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MANUFACTURING OF FIBER –REINFORCED POLYMER COMPOSITE THERMAL INSULATION BY VACUUM TECHNIQUE

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Abstract: *This study aimed to investigate the potential of application of vacuum technique for manufacturing of fiber-reinforced polymer composites used in military purpose as thermal insulation materials for solid rocket motor chamber. Vacuum technique without infusion of resin was utilized to produce different shapes of specimens. Such applied technique successfully resulted in obtaining rectangular plates for mechanical characterization and ablation test, as well as cylindrical motor chambers for inner ballistic examinations. Thermal insulation material was based on unsaturated polyester resin Dion FR 7721-00 which contained alumina tri-hydrate as fire-retardant. Carbon and glass fabrics were used as reinforcements. Rheological properties of the prepared composite were determined using dynamic-mechanical analysis, while the thermal properties were studied by ablation test. Obtained results indicated that vacuum technology was applicable and suitable for manufacturing of fiber-reinforced polymer composites. Developed materials show improved mechanical and thermal properties and could be used as thermal insulation/inhibitor of composite rocket propellant grains.*

Keywords: *Vacuum technique, carbon fabric, glass fabric, polyester resin*

1. INTRODUCTION

The thermal stability of a material is usually expressed in terms of ability to withstand specified conditions and still retain the physical properties required of the material in the given application. Determination of the structure of such materials for thermal protection plays an essential role in the designing of construction elements for rocket motors.

Polymeric ablation materials (PAMs) represent one of the most important parts of thermal protection system used in solid rocket motors (SRMs) [1]. In the most cases, PAMs should have a low density and thermal conductivity to achieve excellent thermal insulation, since SRMs generate significant amount of heat during their operation. PAMs should have good adhesion to propellant [2], and to protect the structural integrity of the SRMs during long-term storage and firing. During exposure of the propellant grain to extreme temperature and pressure, the PAMs decompose generating a protective char layer which has low thermal conductivity and high mechanical strength. Mechanical integrity gives the char layer resistance to the heat diffusion through it and to physico-chemical erosion caused by combustion gases [3].

Ablation materials, which are investigated in this study, are type of, fiber-reinforced polymer composites. There are various methods for producing selected type of composites, such as filament wounding technique, blending, casting and vacuum techniques. Although the filament wounding technique is commonly used for obtaining fiber reinforced composite materials used in rocket and aerospace industries [4], vacuum technique with (Figure 1) or without infusion of resin, shows its benefits related to the best fiber to volume ratio, ability to create light-weight materials with great mechanical strength.

Considering resin selection for the specified application, polyester, phenolic, vinyl ester, and epoxy resin proved to be the best choice for preparation of the PAMs [5]. Beside the listed, the unsaturated polyester (UPe) resins provide high protection in terms of severe conditions, such internal pressure, extreme temperature and corrosion [6], [7]. Consequently, UPe resins are widely used for impregnatation of appropriate fiber reinforcements into multilayer structure of ablative material. Moreover, UPe resins are compatible with the commonly used reinforcement fibers (*e.g.* carbon, glass). Epoxy and UPe resins possess an appropriate temperature range considering the processing conditions, which is crucial for its application in vacuum technique [4], [8].

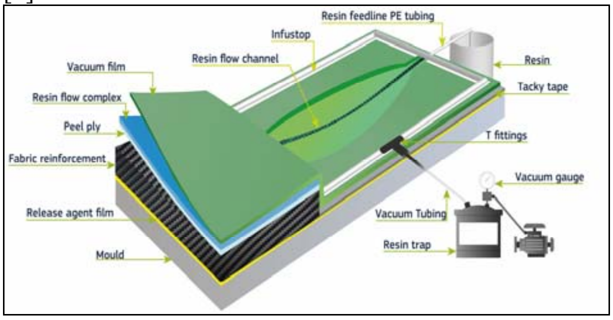

Figure 1. Schematic illustration of vacuum infusion process (reused from http://sicomin.com/products/vacuum-and-infusion/infusion)

Further, various ablative additives, such as fibers [9-12] and inorganic fillers [13–15], could be added to PAMs to improve mechanical properties and to reduce the oxidation rate of the char layer. It is considered that the usage of fibers transforms the polymeric matrix into conductive network, which facilitate the formation of numerous hot spots and accelerate heat diffusion [16–19].

Each component contributes in reaching desired properties in its own way. Therefore, the multilayer structure is preferable to achieve balanced ablation and thermal protective performances of PAMs. So far, the vacuum technique is proved and abundantly applied in manufacturing of insulations for various industrial applications, *e.g.* for hot water storages (thanks, boilers, heat pumps), industrial installations (heat shields, enclosures for valves, tanks), piping (district heating, process heating and cooling), laboratory devices (freezers, incubators, chromatographs, climatic chambers), ovens and dryers.

The main goal of this study was to estimate potential of application the vacuum technique for manufacturing thermal insulation materials for the rocket motor chambers. For that purpose, the self-extinguished UPe resin, which contained alumina tri-hydrate as fire-retardant, reinforced with carbon and glass fabrics was employed.

2. EXPERIMENTAL

2.1. Materials

Developed composites was based on self-extinguished UPe (Dion FR 7721-00, Reichhold, USA) mixed with initiator methyl ethyl ketone peroxide in toluene (MEKP, Sigma Aldrich, Germany) and carbon fabric (style 450-5 Aero, 200 g/cm^2, plain weave (Engineered Cramer Composites, Germany) and glass fabric (Interglas 05507, 200 g/cm^2, plain weave (Engineered Cramer Composites, Germany) as reinforcement.

2.2. Preparation of fiber-reinforced polymer composite

For the dynamic-mechanical and thermal properties determination, the rectangular plate of 250x270 mm dimension was manufactured following the procedure: UPe was applied manually, by brush, over the carbon and glass fabric (in ratio 30 % resin to 70 % of reinforcement) The layers of fabrics were also arranged in two cycles – two layers of carbon, then two layers of glass fabric, and after repeating it twice, 5 layers of glass fabric were added on top of it. Vacuum was applied and enabled curing at room temperature without cavities in material. At the end of the process, extra resin was mechanically removed using lathe, thereby the fibers remained undestructed so this treatment did not affected mechanical characteristics of matherial. The final thickness of plate (determinated with dimension of molde) was 5 mm (Figure 2).

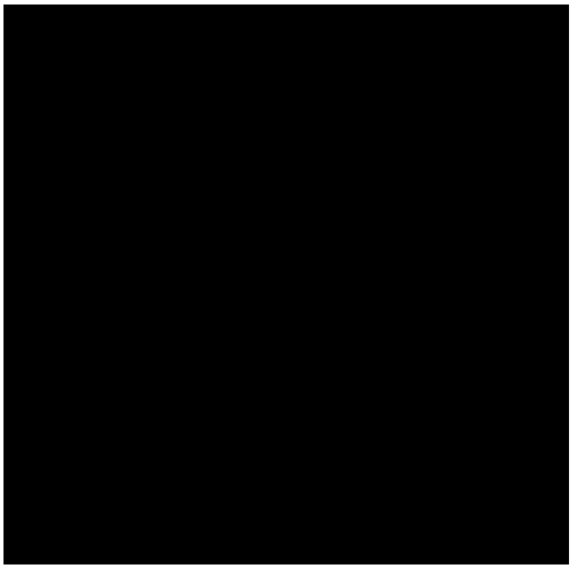

Figure 2. PAM in a shape of rectangular plate

In addition, to prove the potential of the vacuum technique for producing of cylindrical rocket chambers, a 2-inches motor, for inner ballistic characterization of rocket propellants, was manufactured. The 2-inches motor was also manufactured as a rectangular plate applying the UPe resin by brush on mandrel, over layers of carbon and glass reinforcements in the same ratio (70 to 30 % fibres to resin). When all set, vacuum was applied and left to cure at room temperature, constantly under vacuum conditions. Final external diameter was obtained applying mechanical processing (Figure 3). Furthermore, this technique is used for inhibiting double-base propellant grains (DBPG). Employed technique provided successfully coating of cylindrical specimens of DBPG, with and without calotte, which is great technological challenge for conventional techniques (Figure 3 (b)). In addition, satisfied bonding between propellant and composite inhibitor was achieved.

2.3. Characterization methods

Structural characterization of the cured composite was performed using Fourier transforms infrared spectroscopy (FTIR). FTIR spectra were recorded in absorbance mode using a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, within a range of 400-4000 cm^{-1}, at a resolution of 4 cm^{-1} and in 20 scan mode.

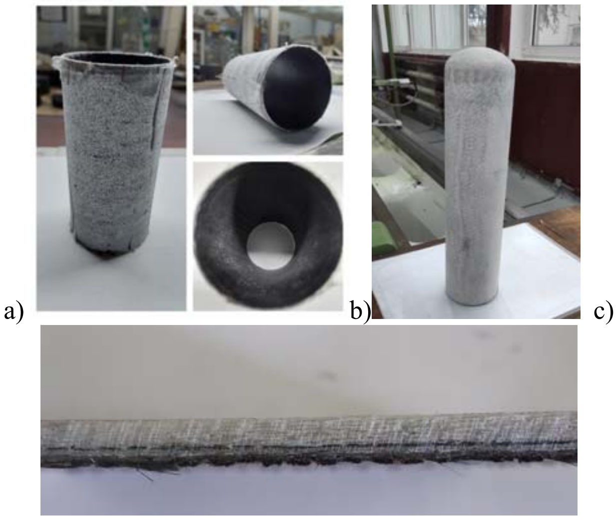

Figure 3. PAM in shape of cylindrical chamber for inner ballistic characterization (a), coated specimen with calotte (b), and cross section of the cured carbon/glass multi-layered composite (c)

Dynamic mechanical analysis (DMA) study of the cured composite samples was performed in torsion deformation mode using the Modular Compact Rheometer MCR–302 (Anton Paar GmbH) equipped with standard fixtures (SRF12) for rectangular bars, temperature chamber (CTD–620) having high temperature stability (±0.1 °C). The standard sample of a rectangular bar shape (44×10×4 mm) was tested by using "temperature ramp test" in temperature range from 40 °C to 170 °C, the heating rate was 5 °C·min^{-1}, and the single angular frequency of 1 Hz, and strain amplitude was 0.1%.

The thermal properties of produced PAM plate based on the cured DION® FR 7721-00 resin as matrix were studied by a modified Oxyacetylene Ablation Testing of Thermal Insulation Materials [20] using an Extech High-Temperature infrared thermometer and an oxyacetylene flame. Samples of standard dimension (100x100x6 mm) were used (Figure 4).

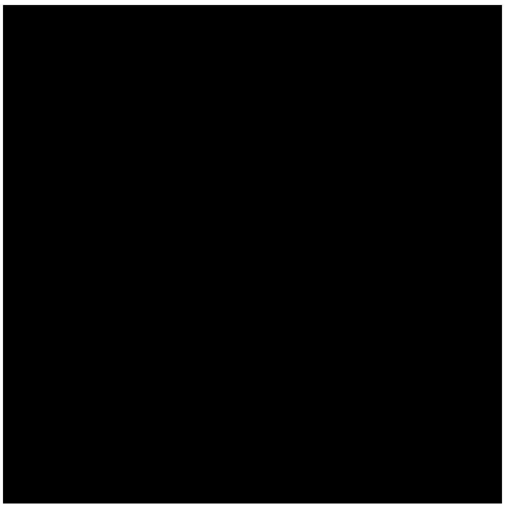

Figure 4. Specimen for modified oxyacetylene torch test

3. RESULTS AND DISCUSION

3.1. Structural characterization

FTIR spectra of uncured neat UPe resin and cured composite, CF and GF are presented in Figure 5.

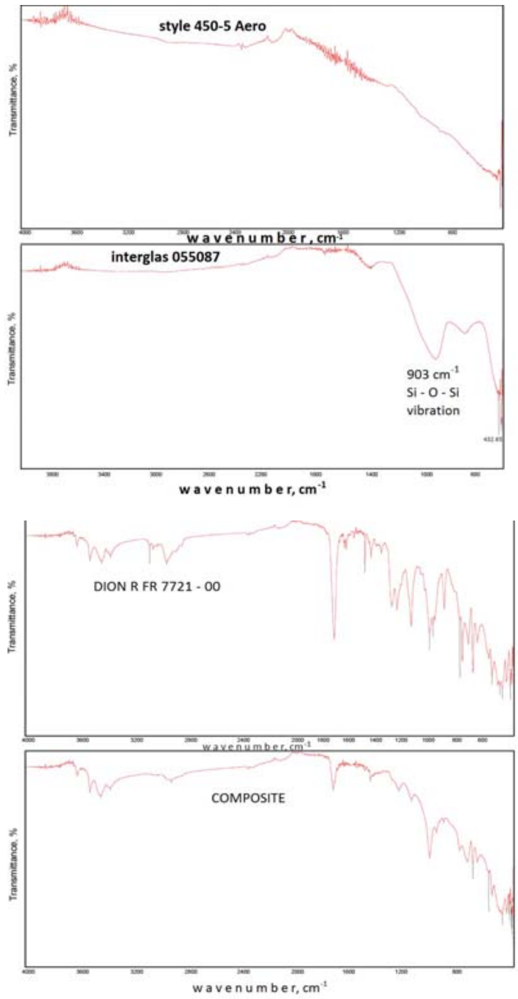

Figure 5. FTIR spectrum of the cured composite UPe_CGF, uncured UPe, carbon fabric (CF) and glass fabric (GF)

The peaks observed in the FTIR spectra of UPe and composite around 3616, 3525, 3444, and 3375 cm^{-1} and the low intensity peak at 697 cm^{-1} originate from hydroxyl (OH) and Al-OH groups stretching vibrations. Symmetric and asymmetric vibrations of CH_3 and CH_2 groups are observed around 3050, 2825, and 2840 cm^{-1}, while their bending vibrations are remarked at about 1454 cm^{-1} [21]. The intensity of these peaks is significantly reduced in FTIR spectrum of cured composite. The band at 1728 cm^{-1} in the FTIR spectrum of the composite originates from carbonyl C=O (ester) group present in the polyester resin [21]. This peak is shifted to a higher wavenumber compared to the neat UPe (1720 cm^{-1}) indicating interactions between UPe and carbon and glass fibers. The peak at 1490 cm^{-1} in UPe originates from the stretching vibration of the C=C and disappears after curing. Si-O-Si vibrations are observed as a broad peak at 903 cm^{-1}.

3.2. Dynamic mechanical analysis (DMA)

DMA is a standard technique abundantly used to examine viscoelastic properties of polymer materials in a wide temperature range. The temperature dependences of storage modulus (*G*'), loss modulus (*G*"), and loss factor (tanδ) of developed composite is shown in Figure 8. *G*' reflects elastic, while *G*" reflects viscous behavior of polymer matrix. In addition, Table 1 shows comparison of some characteristics of analyzed sample, neat UPe resin and composite: storage modulus in glassy state and rubbery plateau (G'_{GS} and G'_{RP}, respectively), glass transition temperature (T_g) and tanδ peak height.

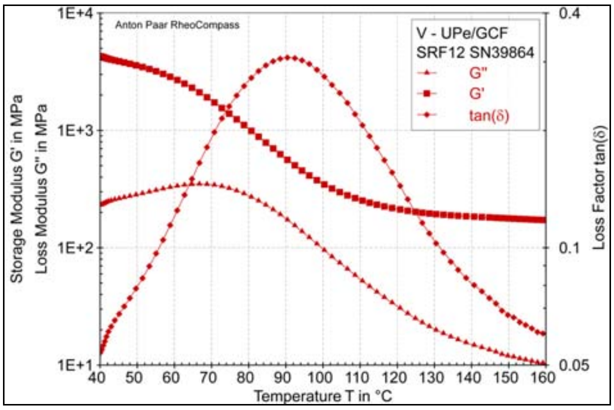

Figure 6. Temperature dependence of storage modulus (*G*') and loss modulus (*G*") of cured UPe CG/FG composite

Table 1. DMA results of UPe and coresponding reinforced composites obtained by different techniques

Sample	G'_{GS}, MPa	G'_{RP}, MPa	T_g, °C	Tanδ peak height
UPe	1698	28.2	110.1	0.43
COMPOSITE	3260	190.2	91.0	0.32

It can be noted that PAM specimen shows higher values of the *G*' in glassy state compared to the neat UPe resin. Such a phenomenon is associated to the strength of fiber/matrix interactions and the way the polymer chains are packed. The temperature increase causes a decrease in *G*' for all samples, which is the consequence of greater movement of the polymer segments. The glass transition temperature (T_g) is determined from tanδ peak position (Figure 6) and it reaches a value of 110.1 °C for UPe resin, and 91.0 °C for composite. The decrease in T_g for composite occurs due to the rigidity of the woven glass and carbon fibers.

3.3. Thermal properties

The thermal properties of developed composite are essential for its use as PAM, namely as thermal insulations in rocket motors. That is why modified ablation test is conducted and it is shown that composite sample has significantly greater thermal stability than the UPe resin. It is remarked that ignition temperature for neat UPe resin is 320 °C, while composite stayed stable even at the higher temperatures. Such phenomenon reflects the contribution of reinforcement to thermal stability of the final material. The carbon and glass fibers transform the UPe matrix into conductive network, which facilitate the formation of numerous hot spots and accelerate heat diffusion. Contrary to this, fibers endothermically absorb heat and give mechanical strength to the charred/carbonaceous material.

Figure 7. Samples of cured composite after ablation test

4. CONCLUSION

The presented study investigates the potential of vacuum technique for manufacturing of fiber-reinforced polymer composites used in military purpose as thermal insulation materials for composite rocket propellants. Self-extinguish UPe resin, reinforced with carbon and glass fibers, prove themselves as adequate materials for processing by this technique. As results, different shapes of specimens, such as cylindrical motor chamber and rectangular plate, were obtained and used for characterization of composite. The vacuum technique is suitable for intended purpose, due to ease of use and economical and environment benefits since there is no waste generation.

The thermal properties of the prepared PAM were determined by modified ablation test, while viscoelastic properties were studied by dynamic–mechanical analysis. Ablative test indicates that vacuum technique is competitive with other similar techniques used for PAM preparation. Obtained material has significantly greater thermal stability than the UPe resin.

ACKNOWLEDGEMENT

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References

[1] Ji, Y.; Han, S.; C hen, Z.; Wu, H.; Guo, S. Understanding the role of carbon fiber skeletons in silicone rubber-based ablative composites. Polymers 2022, 14, 268.

[2] George, K.; Panda, B.P.; Mohanty, S.; Sanjay, K.N. Recent developments in elastomeric heat shielding materials for solid rocket motor casing application for future perspective. Polym. Adv. Technol. 2019, 29, 8–21.

[3] Ji, Y.; Han, S.; Xia, L.; Li, C.; Wu, H.; Guo, S. Synergetic effect of aramid fiber and carbon fiber to enhance ablative resistance of EPDM-based

insulators via constructing high-strength char layer. Compos. Sci. Technol. 2021, 201, 108494.

[4] J. Bassler, “Colorado State University Rocket team builds newly designed rocket fuselage with filament winding equipment provided by Prodigm, Lattice Composites resins, and Composites One carbon fibers,” Reinf. Plast., vol. 64, no. 2, pp. 92–96, 2020, doi: 10.1016/j.repl.2019.07.003.

[5] M. Natali, J. M. Kenny, and L. Torre, “Science and technology of polymeric ablative materials for thermal protection systems and propulsion devices: A review,” Prog. Mater. Sci., vol. 84, pp. 192–275, Dec. 2016, doi: 10.1016/j.pmatsci.2016.08.003.

[6] J. H. S. Almeida, M. L. Ribeiro, V. Tita, and S. C. Amico, “Damage modeling for carbon fiber/epoxy filament wound composite tubes under radial compression,” Compos. Struct., vol. 160, pp. 204–210, 2017, doi: 10.1016/j.compstruct.2016.10.036.

[7] J. Bassler, “Colorado State University Rocket team builds newly designed rocket fuselage with filament winding equipment provided by Prodigm, Lattice Composites resins, and Composites One carbon fibers,” Reinf. Plast., vol. 64, no. 2, pp. 92–96, 2020, doi: 10.1016/j.repl.2019.07.003.

[8] H. Boussetta, M. Beyaoui, A. Laksimi, L. Walha, and M. Haddar, “Study of the filament wound glass/polyester composite damage behavior by acoustic emission data unsupervised learning,” Appl. Acoust., vol. 127, pp. 175–183, 2017, doi: 10.1016/j.apacoust.2017.06.004.

[9] Sun, H.; Yang, Y.; Ge, X. Effect of various fibers on the ablation resistance of poly(diaryloxyphosphazene) elastomer. J. Appl. Polym. Sci. 2020, 137, 48534.

[10] Gao, G.; Zhang, Z.; Li, X.; Meng, Q.; Zheng, Y. An excellent ablative composite based on PBO reinforced EPDM. Polym. Bull. 2010, 4, 607–622.

[11] Asghar, M.; Iqbal, N.; Iqbal, S.S.; Farooq, M.; Jamil, T. Ablation and thermo-mechanical tailoring of EPDM rubber using carbon fibers. J. Polym. Eng. 2016, 36, 713–722.

[12] El-Dakhakhny, A.M.; Ahmed, A.F.; Rutkeviˇcius, M.; El-Marsafy, S.; Abadeer, E. Effects of aramid fibers and colloidal particle fillers in composite ethylene propylene diene monomer rubber thermal insulators for rocket motor insulation. J. Compos. iliMater. 2018, 52, 1989–1995.

[13] Torre, L.; Kenny, J.M.; Boghetich, G.; Maffezzoli, A. Degradation behaviour of a composite material for thermal protection systems. Part III e char characterization. J. Mater. Sci. 2000, 35, 4563–4566.

[14] Farajpour, T.; Bayat, Y.; Abdollahi, M.; Keshavarz, M.H. Effect of borax on the thermal and mechanical properties of ethylenepropylene-diene terpolymer rubber-based heat insulator. J. Appl. Polym. Sci. 2015, 132, 41936.

[15] Dan, Z.; Zhang, C.; Hu, H.; Zhang, Y. Ablation behavior and mechanism of 3D C/ZrC composite in oxyacetylene torch environment. Compos. Sci. Technol. 2011, 71, 1392–1396.

[16] Jaramillo, M.; Koo, J.H.; Natali, M. Compressive char strength of thermoplastic polyurethane elastomer nanocomposites. Polym. Adv. Technol. 2014, 25, 742–751.

[17] Natali, M.; Koo, J.H.; Allcorn, E.; Ezekoye, O.A. An in-situ ablation recession rate sensor for carbon/carbon ablatives based on commercial ultra-miniature thermocouples. Sens. Actuators B Chem. 2014, 196, 46–56.

[18] Ren, J.; Qin, Y.; Peng, Z.; Li, Z. Influence of composite structure design on the ablation performance of ethylene propylene diene monomer composites. e-Polymers 2021, 21, 151–159.

[19] Liwei, Y.; Hao, Z.; Shengtai, Z.; Huawei, Z.; Yang, C.; Mei, L. Improving ablation properties of liquid silicone rubber composites by in situ construction of rich-porous char layer. J. Appl. Polym. Sci. 2021, 138, 50030.

[20] [ASTM International, “Oxyacetylene Ablation Testing of Thermal Insulation Materials.”

[21] A. Drah et al., “Effect of surface activation of alumina particles on the performances of thermosetting-based composite materials,” J. Compos. Mater., p. 002199831983913, Mar. 2019, doi: 10.1177/0021998319839133.