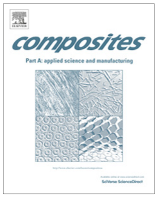
Composites: Part A 56 (2014) 172–180

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa



# Improving the mechanical properties of multiwalled carbon nanotube/epoxy nanocomposites using polymerization in a stirring plasma system

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ARTICLE INFO

*Article history:*
Received 13 August 2013
Received in revised form 3 October 2013
Accepted 11 October 2013
Available online 20 October 2013

*Keywords:*
A. Particle-reinforcement
B. Mechanical properties
E. Surface treatments

ABSTRACT

Uniform treatment of multiwalled carbon nanotubes by plasma treatment has been investigated using a custom-built stirring plasma system. A thin plasma polymer with high levels of amine groups has been deposited on MWCNTs using a combination of continuous wave and pulsed plasma polymerization of heptylamine in the stirring plasma system. Scanning electron microscopy showed that the plasma polymerization improved the dispersion and interfacial bonding of the MWCNTs with an epoxy resin at loadings of 0.1, 0.3 and 0.5 wt%. The flexural and thermal mechanical properties of plasma polymerized MWCNT/epoxy nanocomposites were also significantly improved while untreated MWCNT/epoxy nanocomposites showed an opposite trend. The epoxy with 0.5 wt% plasma polymerized MWCNTs had the greatest increase in flexural properties, with the flexural modulus, flexural strength and toughness increasing by about 22%, 17% and 70%, respectively.

## 1. Introduction

Carbon nanotubes (CNTs) are ideal candidates as nanofillers for the preparation of polymer nanocomposites, owing to their remarkable mechanical, electrical and thermal properties [1–3]. However, in order to fully exploit their unique properties in composites the critical challenges of dispersing high levels of CNTs and providing strong interfacial bonding with the polymers for good load transfer, need to be addressed [4,5]. This requires functionalization of the surface of carbon nanotubes. In order to avoid wet chemical methods and possible damage to the nanotube structure, a plasma method has been developed. It is a dry process and one-step treatment that introduces functional groups on the carbon nanotube surface, without the complex procedures of filtration, washing and drying and multistep reactions required by most chemical functionalization treatments. Moreover, it does this without damaging the nanotube structure [6–11].

However, nanomaterials are difficult to deal with in plasma systems due to their aggregation and their large surface area [12,13]. If they are simply placed in the plasma system then only the surface regions of the nanomaterial that can be reached by the plasma will be modified. Equipment that can provide uniform treatment is essential. Plasma fluidized-bed reactors have been investigated as a means to modify different microsized polymer powders by plasma polymerization [13–15]. Recently, Shi et al. [16] used a fluidized-bed reactor with continuous wave (CW) plasma polymerization to produce a thin plasma polymer on carbon nanotubes. However, CW plasma polymerization as an ‘atomic polymerization’ [17] causes high fragmentation of the monomer and leads to highly cross-linked plasma polymers with little resemblance to the chemical structure or functionality of the original monomer. This could compromise chemical bonding to a polymer matrix and hence degrade the properties of the resulting nanotube-reinforced polymers.

In this study, an easily constructed stirring plasma system, where nanomaterials can be continuously stirred during plasma treatment, has been used to address the challenge of achieving uniform treatment and easy handling. In our previous work [18], direct amino-functionalization of MWCNTs by a combined plasma mode in a nitrogen plus hydrogen gas mixture was used to improve the nano- and macro-mechanical properties of an epoxy resin. In this study, the MWCNTs were coated with a thin polymer containing amines by a combination of continuous wave and pulsed (CW + P) plasma polymerization of heptylamine (HA). These plasma polymerized MWCNT were tested as reinforcement for the epoxy matrix. It has been previously shown that the plasma polymer obtained by CW + P plasma polymerization characteristically has high retention of desired functional groups and good adhesion to substrates [19,20].

The surface morphology of MWCNTs before and after plasma polymerization was studied by scanning electron microscopy

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http://dx.doi.org/10.1016/j.compositesa.2013.10.009

(SEM). The chemical composition of the nanotubes after plasma polymerization was studied by X-ray photoelectron spectrometry (XPS), Fourier transform infrared spectroscopy (FTIR) and thermo-gravimetric analysis (TGA). Neat epoxy and epoxy nanocomposites containing 0.1 wt%, 0.3 wt% and 0.5 wt% of untreated MWCNTs (u-MWCNTs) or HA plasma polymerized MWCNTs (HAPP-MWCNTs) were prepared. The curing behavior of the epoxy resin system, with and without MWCNTs, was studied by DSC. The mechanical properties of MWCNT/epoxy nanocomposites were determined by DMA and three-point bending tests. The fracture surfaces of the nanocomposites after the three-point bending tests were investigated by SEM in order to evaluate the dispersion of the MWCNTs and their adhesion to the epoxy resin.

## 2. Experimental

### 2.1. Materials

MWCNTs were purchased from Sigma–Aldrich Co., LLC. They were produced by a CoMoCAT® catalytic Chemical Vapor Deposition (CVD) process with a purity of more than 95% carbon. The diameter of the MWCNTs was 15–20 nm and their length was about 5 μm. Epon 862 epoxy resin (Bisphenol F) and Epikure W aromatic amine curing agent were purchased from Hexion Specialty Chemicals Inc. The density of Epon 862 epoxy was about 1.17 g/cm$^3$ and the viscosity was about 25–45 P and the curing agent was about 1–3 P at 25 °C (1 P is equal to 1 g/cm s). The mixing ratio of Epon 862 epoxy to Epikure W curing agent was 100:26.4 by weight. Heptylamine ($CH_3(CH_2)_6NH_2$, 99% purity, Sigma Aldrich) was used as the monomer for plasma polymerization.

### 2.2. Plasma polymerization of heptylamine

Plasma polymerization of heptylamine on MWCNTs was conducted in a custom-built RF 13.56 MHz stirring plasma system (Fig. 1). The stirring plasma reactor consists of a Pyrex glass tube about 40 cm high and 4 cm in internal diameter connected to a round flask. The connection between the glass tube and the round flask is well sealed using vacuum grease and a clamp. This setup makes sample collection easy. The round flask is located on a magnetic stirrer which allows control of the stirring speed as well as temperature. A magnetic bar is used to stir the powders during plasma treatment. The plasma electrode had three coils (from 4 to 6 cm in diameter), made from copper wire (3.74 mm in diameter), mounted on the outside of the round flask in which the plasma was produced and the nanotubes were treated. The CNTs and rotating bar are at the base but within the plasma. It would be straightforward to increase the scale of the system or have multiple stirrers or multiple chambers.

About 200 mg of MWCNTs was placed inside the reactor and stirred by the magnetic bar (750 rpm). A fresh batch of the monomer liquid was placed in a round bottom flask and connected to the reactor chamber by a stainless steel line and a manual flow control valve. The system pressure was maintained at 0.05 mbar by a rotary pump which was protected by a liquid nitrogen trap. The samples were first treated by argon plasma (CW 75 W, $5 \times 10^{-2}$ mbar) for 1 min to activate and clean the surface before HA plasma polymerization. The plasma conditions for the HA polymerization were: (i) CW: continuous wave alone (50 W, 1 min); followed by (ii) P: pulsed alone (peak RF power 100 W, duty cycle 1/10, 10 min). The chamber pressure was maintained at 0.05 mbar for plasma polymerization.

### 2.3. Nanocomposite preparation

Neat epoxy, u-MWCNT/epoxy and HAPP-MWCNT/epoxy nanocomposites were fabricated. Neat epoxy samples were prepared by manually mixing Epon 862 epoxy resin and Epikure W curing agent (100:26.4). The mixture was degassed with stirring at 500 rpm under vacuum for 30 min at room temperature before curing.

Epoxy nanocomposites containing 0.1 wt%, 0.3 wt% and 0.5 wt% of u-MWCNTs or HAPP-MWCNTs were prepared. MWCNTs or the freshly plasma polymerized MWCNTs were dispersed in Epon 862 epoxy resin by probe sonication (UIP100hd, 1000 W, 20 kHz) at 30% amplitude for 30 min with a pulsing rate of 2:1 (4 s on, 2 s off).

The pulsing rate can be varied to help keep the temperature stable. Additionally, in order to avoid overheating of the MWCNT/epoxy mixture during sonication, the mixing beaker was immersed in ice water to keep the mixture at about 25 °C. After the sonication, the curing agent was added to the MWCNT/epoxy mixture and then the mixture was stirred at 500 rpm for 30 min under vacuum at room temperature to degas in order to remove entrapped air and voids. All resin systems were injected into an aluminum mould and cured in an oven at 177 °C for 2.5 h.

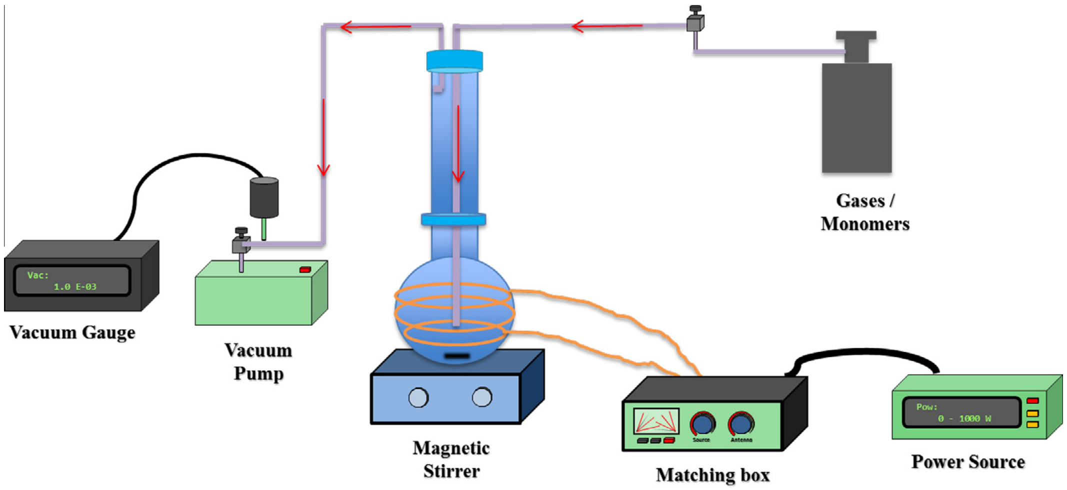

**Fig. 1.** Schematic diagram of the stirring plasma system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)