The influence of metal-organic frameworks on ultra-temperature thermal insulation

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Abstract. The present study focuses on examining how metal-organic frameworks (MOFs) influence the thermal and ablative characteristics of Acrylonitrile butadiene rubber (NBR) matrix-based heat shielding material. Particularly, MIL-88 (MOFs) were synthesized, followed by their incorporation into NBR composite materials. Characterization tools that involved X-ray diffraction (XRD), Scan electron microscope (SEM), Fourier-transform Infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA) were utilized as techniques to analyze the properties of both the MOFs and NBR composite materials. Mechanical tests, thermal conductivity measurements, and ablative performance evaluations were carried out to study how the introduction of MOF influences composites mechanical strength, thermal properties, and ablative resistance. The results show that adding MIL-88 enhances the thermal resistance of NBR composite materials thus contributing to the formation of a dense char layer with increased graphitization during combustion. This structure layer is an efficient barrier to heat and mass transfer, enhancing ablative resistance for thermal insulation materials.

Keywords: Thermal insulation, Solid rocket motors, Ablation rate, MIL-88, NBR, EPDM, Polyurethane, Silicon rubber, Kevlar, APP, MOF.

1. Introduction

The aerospace industry, in collaboration with academic researchers, focuses on developing advanced thermal insulating materials for specific applications within rocket motor casings. Composite materials great importance in solid rocket motors, especially at launch times, where their internal temperatures can reach 3000 K and pressures go beyond 10 MPa. Such a high temperature would cause a severe failure of the motor structure if it reached the outer rocket motor casing. Hence, a thermal shield layer (insulation) is a part and parcel of being located in the design of the rocket motor between the propellant and the metal case. Composite materials act as the primary protective layers, which are known to prevent heat transfer during propulsion. These materials provide structural stability to the casing and thus reduce turbulence and protect it from damage, particularly under severe operating conditions [1,2].

Elastomeric composite materials such as NBR, ethylene propylene diene rubber (EPDM), silicon rubber, and thermoplastic polyurethane (TPU) are used widely because of their promising features including high tensile strength and thermal resistance. NBR-based Elastomeric composite materials have drawn much attention because of their polar structure, low thermal conductivity, and commendable mechanical strength. Recent academic research has concentrated on the enhancement of

the mechanical thermal and ablation properties of elastomeric composite materials to eliminate the limited capability of elastomeric composites to form resilient char layers under high-pressure and high-temperature flames. This enhancement strategy involves incorporating nano and micromaterials such as nano-silica, fibers, and organoclay into elastomeric composites. The incorporation of these advanced materials is aimed at solving the limitation of limited char formation of elastomers to enhance their ability to withstand high-pressure and high-temperature flames [3].

Recently, intensive research was carried out in the direction of increasing the thermal resistance of elastomeric-based heat-insulating systems by introducing flame retardant additives. t has been established that non-halogen flame retardants, especially those with phosphorus additives, offer desirable properties, including efficiency and minimal toxicity. However, problems like poor compatibility and interface defects are the main obstacles to the production of high-quality thermal insulation. Moreover, the complex manufacturing processes and the higher cost of these flame retardants might limit their widespread use, hence the need to find new alternatives for improving the thermal resistance and mechanical properties of thermal insulation materials. The most recent studies have discovered new flame retardants involving metal ions coordinated with organic linkers called metal-organic frameworks (MOFs), aiming to take advantage of the positive attributes of both organic and inorganic flame retardants by introducing this promising avenue into flame retardant technology [4].

In the last decade, metal-organic frameworks (MOFs) have emerged as novel flame retardants for polymer matrices, forming two or three-dimensional structures with metal ions or clusters coordinated to organic ligands. The flame retardancy of MOFs operates through different mechanisms. During the decomposition of MOFs, non-flammable gases such as carbon dioxide, and water are released which dilute the concentration of flammable gases and reduce ignition probability. Then, MOFs create the char layer impeding heat, flames, and combustion gases. Moreover, the metallic constituents function as catalysts, aiding char formation and reducing the emission of flammable gases. The presence of metal oxides promotes heat absorption, which decreases flame temperature and restrains fire spread in the surrounding environment [5].

In this study, MIL-88(Fe) was synthesized and introduced at a concentration of 4 parts per hundred rubber, (phr) into NBR composite materials. The aim is to investigate the impact of MIL-88(Fe) on thermal insulation in ultra-high temperature applications on the thermal stability and resistance, as well as the mechanical, physical, and thermal properties of the NBR composite materials. This study seeks to expand research in the field by elucidating the positive effects of MOF on thermal insulation.

2. Experimental work

2.1. Materials

For the preparation of MOFs, 1,4-Benzenedicarboxylic acid, also known as terephthalic acid (H_2BDC, 98%), Ethanol (EtOH, 98%), N, N-dimethyl formamide (anhydrous DMF, 99.8%), and Iron(III) chloride hexahydrate ($FeCl_3.6H_2O$, 98.5%) were provided from Sigma-Aldrich, Canada. For NBR-based heat shielding materials, Acrylonitrile butadiene rubber (Acrylonitrile content, 34%), Dibutyl phthalate (DBP, 99%), Sulphur (S, 99%), Zinc oxide (ZnO, 98%), Stearic acid (97%), Tetramethyl thiuriam disulfide (TMTD, 99%), Silicon dioxide (SiO_2, 99%), N, N-diphenyl-p-phenylenediamine (H, 97%) Kevlar (KP, 99%), and Ammonium polyphosphate (APP, 99%) were provided by Shandong chemicals Co., China.

2.2. MOF Synthesis

The preparation of MIL-88(Fe) was carried out according to the published Chongli Zhong method as shown in figure 1(a) [6]. 0.25 g of terephthalic acid (H_2BDC) (1mmol) and 0.81 g of Iron(III) chloride hexahydrate ($FeCl_3.6H_2O$) (1mmol) were dissolved in 60 ml of N, N-dimethyl formamide (DMF) the solution was heated for 24 hr at 110°C to complete the reaction, the solution was cooled to room temperature. The reaction produced an orange-colored suspension, which was centrifuged at 5,000 rpm for 15 minutes. The precipitate solids were washed with DMF two times and ethanol three times. Then the product was dried overnight at 85°C.

a) b)

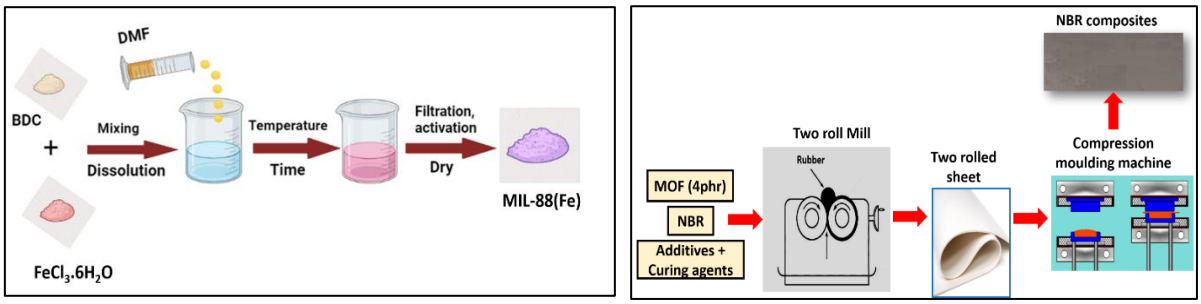

Figure 1. Schematic diagram illustrating the synthesis of MIL-88(Fe)(a). Additionally, the manufacturing process of NBR-based thermal insulation(b).

2.3. Fabrication of NBR-MOFs composites

The preparation of NBR composite materials, which were carried out using the method described in figure 1(b). Whereby NBR was passed between the two rolls mixing mill several times at 65°C and a constant speed of 50 rpm for 15 min. DBP was introduced into the NBR matrix as a plasticizer, alongside other additives including KP and SiO_2 for enhancing heat resistance, APP for flame retardancy, ZnO and stearic acid as curing activators, and H for antiaging properties. These additives were gradually incorporated into the nitrile rubber to optimize its performance characteristics, and then 4 phr (part per hundred rubber) from MOF was added into the NBR matrix. After obtaining a homogeneous rubber compound, the TMTD as a curing accelerator and sulfur as a curing agent were added to the NBR matrix, following the formulations in table 1. Finally, the compounds were vulcanized in molds at 160°C and 15 MPa to reach the optimal cure time T90. After-vulcanization, 100 × 100 × 3 mm^3 specimens were used to determine the ablation rate in an oxyacetylene test, while 150 × 150 × 3 mm^3 specimens were used to assess the mechanical properties of the compounds [7].

Table 1. Formation of insulation material for rocket motors based on NBR.

Ingredients		NPR	DBP	KP	SiO_2	APP	ZnO	TMTD	Stearic acid	S	H	MIL-88(Fe)
Loading level (phr)	NM0	100	15	20	10	30	5	0.5	1.5	0.5	1.5	-
	NM1	100	15	20	10	30	5	0.5	1.5	0.5	1.5	4

2.4. Characterization

Powder X-ray diffraction (PXRD) data for MOF were obtained using a Bruker D8 Advance X-ray diffractometer, scanning from 5° to 50° with a 0.02° increment. Fourier-transform infrared (FTIR) spectra were recorded for MOFs using a Perkin Elmer Spectrum one FTIR spectrometer. Thermogravimetric analysis (TGA) was conducted on MOF up to 600°C and NBR composites up to 800°C using a heating rate of 10°C per minute. Scanning electron microscopy (SEM) analysis was carried out for MOFs and NBR composites. additionally, mechanical and density tests for NBR composites were performed according to the ASTM standards. The measurement of thermal conductivity for the samples was conducted utilizing Lee's Disc Apparatus according to ASTM D7340-07(2018) standards. Raman spectroscopy (CRS, Jobin Yvon, France) to evaluate the intensity of char layers. The ablation performance of insulators based on NBR was characterized using the oxyacetylene flame test, showing erosion and breakdown of ablate components with the calculated ablation rates within the ASTM E-285-80 standards.

$$R_d = \frac{d_1 - d_2}{t} \quad (1), \qquad R_m = \frac{m_1 - m_2}{t} \quad (2)$$

The linear ablation rate (R_d) in equation (1) and mass ablation rate (R_m) in equation (2) are used to analyze material loss thickness, resistance to high-speed heat flow, and indicates the rate of mass loss

caused by the flow of pyrolysis gas and the char layer losses. Additionally, a thermocouple measured the maximum back-face temperature ($T_{max,b}$) to determine thermal insulation properties.

3. Results and Discussion

3.1. MOF characterization

XRD spectra were used to analyze the structural characteristics of prepared MOF, showing significant agreement with simulated patterns. Diffraction peaks of prepared MIL-88(Fe) were found at 2θ values of 9.35°, 9.9°, 12.55°, and 13.81°, with the possible slight deviations resulting from solvents-induced structural changes during the preparation of the samples as shown in figure 2(a). FTIR spectra of MIL-88(Fe) revealed characteristic peaks: symmetric and asymmetric vibrations of carbonyl groups at 1600 cm^{-1} and 1350 cm^{-1}, and in-plane/out-of-plane bending of C-H bonds at 1040 cm^{-1}. Lower wavenumber absorption peaks corresponding to Fe-O bonds were noted around 550 cm^{-1} as shown in figure 2(b) [8].

a) b)

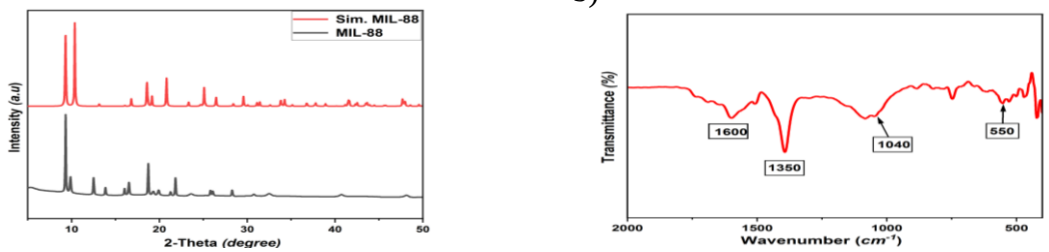

Figure 2. The XRD pattern of both simulated and measured for MIL-88 (a). Additionally, showcases the FTIR spectra for MIL-88 (b).

SEM analysis, as depicted in figure 3(a), revealed that MIL-88 crystals exhibit a hexagonal bipyramidal morphology. The thermal stability of MIL-88 was assessed via TGA and derivative thermogravimetric analysis (DTG) analysis, revealing multi-step decomposition attributed to its complex structure. TGA curves displayed initial weight loss from solvent removal, followed by distinct stages indicating framework breakdown, resulting in char residue and metal oxides. MIL-88 exhibited slight weight loss around 200°C due to solvent desorption, followed by a major degradation stage (300°C to 450°C) where the framework disintegrated as the BDC linker separated. Beyond 500°C, no considerable loss in weight was detected, indicating residue ferric oxides and char residue post-decomposition as depicted in figure 3(b) [9].

a) b)

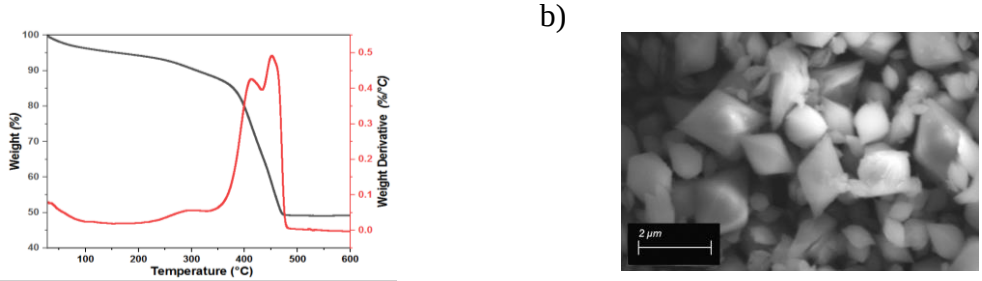

Figure 3. The weight loss from TGA and DTG curves (a). Additionally, SEM micrographs (b) of the as-synthesized MIL-88.

3.2. Characterization of thermal insulation

SEM analysis showed improved morphology in the NBR matrix with MOF as compared with the NBR composite without MOF as shown in figure 4. Incorporating MOFs enhanced uniformity between additives and NBR due to organic linkers, fostering better compatibility and dispersion. Organic linkers in MOFs act as dispersing agents, reducing processing time for a well-integrated composite material.

a) b)

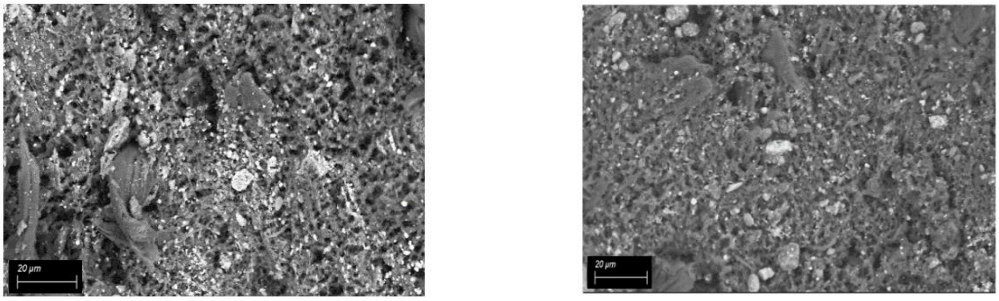

Figure 4. SEM images depicting the surface (EHSMs) NM0 (a) and NM1 (b).

Adding a flame retardant typically reduces polymer mechanical behavior. NBR compositions without MOFs had a tensile strength of 10.15 MPa, elongation of 45.2%, and hardness of 78 shore-A. However, with 4 phr of MIL-88, NM1 showed increased tensile strength (11.4 MPa), elongation (55.2%), and hardness (81 shore-A), marking gains of 12.32%, 22.1%, and 3.85% respectively as shown in figure 5(a). The enhancement in mechanical properties with the addition of MIL-88 is attributed to the organic component of MOFs, which improves interfacial compatibility within the rubber matrix. MOFs contribute to increased resilience and elasticity in rubber composites by enhancing the interaction between additives and the rubber matrix.

The density of NBR-based HSMs remained largely unaffected overall, indicating the minimal impact of MIL-88 on density requirements for SRM. Thermal conductivity decreases with MOF addition to NBR, as shown in figure 5(b), due to the hybrid nature of MOFs, which create interfaces hindering heat flow. These hybrid materials, comprising different materials with distinct properties, exhibit varied thermal conductivities due to inherent differences, forming barriers to heat flow at their interfaces.

a) b)

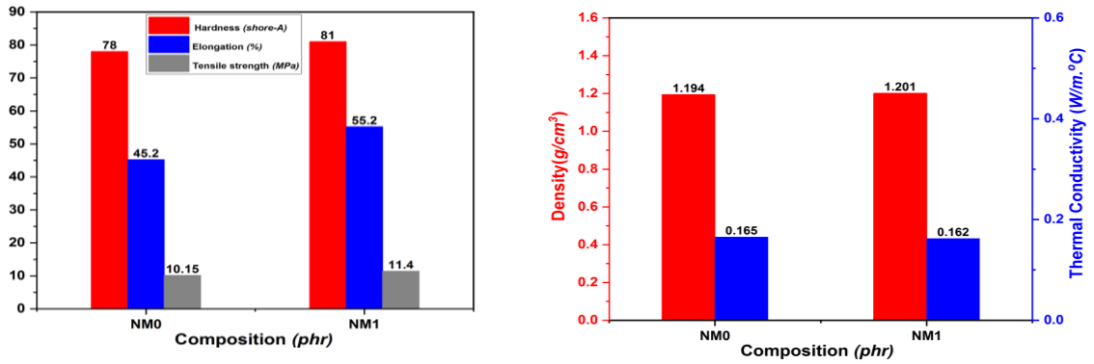

Figure 5. The effect of MIL-88 in NBR composite materials on the mechanical properties (a) and, additionally, on thermal conductivity and density (b).

The TGA and DTG analysis of NBR-based insulators (figure 6) revealed a two-step thermal decomposition process, with the initial degradation occurring around 225°C, primarily affecting rubber compounds containing APP and low molecular compounds like plasticizers. The incorporation of 4 phr of MIL-88 resulted in a slight increase in the onset degradation temperature, indicating improved thermal stability of the composition. The decomposition of organic components concluded above 500°C, leaving weight residue attributed to char from the matrix with additives and metal oxides from the MOF, which are formed during the decomposition of organic ligands in the MOF structure. Notably, MIL-88 demonstrated enhanced catalytic effects on charring, as evidenced by higher weight residues at 800°C for compositions containing the MOF compared to those without.

a) b)

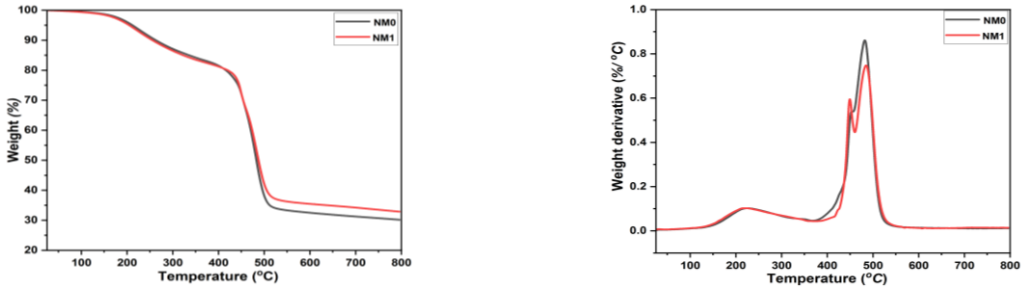

Figure 6. The weight loss from (TGA) (a) and the (DTG) curves (b) of NBR-based insulators.

The char, resulting from the decomposition of NBR composites with MOFs, offers inadequate protection against high-speed, high-temperature oxy-acetylene flame, as indicated in figure 7. NM1 shows improved ablative resistance, reducing linear ablation rate by 6.1% to 0.0195 mm/s compared to NM0, with a decreased mass ablation rate by 11.6% to 0.069 (g/s) for NM0 as shown in figure 7(a). These findings underscore the role of MOFs in enhancing ablative resistance, crucial for maintaining a specific distance between high-temperature external environments and inner objects for superior thermal insulation. The combination of NBR composites and MIL-88 forms a thick, resistant char network, acting as a barrier against heat and decomposition products, thus retarding combustion. Back-face temperatures of ablative composites affirm MOF efficacy in maintaining acceptable temperature levels, crucial for solid rocket motor thermal protection systems. Figure 7(b) illustrates a decrease in back-face temperatures and char layer thickness with increasing MOF proportion, indicating reduced heat transfer owing to MOF low thermal conductivity. NM1 demonstrates superior thermal insulation with the lowest back-face temperature, owing to its outstanding ablative resistance and acceptable heat transfer properties.

a) b)

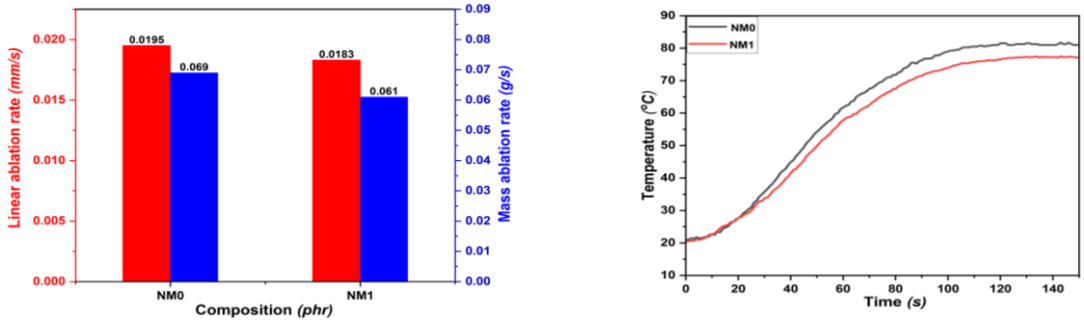

Figure 7. Ablation rate (a) and back face temperature (b) of NBR-based insulators.

The assessment of MOF influences on char formation in NBR composites reveals that the charred structure of ablated specimens exhibits surface defects such as roughness and holes as shown in figure 8(a), suggesting a non-uniform structure. However, morphological analysis shows that specimens with MOF addition exhibit fewer defects compared to those without as shown in figure 8(b). Furthermore, the surface of the char layer is coated with particles, suggesting the generation of metal oxides during the combustion process, which act as an efficient barrier. These findings suggest that the inclusion of 4 phr of MIL-88 facilitates the formation of a consecutive and dense char layer, functioning as a barrier to safeguard the substrate, hinder oxygen and diffusion of volatile pyrolysis products, and mitigate energy returned from flames, consequently enhancing ablation resistance [10].

a) b)

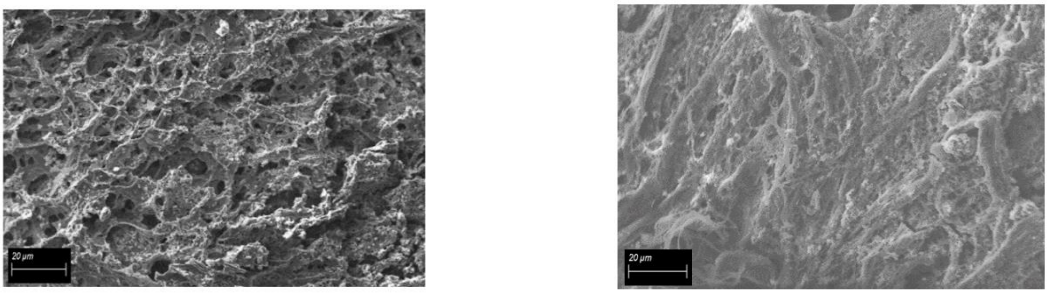

Figure 8. SEM images of char residues for NM0 (a) and NM1 (b) after ablation test.

The evaluation of char residues graphitization degree via Raman spectra reveals two prominent peaks corresponding to G and D bands, indicative of crystalline graphite and glassy or disordered carbons, respectively. The ratio of the integrated intensity of D and G bands (I_D/I_G) serves as a measure of graphitization degree, where a higher I_D/I_G value implies lower graphitization [11]. In this study, NBR composite materials without MOF exhibit an I_D/I_G ratio of 0.86, while NM1 composites show ratios of 0.81, indicating enhanced graphitization as shown in figure 9. This suggests the catalytic charring effect of MOFs, leading to the production of graphitized carbon during combustion. The dense char layer with increased graphitization acts as an efficient barrier, reducing heat and mass flow, impeding organic volatiles release, and inhibiting flame spread. Overall, the incorporation of MOFs not only boosts the formation of char layers but also enhances the degree of graphitization, thereby improving thermal insulation resistance to fire.

a) b)

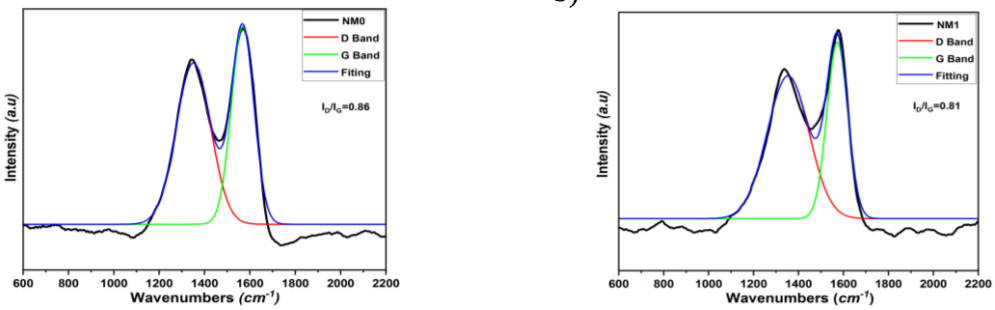

Figure 9. Raman spectra of the char residues for NM0 and NM1 after ablation test.

4. Conclusion

The addition of Metal-Organic Frameworks, MIL-88 into NBR-based heat shielding composites greatly improves their thermal and ablation performance, by notable reductions in liner and mass ablation rates by 6.1% and 11.6%, respectively. The synthesized MIL-88 displays a well-defined structure and improved thermal stability which promotes the formation of a compact char layer with increased graphitization during burning. This char layer works as an excellent thermal barrier against both heat and mass transfer and this contributes to increased ablative resistance and thermal insulation. Mechanical tests have shown increased tensile strength, elongation, and hardness of 12.32%, 22.1%, and 3.85% respectively, with the presence of MIL-88 which shows good material integrity. Moreover, thermal conductivity measurements demonstrate a decrease in heat transfer with MOF addition, further improving thermal insulation. This highlights the possibility of MOFs serving as enhancers in elastomer-based heat shielding materials, finding new doors of highly efficient thermal protection systems in aerospace and other high-temperature applications.

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