Smart membrane absorbing electromagnetic waves based on polyvinyl chloride/graphene composites

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Abstract
The rapid proliferation and intensive use of electronic devices have led to an increase in electronic pollution, such as electronic noise, electromagnetic interference (EMI), and radiofrequency interference (RFI), which cause malfunctions of electronic devices. The emergence of flexible polymer composites has a remarkable potential for electromagnetic shielding depending on their unique characteristics, such as their electrical, thermal, mechanical, and magnetic properties, which are very useful for suppressing electromagnetic noise. Graphene (G) and its composites can serve as better shielding materials against these interferences due to their lightweight and high corrosion resistance. Researchers are still grappling with the need for flexible and scalable smart composite materials to prevent radioactive pollution from electronic devices. The inclusion of next-generation graphene (G) conductive fillers loaded with polyvinyl chloride (PVC) / graphene is the subject of our current research (G). Due to the absorption-dominated shielding process, the composite has an extraordinarily low percolation threshold and a high shielding efficiency (SE) against electromagnetic interference (EMI). The distribution and dispersion patterns of graphene particles in the matrix phase were validated by SEM electron micrographs. The composite, which contains just 40% graphene by weight, has an EMI SE value of 26 dB in the frequency range of 10 to 15 GHz and is only 2 mm thick. In this case, we believe that promoting a scalable and industrially viable G/PVC composite, which is a novel and strong candidate in the burgeoning field of high-stress electromagnetic shielding applications in the future, is the best option.

1. Introduction

Nowadays, the proliferation of electrical and electronic devices and equipment containing electrical and/or electronic components (for example, radio and television receivers, industrial machines, etc.) has increased electromagnetic interference (EMI) problems. In order to prevent the malfunction of the equipment and to ensure a satisfactory electromagnetic environment for radio communications, the equipment must be protected by shields, called electromagnetic shielding, that comply with international electromagnetic compatibility (EMC) standards.

Conventional metals with good electrical conductivity, such as copper, aluminum, and nickel, have good electromagnetic shielding performance. However, in some applications, the shielding material must, in addition to being effective, be lightweight and flexible. Therefore, great attention has been devoted to the development of such materials from polymers conductive because of their low density, their ease of synthesis, their easy variation of electrical properties, and their low cost.

Polymer science focuses primarily on the development and manufacture of new materials for advanced applications. It plays an important role in the synthetic and methodological advancement of polymers, such as
polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), and polystyrene (PS), which are synthesized on an industrial scale [1]. Polymer composites based on these polymers with appropriate nanofillers have appropriate thermal and mechanical properties (high tensile strength, modulus of elasticity, flexibility) for electromagnetic shielding compared to other granular and ceramic composites [2].

PVC is one of the most widely used polymeric materials due to its low cost, high mechanical strength, good fire resistance, and good chemical resistance [3]. It is the second most commonly used thermoplastic, after PE. Carbon fillers not only improve their thermal stability but also increase their mechanical resistance [4]. Carbon-based nanofillers, such as carbon nanotubes (CNT), graphene (G), graphene oxide (GO), and carbon black (CB), is used to obtain some improved properties of the polymer matrix. The dispersion of the conductive charges of this carbon-based material in PVC (a non-conductive polymer) leads to the formation of conductive polymer composites.

Various methods of preparation are available for the preparation of graphene (G), but the modified method of Hammer’s is commonly used for achieving good yield and purity. More of several functional groups (carboxyl, carbonyl, and hydroxyl) are also, often attached to the leaves of G. These functional groups make the G leaves hydrophilic, forming a stable colloidal suspension. Due to its exceptional properties, G has been widely utilized in energy storage, composite materials, chemical sensors, and electronic and optical devices [5].

The oxygen groups present on the surface of G can interact with the halogen atoms in the PVC chain, forming Van der Waals chemical bonds. It has been reported that N-Dimethylformamide (DMF) is one of the best organic solvents for graphene dispersion in PVC [6]. For the manufacture of improved PVC/G composites, the most appropriate way is to establish a covalent bond between G and PVC to improve the mechanical and thermal properties of the matrix [6].

In this study, G was prepared by recycling graphite from used batteries using an electrochemical method [7] and then using the G to reinforce composite materials based on polyvinyl chloride. We measured the shielding effectiveness of the composite against electromagnetic interference from 10 to 15 GHz using the experimental method of the rectangular waveguide.

2. Experimental part

2.1. Elaboration of graphene

In this study, graphite rods from electrical battery devices (as electrodes) and an electrolyte bath (electrochemical cell) composed of H₂SO₄ and H₂O were used for the electrochemical exfoliation process to obtain high-quality, large-area G thin sheets [8].

2.2. Preparation of composite materials

For the preparation of our G/PVC composites, we followed the protocol of Bakli et al [8]. A mass of G ranging from 0% to 40% was dispersed for 15 min in an emulsion of dibutyl sebacate (DBS) under ultrasonic vibration at room temperature. A mass of PVC (SIGMA ALDRICH, 98%) used as the polymer matrix was added to the mixture (G/DBS) in a mold that has the same dimension as the waveguide, and then subjected to a heat treatment at 423 °K for 1.5 h; the film of this composite (40 G%) is presented in figure 1.
In order to study the effect of G loads on the properties of the PVC, a series of composites were made, and the various compositions are summarized in table 1.

### Table 1. Compositions and mass fractions of engineered nanocomposites [8].

| wt% of G in composite | Sample thickness |
|-----------------------|-----------------|
| 0%                    | 2 mm            |
| 1%                    | //              |
| 2%                    | //              |
| 4%                    | //              |
| 6%                    | //              |
| 8%                    | //              |
| 10%                   | //              |
| 20%                   | //              |
| 30%                   | //              |
| 40%                   | //              |

2.3. Characterization

2.3.1. Characterization of the membrane by scanning electron microscopy SEM

The results of the SEM characterization are presented in figure 2, which shows a compact, smooth, and coherent surface. This aspect can be explained by the densification of the polymer during cross-linking in the presence of graphene. These nanomaterials are known for their high elasticity and their ability to bond with polymers, which gives them a better density with a lower occupied volume.

In order to improve the properties of polymers and in response to the development of methods of preparation and characterization of nano-objects, the incorporation of nanocharges into polymeric matrices quickly took place. Several studies have shown that the addition of nano loads, even at low percentages, to a polymeric matrix to obtain a composite significantly improves the properties of the polymer.

![Figure 2. SEM image of PVC/G (40 wt% of G).](image2)

![Figure 3. FT-IR spectrum of PVC and PVC/G (40%).](image3)
2.4. Characterization by Fourier transform infrared spectroscopy FT-IR

The analysis was carried out using the transmission mode and the results obtained are presented in figure 3. The overlay of the spectra shows that the two materials, PVC and PVC/G, had the same composition with the presence of the same characteristic bands. Furthermore, it is noted that the intensity of the characteristic peaks at the C-Cl functional groups decreased when 40% graphene was added, and this can be explained by the fact that the amount of graphene added was high.

2.4.1. Characterization by differential thermal analysis (DTA)

The measurement consists of determining and measuring the change in thermal flux emitted or received by a sample when subjected to temperature programming. These measurements provide qualitative and quantitative information on thermal transformations. A PVC/G composite containing 40% G and PVC alone was also performed, and the resulting thermogram overlay is shown in figure 4.

The DTA thermograms have two endothermic peaks that correspond to the decomposition of PVC. The first decomposition, which occurs at $T = 300\, ^\circ\text{C}$, is attributed to the degradation of PVC, the removal of HCl, and the formation of conjugated double bonds, while the second decomposition corresponds to the thermal cracking of the residue PVC carbon polymer sequences. The superposition of the two thermograms shows a decrease in the decomposition temperature as a result of the insertion of graphene. The peak temperatures are shown in table 2 below.

3. Electromagnetic shielding effectiveness SE measurement

The network analyzer is an electronic device that allows the characterization of components used in microwave circuits, such as amplifiers, attenuators, cables, and any device having an impact on the transmitted or received signal. Indeed, it makes it possible to measure the scattering parameters, noted $S$. From these parameters, quantities such as power, gain, attenuation, reflection coefficient, or impedance are calculated. There are two
main families of network analyzers. A rectangular waveguide is a technique based on the quadrupole structure and allows the parameters (reflection coefficient and transmission coefficient) to be measured using the network analyzer. In addition, it makes it possible to characterize the permittivity and permeability of the sample as well as its electromagnetic shielding properties.

For the measurement of the electromagnetic effectiveness SE, the PVC/G flexible membrane was inserted into the waveguide support of a KEYSIGHT N5222A Vector network analyzer as shown in figure 5.

The frequency (10–15 GHz), used in military and civilian communications, was used for the SE shielding experiments. From a two-port vector network measurement, the broadcast parameters $S_{11} = b_1/a_1, S_{21} = b_2/a_1$, where (a) and (b) are normalized incidents and reflected waves, and $S_{11}, S_{21}$ are reflection coefficients.

The different phenomena that contribute to shielding effectiveness are [9, 10]:

• Losses by reflection: the reflection on the left wall is due to the mismatch of the electromagnetic wave encountering a change of the medium.

• Losses by absorption: absorption is a loss due to the passage of the electromagnetic wave through a certain thickness of the material. A proportion penetrates the wall and is attenuated by a factor $\exp(-\alpha z)$. $\alpha = 1/\delta$ and $\delta$ is the skin thickness.

• Losses by multiple reflections: these reflections are ignored if $t \gg \delta$ and only the initial transmission will be considered. When the thickness of the material is small compared to the thickness of the skin, there are multiple reflections between the walls of the shielding.

• The sum of these terms significantly decreases the total shielding effectiveness.

• The process involves the measurement of the reflected ($S_{11}$) and emitted ($S_{21}$) signals and the absorption signal of electromagnetic waves by the following equations, respectively:

$$SE(R) = 10 \log \left| 1 / |S21|^2 \right| = -10 \log (1 - R)$$

$$SE(A) = 10 \log \left| 1 - S11^2 / S21^2 \right| = -10 \log (1 - R)$$

$$SE = SE(R) + SE(A)$$

4. Results and discussion

Measurement of the shielding effectiveness parameters of composites has become increasingly important, particularly in the areas of electromagnetic interference (EMI) and radio frequency interference (RFI) research. It involves characterizing the dielectric parameters of the material, such as the permittivity and permeability and the effectiveness of electromagnetic shielding, which have proven useful in many areas of research and development. This is why we characterized our samples (PVC/G composites) from the point of view of the SE shielding according to the percentage of G loads and according to the frequency.

In order to maximize the SE of the G/PVC composite at a given G load, each G must be dispersed in the polymer matrix. A uniform dispersion was possible thanks to the ultrasonic vibration (figure 6), which is an optimal method for a high-load mixing dispersion.

The effects associated with the use of ultrasound vibrations are attributed to the ultrasound-induced increase in polymer chain relaxation from secondary interaction and the resulting increase in reptation and entanglement from stretched states.

Researchers claim that the quality of graphene prepared by ultrasound is much higher than that of graphene obtained by the Hummer method, where the graphite is exfoliated and oxidized [11].
The reflection (R), absorbance (A), and transmittance (T) properties of a sheet of PVC/G were measured using the rectangular waveguide in a frequency range from 10 GHz to 15 GHz and for various percentages of G. The results of these measurements are presented in table 3.

4.1. SE (R) and SE (A) as a function of the percentage of G (GW%)

4.1.1. The shielding efficiency
The parameter S21 (transmittance parameter) of the G/PVC samples is removed by the waveguide. From this parameter and using the expressions (equation: 3) and the implemented software, the trace SE is in the continuation of figure 7.

Figure 7 shows the variation in the shielding efficiency of a plate (PVC/G), using the rectangular guide in the range of 10 GHz to 16 GHz. We find that the shielding efficiency was about 4.5 dB for 0% of G and 26 dB for about 40% of G. Some oscillations were observed due to the existence of internal resonances in the electric field.

At only 1mm thick, the composite demonstrated a value of 7.88 percent by weight and an EMI SE value of 43.39 dB in the X-band frequency range with only 20% by weight of (Ketjen 600JD, K-CB) filled with carboxylated nitrile butadiene rubber (XNBR) [12].

According to Sabyasachi Ghosh and his collaborators, the electromagnetic interference (EMI) shielding effectiveness of the manufactured coated textiles (rGO/Ag) was 27.36 dB in the X band [13].

The minima that SE is exposed to at these resonances have been clearly dampened to improve SE at these frequencies.

These data show that the shielding efficiency depends on the percentage of conductive charge in the composite up to a certain peak of saturation.

| SE%  | 10GHz  | 12GHz  | 15GHz  |
|-----|-------|-------|-------|
|     | A     | T     | A     | T     | A     | T     |
| 0%  | -3.41 | -2.68 | -21.82 | -2.73 | -15.28 | -3.58 | -2.02 | -4.48 | -17.67 |
| 1%  | -8.46 | -2.20 | -21.70 | -3.52 | -16.09 | 5.47  | 6.56  | -21.33 | -4.53  |
| 2%  | -3.19 | -2.91 | -20.11 | -16.3 | -3.92  | 3.92  | -2.10 | -4.35  | -17.63 |
| 4%  | -4.18 | -2.09 | -27.66 | -2.62 | -3.80  | -14.34 | -1.82 | -4.68  | -25.19 |
| 6%  | -3.24 | -2.80 | -26.46 | -2.18 | -4.44  | -14.42 | -1.84 | -4.69  | -21.99 |
| 8%  | -6.30 | -2.63 | -31.15 | -6.06 | -4.53  | -15.95 | -5.69 | -3.55  | -23.59 |
| 10% | -3.54 | -2.53 | -83.41 | -1.99 | -5.10  | -12.20 | -2.07 | -4.24  | -24.38 |
| 20% | 0.03  | -3.07 | -38.61 | -2.62 | -5.69  | -10.85 | -1.9  | -4.92  | -60.72 |
| 30% | -1.53 | -5.34 | -22.97 | -6.98 | -6.98  | -6.98  | -6.98 | -1.29  | -6.89  | -16.11 |
| 40% | -1.25 | -9.01 | -9.01  | -6.98 | -6.98  | -6.98  | -1.74 | -7.80  | -7.80  |

The reflection (R), absorbance (A), and transmittance (T) properties of a sheet of PVC/G were measured using the rectangular waveguide in a frequency range from 10 GHz to 15 GHz and for various percentages of G. The results of these measurements are presented in table 3.
4.1.2. Frequency effect
The results obtained for the frequency effect on the composite (PVC/G) are presented in figure 8.

Figure 8 shows the variation in the shielding efficiency of the composites (PVC/G) with various percentages of G, using the network analyzer in the range of 10 GHz to 15 GHz. We note that SE shielding efficiency increases exponentially with frequency. It varies from 4 dB to 26 dB for 10 GHz to 15 GHz. The electromagnetic shielding of the 40% G (PVC/G) was 24 dB, 25 dB, and 26 dB for the frequencies of 10, 12, and 15 GHz.

5. Conclusions
In summary, a new rentable and industrially viable G/PVC composite material has been developed via a ‘molding in solution’ approach. With only 2 mm of thickness, the composite above contains high-quality EMI with a SE of 26 dB.

The distribution and dispersion of G particles in PVC matrices were discovered using a scanning electron microscope (SEM).

The structural characterization by FT-IR showed that the composites have the same composition, but the addition of a percentage of graphene resulted in a slight modification of the characteristic peaks of the C-Cl group. DTA thermal characterization showed a decrease in the decomposition temperature of PVC/G due to the catalytic effect of graphene. The measurements show that we have a higher shielding efficiency at the composite (PVC/G) by varying the percentage of conductive charge (graphene).

For frequency, the study has shown that our material is reliable for high frequencies, so the efficiency increases by increasing the frequency range. Finally, the introduction of graphene results in a significant improvement in the shielding efficiency of the nanocomposite. This efficiency offers attenuation close to 70% at high frequency.

It could be useful in flexible electronic applications as a ‘global’ composite material. Following that, the difficult problem of producing a cost-effective intelligent composite material can be solved by applying a low-cost composite material (G/PVC) to a flexible electronic application, resulting in a reduction in manufacturing costs for the back-end.

Data availability statement
The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.
Declaration of interest statement

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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