Effect of ZnO-GO Particles on the Photopolymerization and Photo-Cleaning of Epoxy Coating

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In this paper, we fabricate Epoxy/ZnO-GO composite films using photoinduced cationic ring opening polymerization processes with self-cleaning ability and improved thermal properties under the photo exposure. The presence of ZnO nanoparticles on the GO surface aids in achieving good self-cleaning properties by removing model dirt, methylene blue, (within 1-2 h) under sunlight. An increase of almost 15 °C in the thermal stability was obtained by introduction of 0.6 wt% ZnO-GO to the epoxy matrix. Therefore, the nanocomposite could be a promising futuristic material for many advanced applications and used as a surface coating material where it can remove the presence of organic dirt and provide a clean surface.

Keywords: Photo-polymerization, Photo-cleaning, ZnO-GO

1. Introduction
Smart polymers have carved a distinct niche in materials science over the last few decades [1,2]. Epoxy systems are some of the most important thermosetting polymeric materials that are widely used as polymer matrices for composite materials, coatings, adhesives and electronic encapsulants. Therefore, the combination of reinforcement [3-5] make the application of nanofillers in polymer blends in most cases more effective in comparison with single polymer matrix nanocomposites.

Semiconductor photocatalysts, such as ZnO, are widely applied for photodegradation of organic compounds, especially for decontamination of air and water [6]. The self-cleaning properties of ZnO originate from the photocatalytic oxidative decomposition of organic contaminants. Until now, ZnO photocatalyst has been widely used because of its strong oxidizing power, non-toxic nature, and low cost [7-11]. ZnO is a wide band-gap semiconductor oxide (3.37 eV) with a conduction band edge located at approximately the same level as that of TiO2. More attractively, the electron mobility of ZnO has been proven to be higher than that of TiO2 [12]. However, the electron-hole pairs have a high recombination rate in the single phase semiconductor and hence, this has hampered its practical applicability [13]. Particularly, the fabrication of semiconductor composites has attracted substantial research efforts motivated by the desire to improve the photocatalytic efficiency [14-18]. The recent studies have revealed that the ZnO-Grapehene Oxide (GO) composites simultaneously covered three excellent attributes: the increasing adsorptivity of pollutants, extended light absorption range, and efficient charge transportation and separation [19,20], which are the ideal traits of a photocatalyst we have been pursuing for. In this vein, a ZnO-GO hybrid exhibited improved photocatalytic activity under visible light or sunlight. Therefore, an attempt has been made to achieve combined attributes of self-cleaning and mechanical properties in epoxy nanocomposites coatings. Also, the effect of loading of the hybrid on
tuning the self-cleaning and thermal properties of the nanocomposite was investigated.

2. Experimental

2.1. Materials

Epoxy resin, 1,6-hexanediol diglycidyl ether (Araldite DY-H/CH, HDGE) was purchased from Huntsman. (4-Methylphenyl) [4-(2-methylpropyl) phenyl]iodonium hexafluorophosphate (Irgacure 250), a liquid cationic photoinitiator (75% solution in propylene carbonate) was supplied from BASF and hydrazine monohydrate, as reducing agent was purchased from TCI, Japan. Methylene blue (MB) was bought from Merck with molecular weight of 319.85 g/mol. All the chemicals were used as received without further purification. ZnO-GO was synthesized as previously reported in the literature [21].

2.2. Sample preparation

ZnO-GO nanoparticles were directly dispersed in the range between 0.2 and 0.6 wt% in the solution of the epoxy resin by means of sonicator machine at the frequency of 25 kHz for 30 min. The temperature was maintained between 60 °C and 70 °C during sonication. A given amount of cationic photoinitiator was added and homogenous formulations were obtained through a mechanical mixing. The formulations were poured in closed glass molds and UV irradiated at a light intensity of 50 mW/cm² under nitrogen atmosphere.

2.3. Sample characterization

The kinetic of the photopolymerization was followed by Real-Time FT-IR spectroscopy, employing a Thermo-Nicolet 5700 instrument. The formulations were coated onto a silicon wafer with a thickness of 50 μm. The samples were exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam, which analyzes the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy conversion was followed by monitoring the decrease in the absorbance of the typical epoxy peak centered at 760 cm⁻¹. A medium pressure mercury lamp equipped with an optical guide (Hamamatsu LC8) was used to induce the photopolymerization. The light intensity on the surface of the sample was about 50 mW/cm².

SEM images for the worn surfaces and wear debris of the epoxy composites were obtained by a JEOL JSM-6300 microscope.

Transmission electron microscopy (TEM) analysis was performed with a JEOL 2100X electron microscope at an operating voltage of 200 kV.

The self-cleaning properties of the nanocomposite were evaluated by photocatalytic degradation of methylene blue (MB) as a model compound. In the typical test, the nanocomposite film (average weight 0.8–1.0 g) was chopped in to small pieces (dimensions almost 5×5 mm²) and these chopped polymer films were immersed in 50 mL of MB solution (60 ppm). Then the solution was kept in the dark for 1 h to obtain equilibrium. Afterward, the solution was exposed to sunlight (sunny day, average temperature: 38 ± 1 °C, humidity: 62 ± 1%, and light intensity: 90000–100000 lux) for photodegradation of the dye. The concentration change of MB was monitored by measuring the photo absorbance intensity at 664 nm at particular irradiation time intervals.

Thermogravimetric analyses (TGA) of the nanohybrid and nanocomposites were carried out by using a thermal analyzer, TGA 4000 (Perkin Elmer, USA) with a nitrogen flow rate of 30 mL min⁻¹ at a heating rate of 10 °C min⁻¹.

3. Results and discussion

3.1. ZnO-GO characterization

FTIR is used to identify the elemental constituents of a material. The characteristic peaks exhibited by FTIR spectrums of both ZnO-GO hybrid and their corresponding ZnO and GO were presented in Fig. 1. All ZnO characteristic peaks appeared at the ZnO-GO hybrid with slight peaks shifting due to presence of the GO that confirm ZnO immobilization onto the GO surface. Where the two FTIR spectrums of ZnO and ZnO-GO hybrid showed identical characteristic peaks at about 530 cm⁻¹ in case of pure ZnO which corresponds to the Zn-O bond stretching vibration. The light intensity on the surface of the sample was about 50 mW/cm².

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well-dispersed on the surface of the GO sheet (Fig. 2). This suggests that ZnO nanoparticles have a well-ordered structure and a high degree of crystallinity.

**Fig. 1.** FTIR spectra of GO, ZnO and ZnO-GO.

**3.2. UV curing process**

The cationic photopolymerization process was investigated by RT-FTIR analyzes; the conversion curves as a function of irradiation time are reported in Fig. 3. While the plateau value gives the final epoxy group conversion, the slope of the curve gives an indication of the polymerization rate. It is possible to observe that ZnO-GO did not strongly influence the epoxy ring-opening process. However, at sufficiently high ZnO-GO concentration, the overall conversions are lower.

This behavior can be explained in terms of competing reactions of the intermediate phenyliodinium radical cations. It is known that intermediate phenyliodinium radical cations abstract hydrogen from ZnO-GO or solvent and form protons capable of initiating cationic polymerization directly (Fig. 4.) [25,26].

**Fig. 2.** a) SEM and b) TEM micrographs of ZnO-GO.

**Fig. 3.** RT-IR spectra of the photo-curable systems containing different modified ZnO-GO.

**3.3. Sunlight induced self-cleaning properties of nanocomposites**

In this study, MB was chosen as model dirt for testing sunlight induced self-cleaning properties of the prepared nanocomposites. Photocatalytic degradation of the dye was investigated using chopped pieces of the nanocomposite film under exposure to sunlight. The degradation of aqueous MB solution based on its concentration changes with time is shown in Fig. 5. Pure ZnO nanoparticles can degrade the dye but their efficiency is very poor due to the high recombination rate of generated hole/electron (h⁺/e⁻) pairs. Therefore, nanohybrids are used to address the above shortcomings. It is well-known that nanohybrid showed enhanced photocatalytic activity over pure nanoparticles [27].

Hence, sunlight induced photocatalytic degradation of MB solution led to a significant reduction in MB concentration when Epoxy/ZnO-GO nanocomposites were taken as photocatalysts. After illumination starts absorbance spectrum (Fig. 5) showed that peak value reduces moderately. This shows that during experiment absorbance value decrease with exposure to time and finally after 3 h
absorbance peak become nearly smooth while solution blue color also become color less with passing time. Whereas, pristine epoxy and the epoxy-GO nanocomposite did not show significant degradation efficiency. As ZnO nanoparticles are only responsible for degradation of the dye so the presence of a high amount of ZnO nanoparticles in the nanocomposite enhanced the dye degradation rate. Therefore, pristine epoxy and the epoxy-GO nanocomposite did not show effective dye degradation. During degradation GO absorbs the energy of sunlight and emits shorter wavelengths of light. The emitted energy excites the ZnO nanoparticles to generate h⁺/e⁻ pairs which react with water and O₂ to form reactive oxygen species (ROS) such as °OH and °O₂. These ROS actually degrade the dye molecules [28,29]. A blank test without epoxy or its nanocomposites was also performed and extremely slow degradation (only 10%) of the MB was found after 180 minutes of direct sunlight irradiation. Therefore, it can be used as a surface coating material where it can remove the presence of organic dirt and provide a clean surface.

3.4. Thermal properties

The thermal profiles of Epoxy/ZnO-GO composites were explored in Fig. 6. It can be seen that dispersion of ZnO-GO in epoxy enhanced thermal stability compared to pure epoxy. The barrier properties of the nanohybrid are mainly responsible for improving the thermal stabilization of the nanocomposite. Also, the presence of an inorganic component provides additional heat insulating capacity, which stabilizes the nanocomposite against thermal decomposition. Moreover, the presence of strong covalent and non-covalent interactions between the nanohybrid and epoxy matrix enhances the thermal stability of the nanocomposites [30,31].

Fig. 6. TGA thermograms of epoxy and its nanocomposites.

4. Conclusions

Polymeric nanocomposite systems based on an epoxy resin and GO layer modified with ZnO particle were prepared. The kinetics of the photopolymerization process, monitored by Real-Time Infrared Spectroscopy, showed very low influence of the presence of the ZnO-GO on the curing reaction. All the nanocomposites exhibited excellent thermal properties and self-cleaning ability.

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