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Rapid microwave processing of epoxy nanocomposites using carbon nanotubes

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Abstract: Microwave processing is one of the rapid processing techniques for manufacturing nanocomposites. There is very little work focussing on the addition of CNTs for shortening the curing time of epoxy nanocomposites. Using microwave energy, the effect of CNT addition on the curing of epoxy nanocomposites was researched in this work. Differential scanning calorimetry (DSC) was used to determine the degree of cure for epoxy and nanocomposite samples. CNT addition significantly reduced the duration for complete curing of epoxy nanocomposites. As compared to monolithic cured epoxy, 20.5% of decrease in time and 12.5% decrease in spent consumed energy were observed for 0.2 wt.% CNT filled epoxy nanocomposite.

Key Words: Carbon nanotubes, Epoxy nanocomposites, Microwave curing.

1. Introduction

In any composite manufacturing setup, researchers and industrialist are always seeking ways to reduce product cost and environmental damage. In this regard, energy and time spent for the manufacturing of a product are the most significant parameters. Therefore, it is important to research innovative technologies available for rapid curing of composites. Some of the attractive options as compared to conventional curing are UV methods, gamma radiation, microwaves and electron beam. The most productive of all are microwave and electron beam processing, both based on electromagnetic oscillations. Electromagnetic oscillations can be divided into two main groups: high frequency currents and ultra-high frequency or microwave radiation. Electron beam has many advantages (Sui et al., 2000 and Wolff-Fabris, 2010) but for curing composites it is responsible for imparting large shrinkage and low glass transition temperature to the thermoset composites (Ghosh and Palmese, 2005). Microwave radiation is electromagnetic radiation with a wavelength in the range of 1 mm (300 GHz) to 30 cm (1 MHz) (Pinprayoon, 2007).

Microwave energy is a very attractive option because it uses less energy and less time to produce composites (Meyer and Herbeck, 2005, Das et al., 2009, Ku and Yusaf, 2008 and Yusoff et al., 2007). The application of high-frequency electric fields for curing the thermosetting composites is a rapid processing technique and it is well known that microwave treatment has numerous advantages compared to thermal heating (Wallace et al., 2006, Rangari et al., 2010 and Chang et al., 2012). The technique offers deep and uniform penetration of microwaves into the sample, capability of preferential heating sites and rapid production rate (Judith, 1999 and Zhou and Hawley, 2003). It is worth mentioning here that microwave heating occurs thoroughly through the entire thickness of the sample. Uniform curing through the thickness of the composite is quite complicated or impossible to achieve during conventional thermal heating (Judith, 1999 and Pinprayoon, 2007). Due to its simplicity and effectiveness, microwaves can also be used to restore any damage in a composite structure (Zhang and Dai, 2006). Microwaves enable to achieve the finished composites in a few minutes maintaining the mechanical properties, and sometimes even exceed it as compared to several hours long conventional thermal curing (Chang et al., 2012 and Papargyris et. al, 2008). Zhou and Hawley (2003) reported stronger crosslinked bonds in thermoset polymers cured by microwaves. The glass transition temperature is much higher for microwave cured samples as compared to those cured with the conventional heat (Wallace et al., 2006).

Looking into the kinetics of microwave curing, the physical cause of the existence of the electromagnetic field is due to the time-varying electric field which creates magnetic field and the changing magnetic field generates the vortex electric field (Cook, 2003 and Mukherji, 2006). Thus, they produce each other and have perpendicular spatial arrangement. By creating an electric field, the electrons move from the cathode to the anode producing waves. Electrical conductivity of pure epoxy system is very low which may lead to uncompleted and uneven curing as reported by Judith (1999). With addition of Carbon nanotubes (CNTs), electrical conductivity of thermosetting resins increases significantly (Gojnya et al., 2006 and Allaoui et al., 2002). Furthermore, due to the

very high electrical conductivity of CNTs (Bandaru, 2007), heat applies directly inside the sample which led to faster processing and obtaining absolutely cured material (Zhou and Hawley, 2003). It was found that absorption of microwave energy is associated with dipolar matrix relaxation and enhanced by the very high electrical conductivity of carbon additives (Paton and Windle, 2008 and Rangari et al., 2010).

To understand the role of CNTs in microwave curing of composite, it is essential to understand microwave curing of polymers. It is possible to heat polymeric molecule because of their polar groups and segments of the dielectric material (Zong et. al, 2005). When a polymer molecule is placed in an alternating electric field, there is a change in its polarity. The energy, consumed to overcome thermal motion, is dissipated in the material and this is responsible for heating up the material. During the movement of charged electron, it displaces the charges and will polarise the material which is placed in the electromagnetic field. Displacement of charge is due to the reorientation of polar molecules (dipolar polarisation) and electro-nuclei dependences (Nightingale and Day, 2002). In other words, under the microwave influence, dipoles of molecules are polarised and aligned in the direction of the field (Boey and Lee, 1990 and Meyer and Herbeck, 2005). Carbon based additives (including CNTs) are good absorbers of energy from microwave frequency electromagnetic fields (Zhao et al., 2006, Bao et al., 2011 Fan et al., 2006 and Menendez et al.,2010). With the addition of very little amount of CNTs (0.04 wt.%), the absorbing property of composites have been increased up to 500 times as reported by Paton and Windle (2008). Zhou and Hawley (2003) reported that addition of carbon in composite materials prevents localised overheating in the microwave processing and also aids in speeding up the curing reaction. Fig. 1 describes the absorption behaviour of carbon black in epoxy resin matrix. It shows that carbon is responsible for heating up the polar groups as well as the long polymeric chain, whereas in the absence of carbon, only polar group is responsible for heating up the polymeric chain (Zhou and Hawley, 2003). Precisely, localised superheating of functional groups in polymer molecule is the main reason of curing in the absence of carbon.

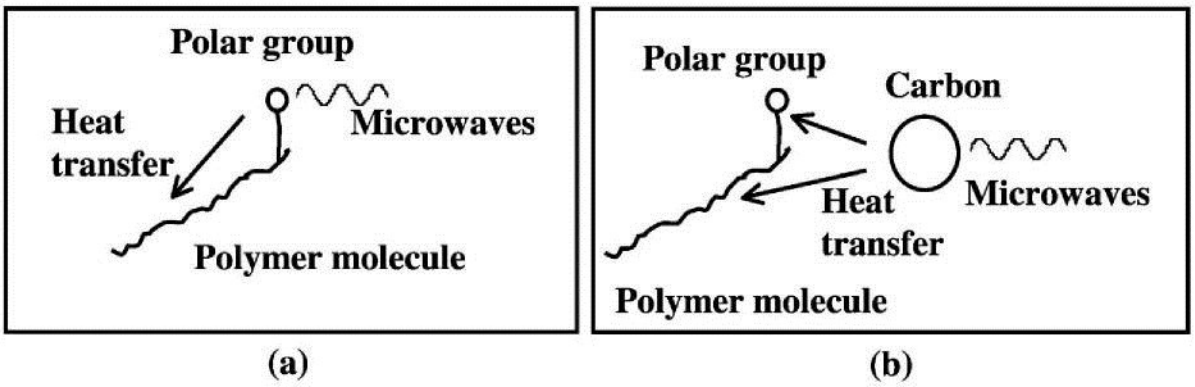

Figure 1. Microwave interactions with: a) neat epoxy; b) and epoxy doped with carbon (Zhou and Hawley, 2003).

Most of the research studies in this area focussed on the kinetics of microwave curing and comparisons were mainly made between the energy and time savings for conventional and microwave heating technologies. There is no research published on the effect of additions of CNT on energy and time for complete microwave curing of epoxy nancomposites. This work systematically reports the reduction in energy and time spent for microwave curing by the incorporation of various amounts of CNTs.

2. Experimental work

2.1 Material

The epoxy resin system used in this study was Araldite LY 5052/ Aradur 5052. Araldite LY 5052 is a low viscosity multifunctional epoxy system supplied by Huntsman, USA. Epoxy resin produced from bisphenol A resin and epichlorohydrin (Chernin et al., 1982). The hardener for this system was Aradur 5052 which is mixture of polyamines (Huntsman, 2010). Commercially available high purified MWNTs supplied by Electrovac, Austria (95% as per TGA, having traces of metal and metal oxide) were used as a reinforcement material. CNTs had density of 0.98 g/cm^3 (as per He pycnometery), specific surface area of 26 m^2/g, average length up to 2500 nm and average diameter of 50 nm. The synthesis method is Chemical Vapour Deposition (CVD). The mix ratio of the components was 100:33 parts by weight which correspond to 24.8 % of hardener

and 75.2 % of resin, according to amine/ epoxy (A/ E) ratio due to high chemical activity of amine groups (Pinprayoon, 2007). The total mass of epoxy system was 15.9 g (3.94 g of hardener and 11.96 g of resin).

2.2 Specimen preparation

The components of resin and hardener were weighted accurately according to the processing data and hand mixed. Pre-calculated amounts of CNTs and epoxy resin were carefully weighed and manually mixed together. MWNTs in the amount of 0.01 wt.%, 0.1 wt.% and 0.2 wt.% were infused in the matrix and dispersed via bath sonication (Ultra 7000, ultrasonic frequency: 42 kHz, power consumption: 50W) for 1 hour. Afterwards each epoxy system was divided into 6 parts and poured into the glass tubes. The tubes were put into the vacuum oven OV-11 (Medline) for 1 hour to remove the presence of air before microwave curing.

2.3 Curing Procedure

The microwave setup used in this study was MARS 6 supplied by CEM Corporation, USA (magnetron frequency 2.45 GHz, power output 1800W). It was used with vessels having self-regulating control of the temperature and pressure. MARS 6 automatically recognises the type and number of vessels that have been loaded, and adjusts the output power and other parameters. The number of glass tube used in this study was 6 (maximum number of vessels is 24). Neat epoxy resin (Epoxy 1) and epoxy system infused with 0.01 wt.% CNTs (Epoxy 2), with 0.1 wt.% CNTs (Epoxy 3), and 0.2 wt.% CNTs (Epoxy 4) were cured under the same conditions. The initial parameters used are: ramp time: 10 min, hold time: 1 min, temperature: 40 ^{o}C and maximum power: 500 W.

2.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) of various specimens was carried out with using Perkin Elmer Pyris 1 apparatus. The samples were cut into small pieces weighing from 5 mg to 10 mg using a engineering blade machine Labotom-3 supplied by Struers, Australia. Specimens were placed in aluminium plates containing a crimped lid with a small hole. The hole is necessary to maintain the constant pressure in the system and prevent deformation or rupture of aluminium pans. The DSC measurements were carried out from 30 ^{o}C to 250 ^{o}C at a high heating rate 10 ^{o}C/ min for three cycles under nitrogen atmosphere. DSC was performed for the neat epoxy and all nanocomposite systems under the same conditions.

3. Results and Discussion

Fig. 2 shows the power profile as a function of time obtained from the microwave curing process. The power profile has the same characteristics for the epoxy and nanocomposite samples during the curing process. Three stages in Fig. 2 can be visualised. Stage 1 (up to 12 sec) of the graph is a sharp decrease in the power. As shown in Fig. 2 during this stage the power decreased rapidly as the default initial power (500 W) was very high for the systems. The fall of the curve extends until about a certain value of consumed power, approximately 110-120 W. Afterwards, the epoxy and nanocomposite systems start to react and absorb the heat from outside. As can be seen from Fig. 2, the chemical reaction occurred over a small period of time, from 12 sec to 154 sec, which would be referred as stage 2. The epoxy-amine reaction is the most dominated reaction during microwave curing process (Wallace et al., 2006 and Mezzenga et al., 2002), whereas the epoxy-hydroxyl groups are more dominated while thermal heating. The reaction can only take place from a certain minimal energy of the incoming particle called the energy threshold of the reaction (Mezzenga et al., 2002). In this study, it can be considered that energy threshold occurs at 12 sec. Furthermore, an active chemical reaction started from 12 sec of the curing process. During stage 2, the microwave energy is absorbed by epoxy system and maximum power consumption was found to be around 220 W. At the third stage of curing (after 154 sec), in all cases, there is no energy consumption observed (Fig. 2). The epoxy resin system consumed all necessary microwave power and no external energy was required for curing. Once the required amount of heat has been absorbed, samples were cured completely (as found later by DSC analysis) and the absorption of heat was no longer detected (Fig. 2).

The area under the power-time curve (Fig. 2) was calculated by integration. Theoretically, it defines the amount of potential energy absorbed during the microwave processing. The obtained values are presented in Tab. 1. This would indicate the amount of energy consumed for curing epoxy samples with and wihout CNTs. It was found that with the smaller addition of CNTs, more energy is required for microwave curing. The area under the curve was evaluated and compared. Conducted experiments allowed to obtain 12.5 % of energy reduction by employing 0.2 wt.% of CNTs into epoxy matrix (Tab. 1). Therefore, it can be concluded that CNTs are responsible for loweing the microwave energy consumption for curing epoxy nanocomposites.

A series of DSC test were conducted in order to observe the degree of cure for epoxy and nanocomposite samples. DSC analysis confirmed that all microwaved epoxy and nanocomposites were completely cured since there was no evidence of chemical reaction during testing. If the system is fully cured, the absorption of heat would not occur and epoxy system can be re-heated and re-cooled (PerkinElmer, 2011) reversibly below its glass transition temperature (Tg). Cyclic execution of this test is an accurate way for analysing degree of cure compared to a single heating cycle. In this work, three heating/ cooling cycles were conducted prior to the reporting of results (Tab. 1). All microwaved samples were fully cured significantly before the curing time described by the supplier (Huntsman, 2010) of the epoxy system. The technical data sheet recommends curing (at room temperature) and post curing (at 100 ^{o}C) time of at least 1680 min.

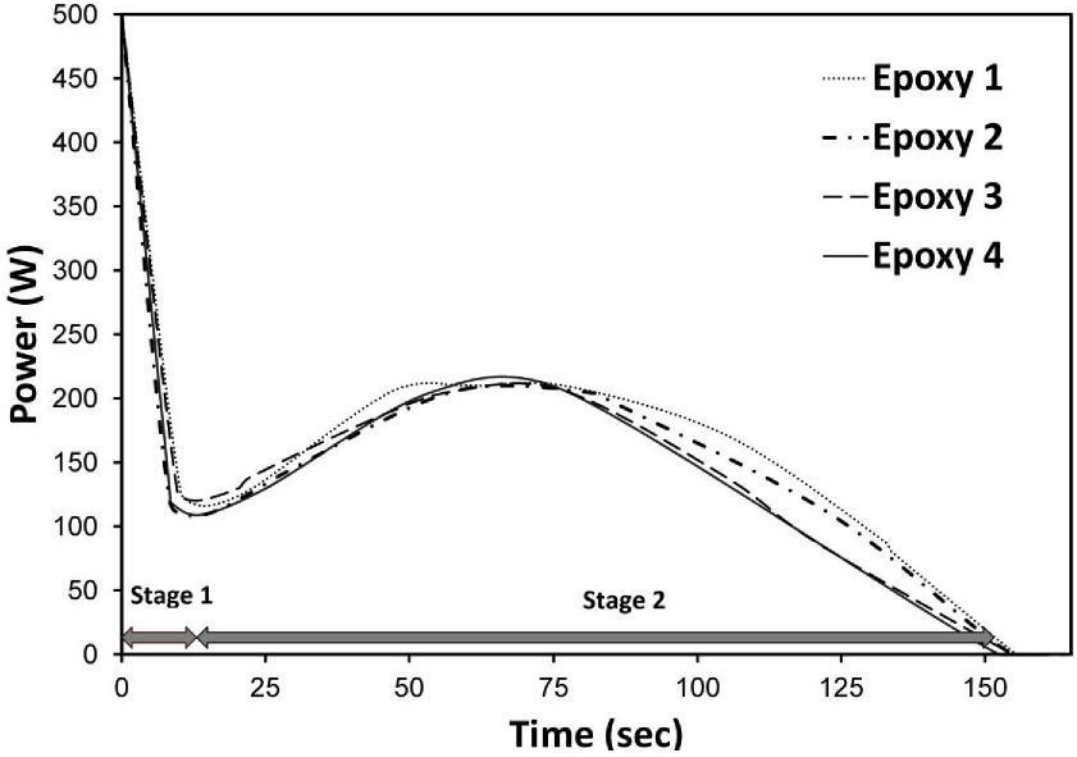

Figure 2. Power profile for the samples obtained using microwave curing.

The temperature of the microwave process could not be controlled or changed manually during the curing process because the microwave oven is programmed to be self-controllable. The temperature-time profile of the microwave heating of epoxy and nanocomposite systems is presented in Fig.3. In contrast to the power-time curves (Fig.2), the temperature profile was divided into two stages of the process. Stage A (up to 325 sec) describes gradual increase of temperature of the microwave curing process. By analysing this stage, it is possible to observe gradual heat release from the chemical reaction. This was attributed to the dipole movements and its polarisation in the electromagnetic field (Yusoff et al., 2007, Boey et al., 1990 and Zhou et al., 2003). Stage B shows gradual reduction of curing temperature due to the process of crosslinking and progressive curing of composites. By the end of this stage, material was fully cured and was hardened. As can be implied from the power-time graphs (Fig. 2), consumption of power took place at stage 2 of the curing (until 154 sec), whereas Fig. 3 shows temperature rising at the same time. Based on these results (Fig. 2 and 3), it can be concluded that after 154 sec of heating process, heat was generated from inside the system during exothermic reaction and no external heating was needed for curing.

At higher temperatures, above 50 ^{o}C, it was found that the monolithic Epoxy 1 (Fig. 3) required more amount of heat as compared to any other system. Monolithic Epoxy 1 had the highest curing temperature of 73 ^{o}C as compared to 58 ^{o}C for Epoxy 4 (0.2 wt.% CNTs) system. Here, a reduction of 20.5 % in temperature can be seen because of the addition of 0.2 wt.% CNTs. Moreover, the higher content of CNTs lowered the temperature required for full curing epoxy nanocomposites (Fig. 3). This could be attributed to the high electrical and thermal properties and selective heating of CNTs which allow producing materials at lower temperatures. CNTs

create conducting paths and absorb microwaves effeciently which may lead to rapid curing. This effect has been currently investigated and would be the subject of next publication. The microwave energy was applied directly to the material and as a result, no further side reactions and heat losses were observed. These facts are also very important from manufacturing perspective because they indidicate significant energy and time saving for manufacturing epoxy nanocomposites.

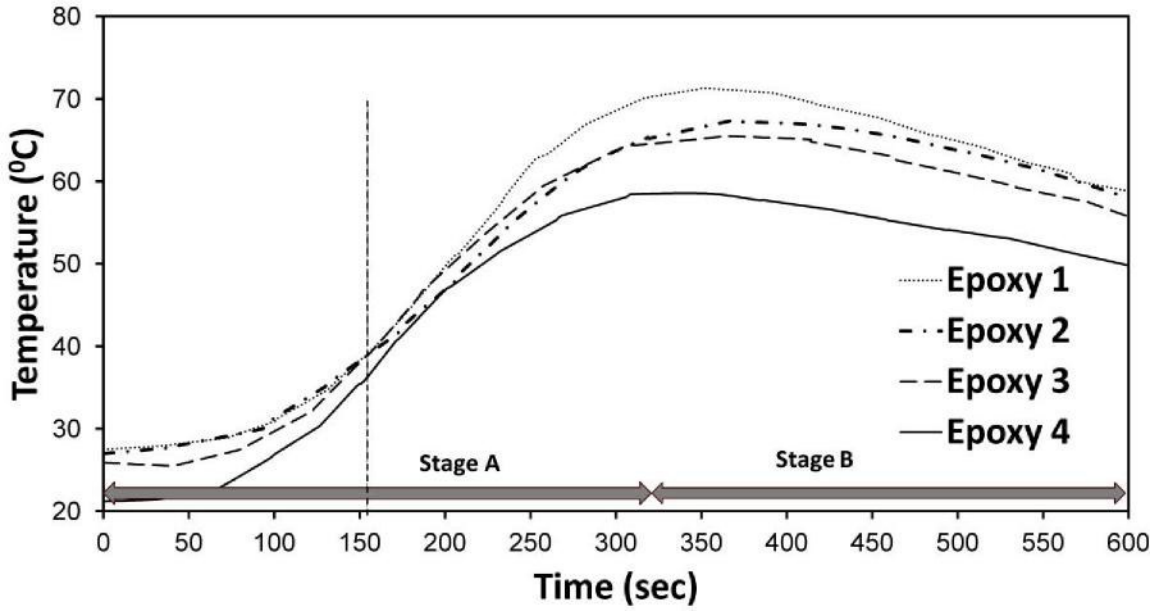

Figure 3. Temperature profile for epoxy and nanocomposite samples. The dotted line shows the point where the energy consumption was 0W.

Table 1. Summary table for microwave cured samples.

Epoxy	wt.% of CNTs	Energy, J	Maximum temperature reached during curing, ^{o}C
Epoxy 1	-	416	71.3
Epoxy 2	0.01	390	67.4
Epoxy 3	0.1	380	65.5
Epoxy 4	0.2	365	58.5

Fig. 4 presents the digital camera captured images of bottoms of the glass tubes with specimens after their full curing in microwave. All samples (Fig. 4) were cured using the same experimental conditions. It was observed that by the addition of CNTs, significant voids were found at the bottom of the tubes. This indicates significant heat was generated by the incorporation of CNTs during microwave curing process. Due to exothermic reaction of curing, heat was generated and as a result, gases were generated which were found trapped in the viscous epoxy melt (Fig. 4b-d). Therefore, for higher concentration of CNTs, exothermic reactions become very active which would produce larger voids in the fully cured samples as found in Fig. 4d. That also mean that lower concentrations of CNTs would be enough for the complete cure CNT based epoxy nanocomposites.

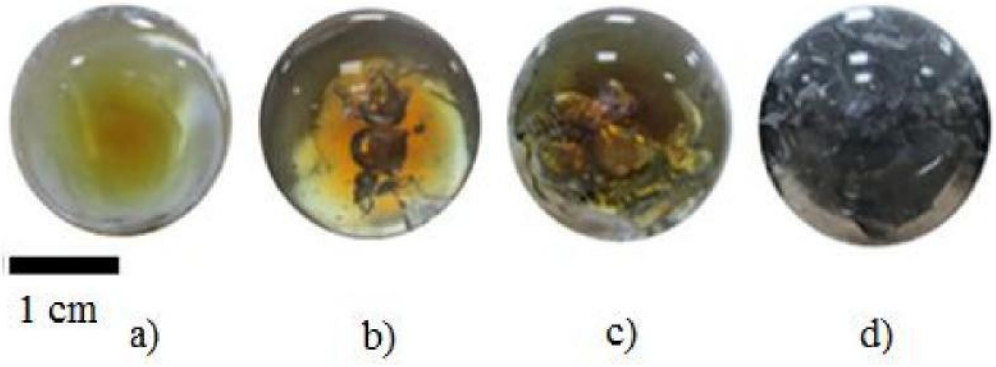

Figure 4. Digital camera captured images of bottoms of the microwaved glass tubes showing: a) neat Epoxy 1; b) Epoxy 2; c) Epoxy 3; and d) Epoxy 4.

5. Conclusion

In this work the effect of CNT addition on the microwave curing of epoxy resin composites was investigated. The results proved that CNTs infusion can further speed up the microwave curing of CNT filled epoxy nanocomposites. CNT filled epoxy nanocomposites can be microwave cured in few minutes with significantly reduced energy consumption compared to monolithic epoxy resin without CNTs. The conducted experiments allowed obtaining 12.5 % of energy and 20.5 % temperature reductions by adding 0.2 wt. % of CNTs in epoxy matrix. DSC analysis confirmed that microwaved CNT filled epoxy nanocomposites were completely cured. This could be attributed to the good electrical and thermal conductivity and microwave absorbing properties of CNTs. In the future, results could be used for rapid processing of multifunctional nanostructured composite materials and this is the subject of an on-going research.

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