THE EFFECT OF AMOUNT OF GRAPHENE FOR THE STUDY OF BARRIER PROPERTIES OF EPOXY-GRA PHE NANO COMPOSITES

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ABSTRACT
The vapor barrier film of epoxy graphene nanocomposites of 0.75 and 1.5 wt% was synthesized by dispersion method. This dispersion of graphene mainly attributes to the excellent water barrier property. When epoxy combined with graphene nanoparticles show significantly increased toughness and dampness capacity of epoxy system. This is mainly due to free volume reduction respect to the pristine polymer. The nanocomposites derived from graphene show excellent electrical, thermal and mechanical properties. The excellent electron transport, high surface area and mechanical properties of graphene epoxy nanocomposites has potential applications in food packaging, anticorrosive coating. The synthesized barrier film of epoxy graphene composites were characterized by differential scanning calorimetric techniques (DSC). The barrier properties were investigated by using electrochemical impedance spectroscopy (EIS).

Key words: Epoxy nanocomposites, Barrier properties, Graphene nanoparticles

INTRODUCTION
The development of novel polymer nanocomposites with the unique features such as high aspect ratio, excellent toughness and strength due to the functionalities such as inorganic nanoparticles such as graphene into polymer matrices, such as epoxy system is one of the most promising research fields in various areas of application [1–4]. The loading of graphene has significantly increased electrical and thermal properties and the mechanical properties of nanocomposites [5–6]. However, with the aim of increasing the barrier properties nanofiller such as graphene used in these materials have strong tendency to agglomerate which would cause in homogeneous dispersion of nanofillers in matrices, and reduction in free volume of these nanocomposites [7]. In this study, the effect of graphene on barrier properties of epoxy system has been evaluated by incorporating reduced concentrations of nanoparticles (i.e., 0.75 and 1.5% by weight) into waterborne epoxy resin. Impregnation of epoxy with graphene filter cake without pre-mixing, extraordinary properties of nanocomposites are exceptionally high surface to volume ratio of the nanofiller and/or its exceptionally high aspect ratio.
MATERIALS AND METHODS

Graphene nano particles used in this work are made of few layers with width of less than 2 µM, an average thickness of about 2 nm and a surface area 500 m²/g. The epoxy system is a commercial water borne resin without corrosion inhibitors. It contains additives such as emulsifying and dispersing agents and surfactants mainly 63% weight of solid TiO₂ [8] (Table 1).

Table 1: Specimen names of different epoxy graphene nanocomposites

<table>
<thead>
<tr>
<th>Plain epoxy system</th>
<th>EPX</th>
</tr>
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<tbody>
<tr>
<td>Loading with 0.75% wt. of graphene</td>
<td>Epgo/EG 0.75</td>
</tr>
<tr>
<td>Loading with containing 1.5% wt of graphene</td>
<td>Epgo/EG 1.5</td>
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In order to evaluate the effect of the nano filler on the epoxy matrix properties, a thermal analysis was carried out taking 10 mg of the sample. Three scans (heating, cooling and heating again) were carried out from 30-250 °C with a heating rate of 10 °C per minute for each specimen.

The barrier properties of the modified epoxy systems were investigated by using Electrochemical Impedance Spectroscopy (EIS). A conventional electrochemical cell was used including a saturated calomel reference electrode (SCE), platinum as counter electrode, and the coated aluminium sample as working electrode [9,10]. A frequency response analyzer (FRA), in conjunction with a potentiostat/galvanostat, 1255 and 1286 Solartron respectively, was employed. The electrolyte used was an air saturated 3.5 wt.% NaCl aqueous solution and the area exposed was of about 5 cm². Measurements were carried out at open circuit potential (OCP) over a frequency range from 10⁵ to 0.02 Hz with an amplitude sinusoidal voltage of 10 mV up to an immersion time of 21 days.[11,12]

RESULTS AND DISCUSSION

The measured water contact angle (see Table 2) of the unfilled epoxy system is about 66.3 °; when the nanoparticles dispersed in the epoxy resin, the contact angle increased to 88.1(Epgo/EG0.75sample) and 102.1(Epgo/EG1.5sample). The increase in the contact angle is mainly due to the increase in amount of graphene nanoparticle which in turn increase the hydrophobicity of the epoxy graphene nanocomposites leading to the reduction of sorption of water with the films. (Table 2)

Table 2: Water Contact angle of epoxy graphene nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Epx</th>
<th>Epgo/EG 0.75</th>
<th>Epgo/EG 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water contact angle (degree)</td>
<td>66.6</td>
<td>88.1</td>
<td>102.3</td>
</tr>
</tbody>
</table>

When exposed to the 3.5% wt of aerated NaCl aqueous solution the epoxy graphene nanocomposites films show increase in the impedance modulus, when compared to no loaded epoxy system, which indicates better barrier properties. Even after one day exposure to the test solution at low frequency is slightly less than 10⁷ Ωcm². The increase in impedance modulus at low frequency was mainly due to the formation of local anodic area for prolonged exposure of nanocomposite surface up to 21 days. This was mainly attributed to the sorption of water and electrolyte which in turn shift impedance modulus at low frequency.
The subsequent shift of phase angle at high frequency as function of immersion time is also constituent with further degradation of nanocomposite films. The increase in phase angle of 90°C with minimum (3 degrees) is observed at frequency of about 0.44 Hz after exposure of one day to test solution.

The decrease in impedance modulus with the time show better stability of loaded epoxy nanocomposites. The lower value of impedance modulus after one day immersion for neat epoxy system accounts for poor barrier properties when compared to graphene loaded epoxy nanocomposites, which shows continuously slightly increased values of impedance modulus up to 21 days. (Fig 1)

The increase in impedance modulus (8 × 10^7 Ω cm^2), value for EG1.5 as function of immersion time show better barrier properties of epoxy graphene nanocomposites. The compact behavior of epoxy graphene nanocomposites was explained on the basis of no full penetration of the electrolyte in the given time interval.

![Figure 1: Mass sorbed vs square root of time](image-url)
Meaningful impedance related to the effect of graphene on the Barrier properties of the epoxy nanocomposites is evaluated at 0.02 Hz are reported. As can be seen from this figure 2, the filled nanocomposites exhibited impedance modulus greater than the unfilled base epoxy for all exposure times showing the noticeable effect due to the use of graphene. In addition, EG1.5 showed an impedance modulus of one order of magnitude greater than that exhibited by the base epoxy for all exposure times.

The water diffusion coefficients through epoxy nanocomposites are calculated from the initial slope of the curve of mass sorbed vs square root of time these water diffusion coefficients of EG 1.5wt%of graphene to the epoxy system are lower than those exhibited by the EG0.75.

The increased performances of epoxy graphene nanocomposites to the barrier effect were mainly due to graphene which induces decreasedwaterdiffusivity. The effect of amount graphene increasesthe pathway length of water through whichother nanoparticles used as a filler.

After the first 4 days of immersion the nanocomposite,show a slight increase, day by day, to the end of immersion time, reaching a steady value, indicating a different water absorption process. The observed behavior of the nano filled epoxy can be attributed to a diffusion mechanism of water adsorption and transport through the nanocomposites.

CONCLUSION

In this work, the addition of nanoparticles to epoxy system led to a slight increase of the hydrophobic character of thenanocomposites. The collected EIS data showed that loaded coatings exhibit improved barrier properties which was attributed diffusion mechanism of water transport through the filled epoxy nanocomposites. The water diffusion coefficients of EG 1.5wt%of graphene to the epoxy system are lower than those exhibited by the EG0.75 which can be attributed to a diffusion mechanism of water adsorption and transport through the nanocomposites.

REFERENCES


