DISPERSION OF GRAPHENE USING THE ELECTROSTATIC REPULSION FORCE IN THE GRAPHENE REINFORCED EPOXY COMPOSITES

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Abstract
In this work, a simple dispersion method with electrostatic repulsion force by using electrospray technique was proposed. The graphene-dispersed epoxy composites were fabricated with respect to the different voltage conditions and the particle volume fraction. UV-Visible Spectrophotometer was used to examine the dispersability of graphene in epoxy composite films according to dispersion method. The mechanical property of the graphene/ epoxy composites was measured by the tensile test and the results were compared to the specimen fabricated by using three roll mill method. The electric field strength on liquid affecting the electrostatic repulsion force between the graphene particles was also calculated at each dispersing conditions and the effect of the electrostatic repulsion force on the dispersion status of graphene was characterized.

1. Introduction

Graphene, a two-dimensional planar sheet of sp^2-hybridized carbon atoms, has attracted significant interests in recent years due to its exceptional thermal conductivity (~5,000 $Wm^{-1} K^{-1}$), electrical conductivity (~200,000 $cm^2 v^{-1} s^{-1}$), high mechanical strength (Young's modulus: ~1.0 TPa), excellent optical transmittance (~97.7%), and a large specific surface area (2630 m^2g^{-1}). These outstanding properties make graphene a promising candidate as the nanofiller for aircraft, space shuttle, electronics products and many other structural applications with high strength, light weight and multi-functional features [1]. Besides, a small amount of nanofillers showed higher mechanical strength than conventional micro scale fillers due to the size effect. However, the use of graphene has been limited in polymer composites because it is difficult to disperse in the polymer resin and organic solvent due to its strong van der Waals interaction between the graphene sheets and a stable chemical characteristic. The agglomerates region can induces the formation of void and crack in the composite materials resulting in decreasing the mechanical strength [2]. Thus, many studies have been carried out to improve the disperability of the graphene in the polymer matrix.

A variety of route for dispersing this material have been developed by using mechanical and chemical approaches such as 3-roll mill, ultrasonication and surface functionalization [3-5]. For the surface modified graphene, it can improve the interfacial bonding strength between two components of the polymer composites. In this regards, Wan et. al has reported the improvement in compatibility and wettability of graphene with epoxy resin resulting 57% enhancement of the tensile strength by the surface treatments of graphene sheets using non-ionic surfactant [3]. In case of the mechanical dispersion method, the aggregated particles can be collapsed by applying strong shear force or ultrasound energy [4]. Although these methods are widely used for dispersing the graphene into the polymer composites, they often cause a decrease in the mechanical strength of the graphene; the oxidation process generates the formation of defect and remains the surplus of chemical reactor on the surface. The dispersion of graphene with mechanical method also has a limitation in a certain particle range. Consequently, new approaches should be considered to solve this problem.

The electrospray is a well-known technique to atomize a liquid jet by electrical forces. When the charged liquid flowing out the nozzle elongates, it is dispersed into fine droplets along the electric field between a nozzle and a counter electrode by the electrostatic repulsion force. In this process, the shape and size of the droplets can be controlled by the flow rate of liquid and the voltage at the nozzle [6]. This process is a very simple and cost-effective method and it can be a promising method to disperse the particles without drawbacks. A few researchers have been studied to disperse the carbon based nanoparticles using this method [7-8]. Wang et. al performed the dispersion of carbon nanotubes (CNTs) by using electrospray technique and the aerosolized CNTs was characterized with size, concentration, and stability by matching the experimental and modeling results [7]. Tian et. al found high quality and mass production capability of novel erythrocyte-like graphene oxide by using the electrospray assisted self-assembly [8].

Here, we present a simple approach for the dispersion of the graphene into the polymer based composites using the electrostatic repulsion force by electrospray technique. The graphene-dispersed epoxy composites were fabricated with respect to the different voltage conditions and the particle contents. Our experiments revealed a dependence of the mechanical strength of graphene reinforced composites on the electrostatic force, and confirmed this dependency by calculating the electric field strength.

2. Experimental

2.1. Materials

The epoxy composed of the bisphenol-A type epoxy resin (YD-114F, Kukdo Chemicals, Korea), and the polyetheramine hardenter (Jeffamine D-230, Huntsman, USA) was used as the polymer matrix. The graphene (C500, Hanwha Nanotech, Korea) as nanofillers was prepared. All of the materials were used as received without further purification.

2.2. Specimen preparation

3-roll mill method: The solution was prepared by adding 1wt% graphene into the epoxy adhesives (Resin : Hardener = 10:8, *w/w*) and it was mixed by using a 3-roll mill (EXAKT 50, EXAKT, Germany). The gap between the rollers was kept 5 μm and the roller speed was fixed at 160 rpm. After repeating this process for 2 times, the mixture was dispersed by the ultrasonication for 10 min at 50°C and then degassed in a vacuum chamber for 20 min. Finally, the solution was poured in mold and cured at 80°C for 4 h.

Electrospray method: 0.5~2 wt% of graphene was added to the epoxy resin and mixed by using an impeller. After 10 min, the solution was inserted into a syringe connected to a power supply and sprayed into collector using the electrospray method as shown in Figure 1. 15~25 kV electric voltage was applied between the spinneret and the collector. The distance between the spinneret and collector drum was kept 10 cm, and the solution feed rate was maintained 0.02 mL/min at room temperature. After this process, the mixture of the dispersed graphene was mixed with the hardener using impeller. The mixture of graphene and epoxy adhesive was degassed in a vacuum chamber for 20 min. Then, the solution was poured into the mold and cured at 80°C for 4 h.

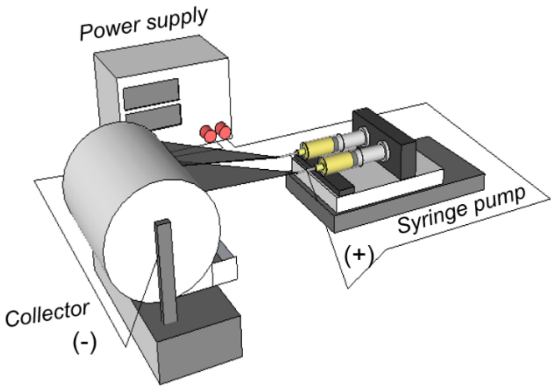


Figure 1. Schematic diagram of the electrospray method

2.3. Characterization

The mechanical properties of the graphene reinforced epoxy composites according to the applied voltage and the concentration of graphene were measured with a universal material testing machine (Model 5567, INSTRON, USA) at a crosshead speed of 2 mm/min. The specimens were prepared in the form of standard dog-bone shapes using a mold according to ASTM standard D638. The tensile strength of the specimens was measured by a strain-gauge bridge bonded on the center of the specimen. The average tensile strength was obtained from 5 samples for each condition. UV-Visible Spectrophotometer was used to examine the dispersability of graphene in epoxy composite films with respect to the applied voltage and the concentration of graphene.

2.4. Electric field and Surface charge density on the liquid jet

The most common approach adopted for the initial stage of spinning is to use slender body theory to obtain a one dimensional problem. General equation was used to calculate the external electric field strength acting on the jet's surface charge [9].
The fluid velocity (υ_0) is given by:

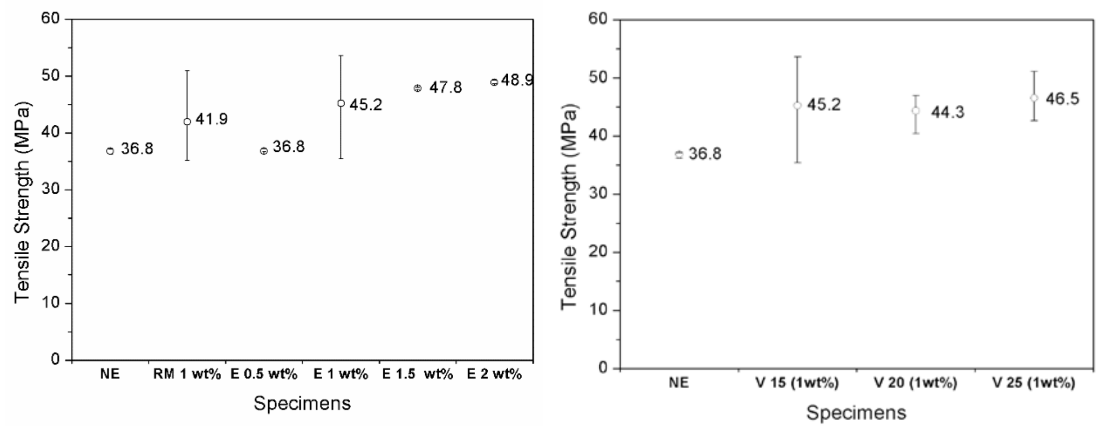
$$\upsilon_0 = \mathrm{Q}/(\pi R_0^2) \tag{1}$$

Where Q is the volume flow rate, R_0 is the jet radius. From this equation, the jet radius was derived. The electric field strength (E_0) along the jet axis is given by:

$$E_0 \; = I/(\pi R_0^2 K) \tag{2}$$

Where I is the current carried by the jet, K is the electrical conductivity of the jet.

3. Results and Discussion



(a) (b)

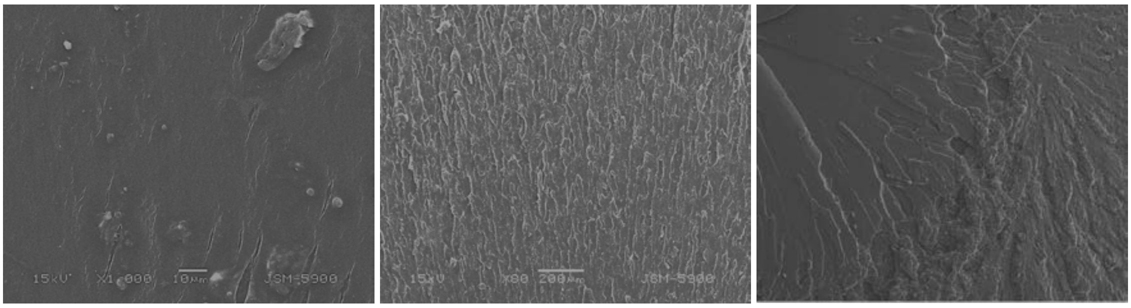
Figure 3. Tensile strength of graphene reinforced epoxy composites: (a) at different concentration of graphene (NE: neat epoxy, RM: Roll mill), (b) at different applied voltage.

Table.1 The calculated electric field strength the different particle concentrations and voltage conditions.

Concentration (wt%) at 15 kV	Label	Electric field strength (V/m)	Voltage (kV) at 1 wt%	Label	Electric field strength (V/m)
0.5	E0.5	3.5×10^{-14}	15	V15	1.82×10^{-14}
1.0	E1	1.82×10^{-14}	20	V20	2.42×10^{-14}
1.5	E1.5	1.27×10^{-14}	25	V25	3.23×10^{-14}
2.0	E2	0.97×10^{-14}			

Figure 2(a) showed the tensile strength of graphene reinforced epoxy composites. The results showed that the tensile strength increased as the concentration of graphene increased. The specimens reinforced with 2 wt% of graphene showed the 33% enhancement of tensile strength as compared to the neat epoxy and 9% compared to the conventional method with 3-roll mill at the same conditions. It showed the tensile strength depends on the dispersion state of graphene. From these results, the electrospray method can increased the effective volume ratio up to 2 wt%. Figure 3(b) showed the effect of the electric field strength with a different applied voltage. As shown in figure 3(b), the tensile strength had a tendency to increase as the applied voltage increased and the maximum value of tensile strengths was found at 25 kV. The field strength acting on the liquid jet was calculated as shown in Table 1. This result shows the electric field strength decreases as the concentration increases. On the other hands, the electric field increases as the applied voltage increases. Considering the equation (1), the increases of concentration accompanies the reduction of the jet radius and the increase of conductivity and current. The applied voltage increases current of the liquids according to the equation (2). From these results, the increase of the applied voltage is effective on the dispersion of graphene at the same concentration conditions.

Figure 3 gives the SEM images of the fracture surface for the neat epoxy and the 1 wt% graphene reinforced epoxy specimen dispersed by the different method. The fracture surfaces of the specimens show the influence of particle addition on the fracture behavior. From the images, it is clear that the roughness of fracture surfaces of the specimens reinforced with graphene is significantly increased compared to that of neat specimen. This surface morphology observed at the all specimens reinforced with graphene is related to the toughening effect of the reinforcing particles.



(a) (b) (c)

Figure 3. SEM image of fracture surface of graphene reinforced composites after the tensile test: (a) neat epoxy, (b) 1 wt% graphene with 3-roll mill method, (c) 1 wt% graphene with electrospray method.

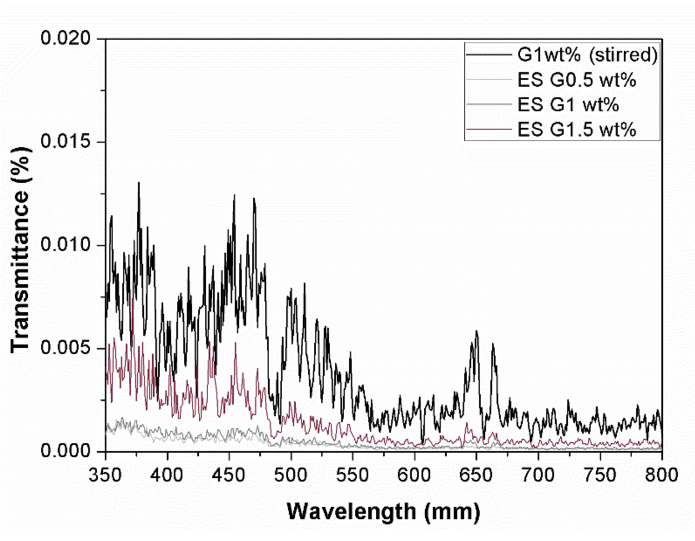


Figure 4. UV-visible spectroscopy at the different dispersion method.

Figure 4 depicts the UV-vis spectra of the graphene in epoxy resin with varying concentration of graphene. The transmittance of specimens was increased as the graphene concentration increased. But, for the same conditions (1wt% graphene), the specimens with the electrospray method decreased compared to that of conventional method. Because the effective area of absorbing UV-visible light became increases as the dispersion state of graphene improved, while the ability of light absorptions of the specimens dispersed by impeller mixing decreased due to the aggregated particles. From the results, it was found that the electrospray is a promising method to disperse conductive particles in the polymer composites

4. Conclusion

In this study, we introduced the electrospray technique to improve the dispersion of graphene in epoxy resin. The tensile strength of the specimens reinforced with graphene was enhanced by 33% compared to the neat epoxy and 9% compared to the conventional method with 3-roll mill at the same conditions. The transmittance of specimens prepared by electrospray was also decreased compared to that of conventional method. These results show the dispersion technique using electrostatic force has great potential to disperse the conductive particles into the polymers.

Acknowledgements

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