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Mechanical and Microwave Absorption Properties of Exfoliated Graphite and Manganese Ferrite Nanoparticles on Polyvinylidene Fluoride Thin Films

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This study presents a simple and efficient method for the development of thin polymer composite films for use in absorbing electromagnetic waves at X-band frequencies. The thin film composites were fabricated by solution casting technique by incorporating the exfoliated graphite, and manganese ferrite nanoparticles into the polyvinylidene fluoride matrix. The composite film consisting of both 3 wt.% of $MnFe_2O_4$ and exfoliated graphite/PVDF showed better absorption properties and achieved a minimum reflection loss of –30.54 at 9.62 GHz in the 8 – 12 GHz frequency range. This synergistic effect of the film was attributed to its β-phase formation, multiple-reflection-absorption effect, and the conduction of fillers at their interfaces. Finally, the mechanical and absorption characteristics of the fabricated thin film composites were also investigated. The results indicated that these composite films hold potential for use in microwave absorption applications in the X band.

Keywords: microwave absorption, X band absorbers, solution casting technique, thin films, mechanical properties.

1. INTRODUCTION

In recent years, concern over microwave absorbers has significantly increased due to the growing prevalence of radar technology. Microwave absorbers are widely used in stealth aircraft operations, particularly in the X band (8 – 12 GHz). Polyvinylidene fluoride (PVDF) based composites were studied extensively for their lightweight, flexibility, mechanical durability, and environmental friendliness. Consequently, addressing and mitigating undesirable electromagnetic radiation became an essential concern. To improve the β-phase of the PVDF matrix, various nanofillers such as ferrites and carbon materials were incorporated into composite materials. This incorporation of nanofillers improved the microwave absorption performance of PVDF-based composites. Among these nanofillers, exfoliated graphite (EG) was particularly noted for its excellent dispersion qualities, large surface area, and high conductivity, making it a highly desirable material for microwave absorption. EG's superior electrical conductivity was attributed to its lower oxygen content compared to other types of graphite [4, 5]. The presence of OH and COOH groups on the surface of EG enables more physical and chemical interactions with polymers, resulting in unique mechanical and thermal properties [6 – 8]. Ferrites are known to be effective in absorbing electromagnetic waves due to their exceptional wave absorption capabilities, abundance of raw materials, and low cost [9 – 11]. Among the ferrites, Manganese ferrite ($MnFe_2O_4$), the most preferred ferrite material among researchers for microwave absorption due to its high surface area and low density. Additionally, $MnFe_2O_4$ has high magnetic permeability, resulting in stronger magnetic properties and higher wave absorption capacity [12, 13]. It can be used in various forms such as nanoparticles, nanostructures, and thin films, with each having unique properties such as continuous anisotropy, size-dependent magnetization saturation, and a high Curie temperature, further enhancing its suitability for electromagnetic wave absorption applications [14, 15]. Recent studies have focused on magnetic nanoparticles combined with PVDF nanocomposite films have emerged as highly promising candidates for various fields [16]. For decades, microwave absorbers have been integral to military uses and other applications like antenna pattern shaping and radar cross-section reduction. Traditional microwave absorbers, such as ferrite, carbon materials, and magnetic nanocomposites, are typically powder materials with high reflection loss [17]. However, these conventional materials are often heavy and inflexible, limiting their effectiveness in lightweight structures like aircraft. The significance of this work lies in its demonstration of improved microwave absorption and mechanical properties through the synergistic use of both carbon and magnetic fillers. Several studies have concentrated separately on microwave absorption and mechanical characteristics, herein this composite offers a balanced performance in both properties. To address these limitations, microwave absorbing materials with

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electroactive polymers offer a solution-by-solution casting method. This approach produces thin, flexible nanocomposite films with excellent frequency responses in the GHz range. Therefore, extensive research is needed on microwave absorption materials. In particular, nanoparticles like carbon and magnetic particles combined with PVDF nanocomposites showed great potential in the X-band frequency range (8 – 12 GHz) [18]. Thus, this work presents a thorough analysis of the electromagnetic wave absorption characteristics of exfoliated graphite and manganese ferrite embedded in a PVDF matrix. This study was tested using vector network analysis, X-ray diffraction, and scanning electron microscopy for microwave absorption at X-band frequency (8 – 12 GHz). The combination of EG and $MnFe_2O_4$ together has a synergistic effect that improves the electrical and magnetic characteristics of thin films. These thin film composites could be employed in a variety of defense and electronic sectors to reduce electromagnetic interference. Furthermore, the nanocomposites developed in this study can be used to construct enclosures for electronic devices and shield them from unwanted electromagnetic waves. The research findings will provide valuable insights into the optimal conditions and significant contributions that can enhance the absorption of microwaves in the prepared composite thin films.

2. EXPERIMENTAL PROCEDURE

Polyvinylidene fluoride (PVDF) was purchased from Thermo Fisher Scientific Pvt Ltd. Exfoliated graphite (EG) and Manganese ferrite ($MnFe_2O_4$) nanoparticles were obtained from Nano research lab, India. Dimethylformamide (DMF) was purchased from Merck Ltd. The PVDF/EG/$MnFe_2O_4$ composite thin films were fabricated by a simple technique called the solution casting method. Initially, the PVDF powder is dissolved in DMF solution for 3 hrs by using a magnetic stirrer. Then EG nano particles were then added to PVDF/DMF solution and mixed well through a magnetic stirrer for 2 hours at 60 °C. And then $MnFe_2O_4$ nanoparticles were added to the prepared PVDF/ EG solution and stirred for 2 hours at 60 °C to get uniform distribution. Finally, the solution was poured into a Petri dish and cast into films at 60 °C for 8 hrs. Likewise, the different composite thin films were fabricated for the various concentrations of the fillers as tabulated in Table 1. The aggregation caused by PVDF polymer could be reduced by increasing the stirring time to get the homogenous polymeric solution and also lowering the filler concentrations.

Table 1. Composition of the fabricated thin film

Sl.No.	Sample designations	Material combinations, wt.%
1	A	Pure PVDF
2	B	3 wt.% EG/PVDF
3	C	1 wt.% of $MnFe_2O_4$ –3 wt.% EG/PVDF
4	D	3 wt.% of $MnFe_2O_4$ –3 wt.% EG/PVDF
5	E	5 wt.% of $MnFe_2O_4$ –3 wt.% EG /PVDF

3. RESULTS AND DISCUSSION

The XRD patterns revealed the presence of distinct crystalline phases within the PVDF sample. As illustrated in Fig. 1, the XRD spectrum observed the electrically active polar β-phase at 20.34° and 36.24°, the non-polar α-phase at 18.54° and 26.5°, and the polar γ-phase at 39.02°. Incorporating carbonaceous and ferrite filler into the PVDF matrix, indicated an increase in the composite's α and β-phases which led to improved dielectric characteristics [16 – 18]. The PVDF's polar phase nucleation was influenced by the interactions near the EG/$MnFe_2O_4$/PVDF interfaces. This phenomenon of interfacial interaction influences the crystallization behaviour and overall properties of thin films. The crystallinity of the composite thin films is enhanced due to the formation of cationic complexes with the functional group of PVDF, which confirms the intercalation of EG with the PVDF polymer system.

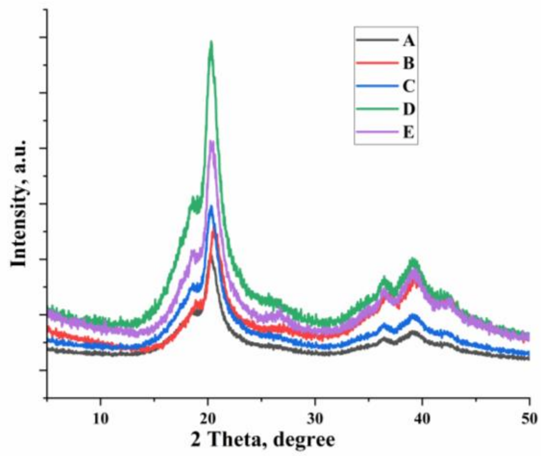
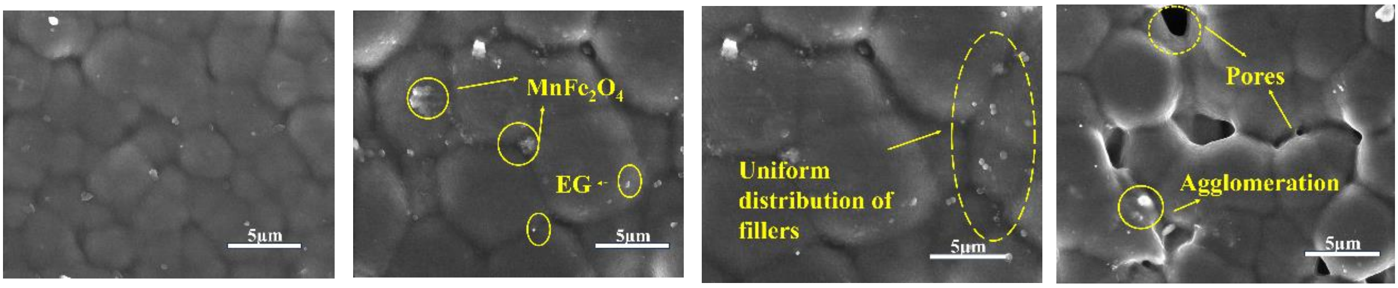


Fig. 1. XRD patterns of the thin films: A – pure PVDF; B – 3 wt.% EG/PVDF; C – 1 wt.% of $MnFe_2O_4$ and 3 wt.% EG/PVDF; D – 3 wt.% of $MnFe_2O_4$ and 3 wt.% EG/PVDF; E – 5 wt.% of $MnFe_2O_4$ and 3 wt.% EG /PVDF

The SEM images shown in Fig. 2 revealed the crystallization of the β-phase within the PVDF films. The SEM images of samples reveal well-defined, uniform, and densely packed EG and manganese iron oxide particles within the PVDF composite films. In Fig. 2 c sample D, where the uniform distribution of nanoparticles on the surface serves as a distinct indicator of β-phase crystallization whereas in Fig. 2 d, sample E shows the presence of agglomeration, voids, and pores due to the high percentage of filler particles.

The incorporation of exfoliated graphite nanoparticles into the PVDF matrix enhanced the polar β-phase of PVDF. These nanoparticles served as nucleation centers, influencing the alignment of dipoles within the PVDF structure. The increased number of nucleation sites promoted the development of the β phase in the composite thin films. For consistent and efficient performance of these thin composite films, it was crucial to maintain a uniform dispersion of reinforcements such as EG and $MnFe_2O_4$ particles to get synergistic effects and a continuous conductive network. However, particle agglomeration led to stress concentration, which negatively impacted the film's tensile properties [19 – 21].



a b c d

Fig. 2. Microstructures of the thin films (a) 3 wt. % EG /PVDF (b) 1 wt. % of $MnFe_2O_4$ -3 wt. % EG /PVDF (c) 3 wt. % of $MnFe_2O_4$ -3 wt. % EG /PVDF (d) 5 wt. % of $MnFe_2O_4$ -3 wt. % EG /PVDF

The Vector Network Analyzer (Agilent N9917A) was connected to the two horn antennas for the analysis of the reflected microwaves [22 – 24]. Stress induces the polymer chain to become oriented, which is essential for the transition to PVDF's β phase [13 – 15]. The maximum tensile strength of samples B-E is 26.65, 28.24, 32.16, and 29.21 MPa respectively, which are compared to the pure PVDF film (24.52 MPa) as shown in Fig. 4. This microwave performance was attributed to the broad surface area, high electrical conductivity, homogeneous dispersion and magnetic response of $MnFe_2O_4$ nanoparticles, which caused electric and magnetic loss. Additionally, dielectric loss was identified as the primary contributor to electromagnetic loss in thin films because of the presence of EG nanoparticles.

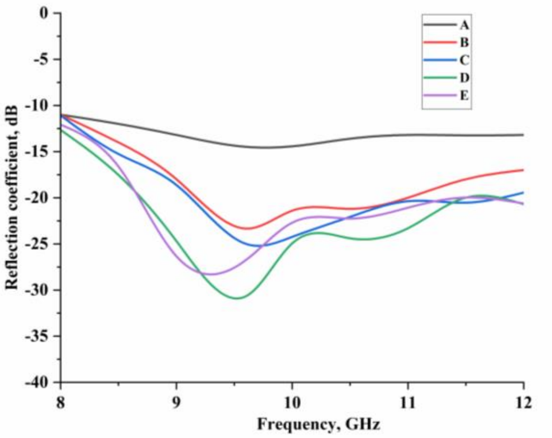


Fig. 3. Reflection coefficient of the thin films at 8 – 12 GHz

In that, two horn antennas were used as a receiver and transmitter, positioned for bistatic radar operations in an anechoic chamber setup. The results showed reduced reflection for PVDF films with carbon and magnetic fillers for all concentrations. Notably, the composite with 3 wt.% of both $MnFe_2O_4$ and EG in the PVDF matrix demonstrated microwave absorption with a minimum reflection loss of –30.54 at 9.62 GHz in the X band in Fig. 3.

The absorption of microwaves is determined by the interaction between electric and magnetic dipoles within the material. The microwave absorption behavior was attributed to the synergistic effect of exfoliated graphite, $MnFe_2O_4$, and PVDF, leading to enhanced dielectric and magnetic dissipation. Stress induces the polymer chain to become oriented, which is essential for the transition to PVDF's β phase [25, 26]. The maximum tensile strength of samples B–E is 26.65, 28.24, 32.16, and 29.21 MPa respectively, which are compared to the pure PVDF film (24.52 MPa) as shown in Fig. 4.

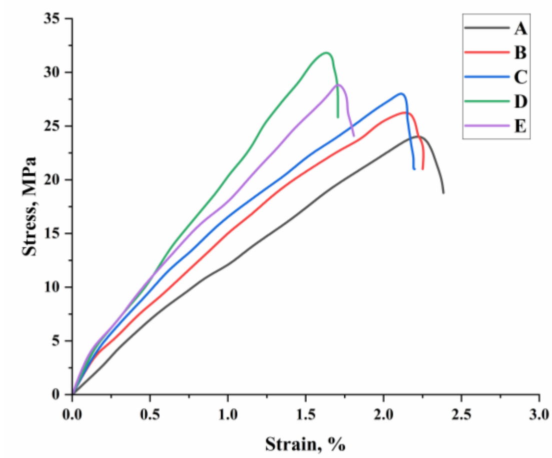


Fig. 4. Tensile properties of the PVDF composite thin films

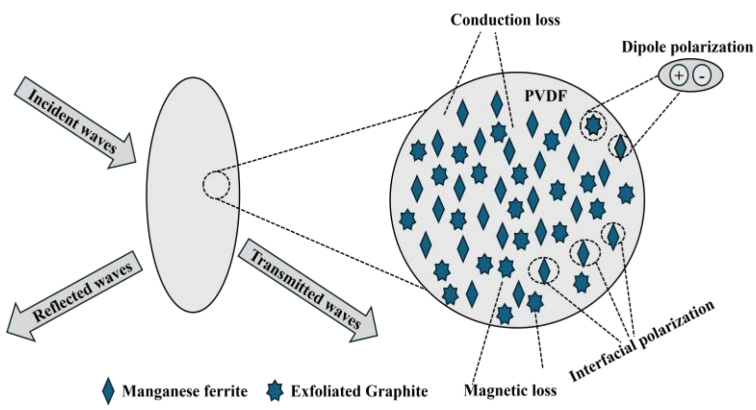


Fig. 5. Schematic diagram of the microwave mechanism of the fabricated PVDF composites

The microwave mechanism of the fabricated PVDF composite thin films is illustrated in the schematic diagram in Fig. 5. The significance of the enhanced microwave absorption achieved through the synergistic use of EG and $MnFe_2O_4$. These fillers improved the dielectric loss, conduction loss, interfacial polarisation, and magnetic loss which offered a balanced performance in microwave absorption properties. The increased polarizability in the EG/$MnFe_2O_4$/PVDF nanocomposite thin films (B, C, D & E) because of the presence of negatively charged fluorine atoms and PVDF was influenced by electrostatic interactions with EG and $MnFe_2O_4$, making it more polarized compared to the pure PVDF sample (A).

4. CONCLUSIONS

In this study, we present an effective and simple method to fabricate microwave absorber composite thin films using a polyvinylidene fluoride (PVDF) matrix with exfoliated graphite and manganese ferrite nanoparticles for microwave absorption. Furthermore, the proposed thin film composite absorber of 3 wt. % of both $MnFe_2O_4$/EG in PVDF has a minimum reflection loss of –30.54 at 9.62 GHz in the X band. Moreover, the maximum tensile strength of samples B-E is 26.65, 28.24, 32.16 and 29.21 MPa respectively, which are compared to the pure PVDF film. Thus, the thin film exhibited improved mechanical properties which makes it suitable for X-band applications. The results indicated that these composite films hold potential for use in electromagnetic wave absorption applications, particularly in stealth aircraft industries Further studies in this research will be focused on identifying superior substitution materials for the matrix and reinforcements. Moreover, simulations of these composites will be investigated to improve microwave absorption.

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