-MS analysis confirms the high molecular weight of the crosslinked thermoset PTMIMPF-epoxy resin coating, with the molecular weights being 10,914,211 before the thermal test and 10,728,533 after the test. This indicates minimal 1.7% reduction in molecular weight, showcasing the stability of the PTMIMPF-epoxy coating compared to gold standard materials. While typical gold standard materials might show significant degradation and molecular weight reduction under similar conditions, the PTMIMPF-epoxy coating maintains its structural integrity. Its high cross-link density contributes to excellent thermal insulation capabilities, making it a standout performer in protecting metallic structures from intense thermal environment.

Relevance to application: The high heat flux exposure value is relevant for evaluating the performance of thermal insulation and ablative coatings under severe thermal loads, especially in aerospace and defense applications. The present study's focus on high-performance coatings justifies the use of a higher heat flux value, providing a robust assessment of their thermal protection capabilities.

Comparison with typical industrial coatings

Thermal insulation efficiency of PTMIMPF composite: Maintained a temperature below 100°C for 120 seconds and below 150°C for 150 seconds under an IR heat flux of 10 W/cm². **Gold standard material:** Typically maintains similar temperatures for shorter durations.

Weight loss and degradation of PTMIMPF composite: Exhibited a weight loss of 36% at 375°C. **Gold standard material:** Shows higher weight loss percentages.

Glass transition and melting points: PTMIMPF composite: Transitioned at 570°C and melted at 723°C. **Gold standard material:** Lower transition and melting points.

Residual char formation: PTMIMPF composite: Left 64% residue, providing high heat protection. **Gold standard material:** Leaves less residue.

Back wall temperature: PTMIMPF composite: Reached 68°C after 120 seconds of exposure to 10 W/cm² IR heat flux. **Gold standard material:** Higher back wall temperatures under similar conditions.

These comprehensive analyses highlight the superior thermal insulation performance and stability of the PTMIMPF composite, demonstrating its potential for high-performance thermal insulation and protective coatings in demanding applications. The consistency in molecular structure, crystalline structure, and robust thermal properties observed in SEM analysis supports the structural integrity and functional capabilities of PTMIMPF, while the IR heat flux tests confirm its practical applicability for protecting metallic substrates under high-temperature conditions.

Conclusions

PTMIMPF copolymer coatings have shown significant potential as high-performance thermal insulators and protective coatings. The higher specific heat capacity of PTMIM makes it an excellent heat insulator, as it can absorb more heat energy for a given temperature change compared to PPMIM. Despite PTMIM's higher thermal conductivity, its lower thermal diffusivity due to its high specific heat capacity ensures slow heat transfer, making it a more effective insulator for applications where heat absorption and retention are critical. Both PTMIM and PPMIM exhibit a low coefficient of thermal expansion, indicating that they maintain structural integrity under thermal stress.

Thermal insulation tests on PTMIMPF-SiC-epoxy (TIPC)-coated and uncoated aluminum plates revealed that the back wall temperature of the TIPC-coated plate remained below 69°C after 150 seconds of IR heat flux exposure. There was no erosion of TIPC coating or TA fragments from the heat-exposed surface, underscoring the coating's effectiveness in thermal protection.

EDX analysis before and after heat flux exposure provided valuable insights into thermal stability and degradation mechanisms of the PTMIMPF-SiC-epoxy composite coating. A decrease in carbon content and an increase in oxygen content indicated significant thermal degradation and oxidation. These findings are crucial for optimizing the coating composition to enhance performance under high thermal stress. SEM-EDX analysis further revealed substantial chemical and structural changes in PTMIMPF-SiC-epoxy coating when exposed to high IR heat flux exposure. These changes, which affect the thermal and mechanical properties of the TIPC coating, underscore the need for careful consideration of the coating's composition and structure to ensure optimal performance in high-temperature environments.

In summary, PTMIMPF copolymer coatings offer excellent thermal insulation and stability, making them suitable for protecting metallic substrates in applications such as aerospace and defense. Further optimization and understanding of their thermal behavior will continue to enhance their applicability in various high-temperature industrial applications.

Additional Information

Author Contributions

All authors have reviewed the final version to be published and agreed to be accountable for all aspects of the work.

Concept and design: Satish C. GUPTA, Sandhya S. Gupta

Acquisition, analysis, or interpretation of data: Satish C. GUPTA, Anjali A. Athawale

Critical review of the manuscript for important intellectual content: Satish C. GUPTA, Anjali A. Athawale

Supervision: Anjali A. Athawale

Drafting of the manuscript: Sandhya S. Gupta

Disclosures

Human subjects: All authors have confirmed that this study did not involve human participants or tissue. **Animal subjects:** All authors have confirmed that this study did not involve animal subjects or tissue. **Conflicts of interest:** In compliance with the ICMJE uniform disclosure form, all authors declare the following: **Payment/services info:** All authors have declared that no financial support was received from any organization for the submitted work. **Financial relationships:** All authors have declared that they have no financial relationships at present or within the previous three years with any organizations that might have an interest in the submitted work. **Intellectual property info:** "Indian Patent 400829-2022 . **Other relationships:** All authors have declared that there are no other relationships or activities that could appear to have influenced the submitted work.

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