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Material Characterisation

Study on dielectric properties of synthesized exfoliated graphite reinforced epoxy composites for microwave processing

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ABSTRACT

In this study, exfoliated graphite (EG) was used as filler to enhance the dielectric properties of composites, which are processed through microwave (MW) curing. EG was synthesized through MW irradiation technique. The detailed characterizations of as-synthesized EG were first carried out. Afterwards, the EG reinforced epoxy composites have been synthesized. The dielectric properties of composites as a function of EG content with and without MW heating were measured at a frequency of 2.45 GHz. The 3 wt% EG/epoxy composite shows an increase of about 43 and 81% in dielectric constant and loss factor, respectively. The dielectric properties are found to decrease after MW curing. Finally, the dynamical mechanical analysis was performed for MW cured samples including thermally cured samples. The glass transition temperature and storage modulus are found to improve by about 24 °C and 58%, respectively for MW cured 3 wt% EG/epoxy composite as compared to neat epoxy counterpart.

1. Introduction

There is a growing demand in recent years to minimize the energy usage for food and materials processing industry [1]. The microwave heating using 2.45 GHz industrial systems appears to be viable option for these applications due to the faster and rapid heating as compared to the conventional heating phenomenon. The microwave heating is now widely accepted in industry for processing of polymer composites. In microwave heating, there is a direct interaction of molecules with the electromagnetic field, and therefore the heat is generated throughout the volume of material [2]. This results in potential advantages of microwave heating over the conventional heating (CV) such as shorter processing time, selective, volumetric, more uniform and efficient heating [2,3]. However, the major issue associated with microwave heating of polymer composites is to deal with low dielectric loss of polymer resin, which consumes long processing time to achieve desired properties of product. The solution to overcome such a problem is to improve the dielectric properties especially the dielectric loss of base polymer matrix by incorporating it with a secondary microwave absorbing filler or susceptors [4]. The susceptors absorb microwave rapidly and provide sufficient heat to the resultant composites. With the incorporation of susceptor material, the sample becomes highly lossy and are more prone to interact with microwaves [5]. However, in order to properly understand the processing of materials through microwave (MW) heating and to define the heating cycle, the knowledge of dielectric properties of matrix and inclusions is quite important. Therefore, prior to heating, the determination of key parameter i.e., complex permittivity ($\varepsilon_r^* = \varepsilon_r' - \varepsilon_r''$) should be carried out for the processing of materials using microwaves [6]. It includes two key parameters, one is dielectric constant (ε_r'), which represents the amount of energy stored within the material and the other is the dielectric loss (ε_r'') denoting the energy loss during microwave heating.

Carbon materials are very good absorbers of microwaves as they can be heated quite rapidly using electromagnetic waves of RF and microwave frequency range [7]. Some studies have reported about the utilization of carbon materials for microwave assisted curing. However, there is still very limited study about the usage of carbon as efficient fillers for the microwave assisted curing due to the unavailability of dielectric properties data of these fillers and the resultant composites at 2.45 GHz. Fotiou et al. reported on the use of carbon nanotubes (CNTs) for MW curing. They observed that the addition of CNT in the polymer resulted in more efficient energy transfer using MWs while maintaining the mechanical performance of material [2]. Benitez et al. reported about the combined use of carbon nanofibers (CNFs) and Microwaves

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(MWs) to enhance the thermal, mechanical and electrical properties of high density polythene [8]. Rangari et al. studied the thermal and mechanical properties using CNFs as additives to evaluate the time saving microwave curing method [9]. They observed improvement in all samples with CNFs infusion in resin, and optimization of properties was achieved for 0.3 wt% CNFs. Vos et al. found that the low loss oxides such as alumina and silica could be heated up to 800 °C using amorphous carbon as susceptor [10]. However, none of these studies have reported about the effect of susceptor material on the dielectric properties of resultant epoxy composite. Therefore in this study, the exfoliated graphite (EG), a derivative of graphite is proposed as a potential microwave absorbing filler in epoxy matrix. More importantly, a detailed study about the effect of inclusion of various amount of EG filler on the dielectric properties of the resultant composite at 2.45 GHz is carried out by measuring the dielectric constant and loss factor of the sample at each stage. To the best of authors' knowledge, such kind of systematic study involving the effect of EG based fillers on the dielectric properties and the microwave curing phenomenon of the resultant composite has not been done earlier. After studying the dielectric properties, the dynamical mechanical analysis (DMA) of MW cured EG/epoxy composites is also done and the results are compared with the conventionally cured composites. The proposed study can be described in following two steps:

1. The first step deals with the synthesis and characterization of EG using microwave irradiation, and experimentally testing the effect of inclusion of various concentrations of EG on dielectric properties of the resultant composite at 2.45 ± 0.05 GHz. Moreover, the effect of MW curing on dielectric properties is also studied.
2. In the second step, a comparison of MW and CV curing of various neat epoxy and EG reinforced epoxy composites is carried out. The comparison is done on the glass transition temperature.

2. Materials and methods

2.1. Materials

Natural flake graphite (NFG) (sigma Aldrich, 99.99%) with an average diameter of 500 μm was used as a primary source for preparing the exfoliated graphite. Perchloric acid ($HClO_4$), nitric acid (HNO_3) and potassium permanganate ($KMnO_4$) were purchased from Qualigens Fine Chemicals, India and used as chemical intercalate and oxidizer to prepare graphite intercalation compound (GIC). Epoxy resin was purchased from M/S Resinova Chemie, India. It consist of two parts. Part I is PG100, (diglycidyl ether of bisphenol-A) and Part II is PHY161 (aromatic amine-based curing agent). The mixing ratio was Part I (10): Part II (1).

2.2. Synthesis of exfoliated graphite

In this method, firstly the graphite intercalation compound (GIC) was prepared. The moisture free natural flake graphite (NFG), potassium permanganate ($KMnO_4$), perchloric acid ($HClO_4$) and nitric acid (HNO_3) were simply mixed together in their weight ratios with a glass rod in a porcelain dish for 300 s. Here, $HClO_4$ is act as an intercalating agent, while HNO_3 and $KMnO_4$ are oxidizing agent. The whole mixture was then kept at ambient condition for 120 s. After that, the resulting GIC were placed in a glass beaker and exposed to microwaves in a domestic microwave oven at 800 W for 20 s. The GIC heated rapidly with microwaves and EG was prepared by fuming and sparking followed by washing with distilled water and kept in an oven for a night to dry [11,12]. The schematic illustrating the preparation of EG from natural flake graphite is shown in Fig. 1.

2.3. Characterization techniques

The X-ray diffraction analysis of NFG, EG and EG/epoxy composites were carried out using a diffractometer (Thermo Electron ARL XTRA) in 2θ range of 10–90° with CuKα (λ = 1.54184 nm), scan rate of 2°/min, steps of 0.05° and time constant of 1 s. The exfoliated volume (EV) of EG was measured using a measuring cylinder with diameter of 40 mm with a capacity of 250 ml. The interplanar spacing d_{hkl} and the peak position were determined with the help of high score plus version 4.6.1. The Horiba Lab Ram HR100 Raman spectroscopic instrument was used to record the Raman spectroscopy of NFG and EG. During recording, a He-Ne laser having wavelength 632 nm was used. To study the surface chemistry of NFG and EG, X-ray photoelectron spectra (XPS) acquired with a PH15000 (Versa Probll, FEI Inc.) spectrometer was used. The analysis of XPS peaks were done by using XPS PEAK version 4.1. The Fourier transform infrared (FTIR) spectra were recorded by Bruker vertex-70 FTIR in the range of 1000–4000 cm^{-1}. The dielectric parameters at microwave frequency of pure epoxy and composite samples were measured using cavity perturbation technique (CPT). This characterization technique is widely accepted by several researchers due to its accuracy and sensitivity as compared to non-resonant techniques. In CPT, the placement of sample under test at its maximum electric field position creates a very small perturbation in the electric field. This causes variations in resonant frequency (fs) and quality factor (Qs) of cavity. These changes in resonance and quality factor are exploited to measure the complex permittivity parameters using the following expression [13].

$$\varepsilon_{r'} = 1 + \left(\frac{2V_c}{AV_s}\right)\left(\frac{f_i - f_s}{f_s}\right) \quad (1)$$

$$\varepsilon_{r'} = \frac{V_c}{AV_s}\left(\frac{1}{Q_s} - \frac{1}{Q_i}\right) \quad (2)$$

where, f and Q are the resonant frequency and quality factor with s and i representing the loaded and unloaded condition of the cavity, and A represents the shape factor with V_c and V_s being the cavity volume and sample volume, respectively. The shape factor A is calculated by calibrating the set up with a known dielectric material having same density as of the specimen. Thermogravimetric analysis (TGA) was carried out under nitrogen gas atmosphere from 35 to 600 °C at a heating rate of 10 °C/min. The storage modulus and glass transition temperature of the MW and CV cured neat epoxy and their EG reinforced composites were obtained using a Pyris Diamond DMA. The samples were heated from 25 to 200 °C in tensile mode with oscillatory frequency of 1 Hz, strain amplitude of 5 μm and heating rate 5 °C/min. The samples with dimensions of length 40 mm, 10 mm in width and 1.6 mm in thickness were freshly prepared. The surface morphology of NFG, EG and EG/epoxy was recorded using JEOL (JSM-6301 F).

3. Results and discussion

3.1. Morphology of exfoliated graphite

SEM micrographs of as received NFG and synthesized EG are shown in Fig. 2. The agglomerated flat morphology of NFG with average particle size of 510 μm is clearly observed in Fig. 2 (a). It is important to note here that after microwave exfoliation at 800 W for 20 s, large volume change in NFG is observed as shown in Fig. 2(b). It can also be observed that plate like structure of NFG after intercalation and exfoliation took the long cylindrical worm like structure, which is due to the expansion of carbon layers along c-axis by intercalated agents as a result of heating at high temperature [11]. Also the micrograph (Fig. 2(b)) reveals that after expansion the separation between the graphite flakes interlayer spacing is increased, resulting into loose and porous structure of EG Ref. [14]. The enormous increase in volume of