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Effect of nitrogen and oxygen doped carbon nanotubes on flammability of epoxy nanocomposites

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ABSTRACT

To overcome the flammability of epoxy resins, novel nitrogen (CN_x) and oxygen (CO_x) doped CNT were synthesized via CVD method and epoxy nanocomposites at 2 wt.%. constant loading were prepared by three roll milling and cured. The structures of the nanotubes were confirmed by XRD, XPS, SEM and Raman and it was found a very high aspect ratio especially for CO_x.

Thermal degradation as well as glass transition temperatures and elastic moduli were measured by TGA, DSC and DMTA. The flammability of epoxy nanocomposites was studied by microscale combustion calorimetry (MCC) and limiting oxygen index (LOI) determination. Results showed that the fire retardant properties of nanocomposites improved significantly specially for CO_x, which presented a very high LOI (35%) and a homogeneous and uniform surface after burning. This effect was tentatively attributed to the very high aspect ratio of CO_x tubes.

1. Introduction

Since the accidental discovery by Sumio Iijima in the soot of the arc-discharge method [1] in 1991, carbon nanotubes (CNTs) have generated a great deal of research in most areas of science and engineering due to their extraordinary properties: stronger than steel, harder than diamond and electrical conductivity higher than copper [2].

It is well understood that CNTs could not be utilized alone without any supporting medium. In the other words, many of these noticeable properties can be best obtained by incorporating the CNTs into some form of matrix to make different composites. In many cases, these composites have employed polymer matrices and nowadays CNT nanocomposites are being used in many research areas and commercial products due to their mechanical, thermal, optical, electrical [3], photocatalytic properties [4], with applications ranging from coatings [5], batteries [6], filters [7], bio sensors [8] to flame retardant additives [9].

Epoxy resins (EP) are low-molecular-weight pre-polymers containing more than one epoxide group, which are cured using a wide variety of curing agents (amines, anhydrides, etc.). The EPs are widely used as advanced matrix resins in the electrical, electronic, aerospace industries and anticorrosion coatings due to their outstanding characteristics such as high tensile and impact strength, good fatigue resistance, micro cracking resistance, chemical and corrosion resistance, excellent electric insulation and low manufacturing cost [10].

However, the development and application of epoxy based composites has been greatly limited by their high flammability [11]; improving the flame retardancy properties of epoxy resins has become therefore very attractive and has absorbed the attention of many researchers for advanced application. Traditionally, halogenated compounds have been widely used to enhance the flame retardant properties of epoxy resins [12]. Currently, various compounds containing metal hydroxides [13,14], nitrogen, phosphorus [15–17], boron and silicon [18,19], have gained much attention as flame retardants for polymer

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materials to replace traditional toxic halogen-containing flame retardants. The major problem encountered with these compounds is the high loadings needed to achieve high level of fire resistance which generally cause deterioration of the mechanical behavior [20]. The arising of nanocomposite technology has provided a revolutionary new solution to flame retardant polymer materials, improving the fire resistance just at a very low loading of nano-fillers (<10 wt.%) [21], compared to conventional fillers such as $Mg(OH)_2$ or $Al(OH)_3$ (40 wt.% to 60 wt.% loading) [22]. Several types of nano-materials such as clays or montmorillonite [21], double layered hydroxides [23], etc. have been incorporated into epoxy resins aiming to improve flame retardancy. The use of CNTs as flame retardants has raised great interest among researchers due to their special properties. CNTs have been used as a flame retardant (Kashiwagi et al. [24]) not only because of significant improvement of the thermal stability of polymer by their free radical scavenger effect, but also by the formation of a structural network and enhancing the mechanical properties of the final polymer nanocomposite [25]. Moreover, the larger surface area of nanotubes can promote the formation of large amount of char residue which prevents the resin from heat degradation, that is to say, they can generate excellent gas barriers which delay the oxidative degradation of resin during the combustion. However, these nano effects will be diminished if nanofillers aggregate together driven by the strong Van der Waals forces. Therefore, high dispersion state of the CNTs constituted a key point for enhancement of the fire retardant properties [26]. Furthermore, the absence of interfacial interaction limits load transfer from epoxy matrix to CNTs due to their atomically smooth non-reactive surface resulting in poor mechanical properties of epoxy nanocomposites [27]. Up to now, different approaches have been suggested to increase the dispersion degree of CNTs such as ultrasonication, pre-dispersed CNTs into polymer, chemical modification through functionalization [28], etc.

Chemical vapor deposition (CVD) [2] is the most popular method of producing CNTs based on the pyrolysis of hydrocarbons over metal catalysts. In comparison with other synthesis methods it has the advantage of producing aligned CNTs bundles in a single step process, without further purification at a relatively low cost and without prior preparation of substrates [29]. Another important advantage is the ease for changing gas composition to prepare doped nanotubes with nitrogen (CN_x) or oxygen (CO_x). Up to know, numerous applications of CN_x have been reported: field emission devices [30], sensors [8], catalysts [31], electrocatalysts for oxygen reduction reaction [32], and batteries [33]. CO_x has also been prepared and studied [34] and interesting applications as catalysts for electrophoresis have been reported [35]. Chemical functionalization of CNTs to obtain CN_x and CO_x is the strategy explored in this paper to increase polymer-nanotube interaction which leads to the enhanced dispersion state of the functionalized CNTs.

These nanotubes were characterized by X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray scattering (XRD), Raman spectroscopy, and thermal stability (TGA). Afterwards, the nanotubes were used as flame retardant nano-fillers in epoxy matrix to prepare polymer composites, using a multistage mixing and curing process. The morphology of the resultant epoxy nanocomposites was analyzed by SEM. Their thermal stability was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Mechanical properties were determined by dynamic mechanical properties (DMA). The flammability of epoxy nanocomposites was characterized by microscale combustion calorimeter (MCC) and limited oxygen index (LOI).

2. Experimental procedures

2.1. Materials

Epoxy resin (Diglycidyl ether of bisphenol-A (DGEBA)) (EP) with an equivalent weight per epoxide group of 480 g mol^{-1} and 4, 4'-diaminodiphenylsulfone (DDS) with an amine equivalent weight of 140 g mol^{-1}, Ferrocene ($FeCp_2$), Benzylamine, Toluene and the solvents were purchased from Aldrich chemical company and used as received.

2.1.1. Synthesis of CNT, CN_x and CO_x

2.1.1.1. Synthesis of CNT. A solution consisting of 95% Toluene and 5% Ferrocene, which was sonicated for 20 min, was prepared. A single furnace equipped with the CVD technique with a flow of 2.5 L min^{-1} of argon gas for 30 min at 850 °C were used to synthesize the CNT. Total obtained weight was in the range 0.9–1.7 g in each synthesis.

2.1.1.2. Synthesis of CN_x. CN_x were produced using a CVD process using a solution containing 5 wt.% of ferrocene ($FeCp_2$) in benzylamine (C_7H_9N). The solution was then heated at 850 °C with the flow of 2.5 L min^{-1} of argon gas for 30 min. An approximate total weight of 1.2 g was obtained per each synthesis.

2.1.1.3. Synthesis of CO_x. In the case of CO_x, a solution containing 94% Toluene, 1% Ethanol and 5% Ferrocene was heated at 850 °C at 2.5 L min^{-1} of argon gas for 30 min.0.8–0.95 g total weight was obtained in each synthesis.

All of these synthesized nanotubes, CO_x, CN_x and CNT were purified and improved their epoxy dispersibility by H_2O_2 –UV method described in our previous work [36].

2.1.2. Preparation of epoxy nanocomposites

Three samples containing 2 wt.% nanotubes (CNT, CN_x or CO_x), were prepared using a three roll mill mixing appropriate amounts of EP and nanotubes at 120 °C to decrease epoxy viscosity. After milling, the mixture was gently stirred at the same temperature to partially eliminate trapped air from the mixture. Stoichiometric amount of DDS was then added to the mixture and the temperature was then increased to 130 °C to dissolve the curing agent for 20 min under vacuum to get a clear, homogeneous and degassed mixture. The mixture was then poured into a preheated Teflon mold and cured in an oven at 140 °C for 5 h and then post cured for 3 h at 180 °C. Specimens for the entire tests were cut from this block. The sample without nanotubes was the reference.

2.2. Instrumentation

X-ray photoelectron spectroscopy (XPS) data were recorded with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyzer and an unmonochromatized Mg Kα X-ray source operating at 150 W with pass energy of 50 eV. The recorded spectra were analyzed using CASAXPS software, and RSF database by peak fitting after Shirley background correction.

X-ray diffraction (XRD) was collected in an automatic X'Pert Philips diffractometer using a Cu source. Data were collected in the 2θ range from 10° to 90° in step-scanning mode with a step size of 0.02° and a counting time of 2 s per step.

Scanning Electron Microscopy (SEM) was performed using a FEI equipment, with a voltage of 10 kV and a secondary electron detector. The nanocomposites samples were sputter-coated in gold prior to the observation.

Raman spectroscopy measurements were carried out in via