

표면 개질된 탄소나노튜브를 사용한 에폭시 복합재료의 마모특성에 관한 연구

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An investigation of tribology properties carbon nanotubes reinforced epoxy composites

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ABSTRACT

Surface modified carbon nanotubes were applied into the epoxy composites to investigate its tribological property. Carbon nanotubes reinforced epoxy composites were fabricated by casting. Effects to the tribological property of loading concentrations and types of surface modification of carbon nanotubes were investigated under sliding condition using linear reciprocal sliding wear tester. The results show that the small amount of carbon nanotubes into the epoxy exhibited lower weight loss than the pure epoxy. It is concluded that the effect of an enormous aspect ratio of carbon nanotubes surface area which wider than conventional fillers that react as interface for stress transfer. As increased the contents of carbon nanotubes, the weight loss from the wear test was reduced. And the surface modified carbon nanotubes show better tribological property than as produced carbon nanotubes. It is due that a surface modification of carbon nanotubes increases the interfacial bonding between carbon nanotubes and epoxy matrix through chemical bonding. Changes in worn surface morphology are also observed by optical microscope and SEM for investigating wear behaviors. Carbon nanotubes in the epoxy matrix near the surface are exposed, because it becomes the lubricating working film on the worn surface. It reduces the friction and results in the lower surface roughness morphology in the epoxy matrix as increasing the contents of the carbon nanotubes.

Key Words: Carbon nanotubes (CNTs), Epoxy matrix, Tribology properties, Surface modification, Interfacial bonding

1. Introduction

Polymer-matrix composites (PMCs), particularly those containing fiber reinforcement, have become increasingly popular for use in structural applications. The primary benefit is the potential for impressive enhancements in strength-to-weight ratios. Other additional benefits, such as improved wear resistance and material property tailorability can be significantly important in special application. The outstanding mechanical properties of carbon nanotubes are due to the high bond strength of the constituent carbon-carbon bonds and their near perfect lattice structure. The high aspect ratio in combination with low density^[1], high strength (Young modulus 1-5TPa) and stiffness^[2,3] make replacement of ordinary filler carbon

black to CNTs give promising potential as a reinforcement material in composites. In processing of CNTs reinforced polymeric composites, the challenging problem is to transfer the unique mechanical properties of CNTs to the polymer matrix. There are few main topics are currently focusing to improve the properties of CNTs reinforced polymer composites. These topics are dispersion, interfacial bonding and alignment of the CNTs in polymer matrix.

An enormous aspect surface area ratio of CNTs ($1000\text{m}^2/\text{g}$ and more) which more wider than conventional fillers will reacted as interface for stress transfer, but these properties also lead the strong tendency of the CNTs to form agglomerates. Therefore an enhancement of polymeric properties related to the

homogenous dispersion in the matrix and better wetting condition with polymer matrix. CNTs which dispersed through ultrasonication reported that can achieve nano-dispersion than dispersion by ball milling and high speed stirrer. The interfacial bonding can be improved by surface modified by chemical functionalization^[4-6] which give better solubility and dispersion level of CNTs in solvent which open provide more opportunity of applications in various fields.

Recently, the improvements of mechanical properties through tensile test of carbon nanotubes reinforced polymer composites have been reported^[7, 8]. Moreover, the tribological behaviors of the carbon nanotubes which incorporated with polymer matrix in carbon-CNTs, polyamide-CNTs and metal matrix nano-composites have been investigated^[9-12]. It was found that additional carbon nanotubes reduced friction and resulted increase of wear resistance compared to the pure polymer substrates matrix. However, few reports have been available on the tribological behavior of CNT reinforced epoxy polymer composites. The main objective of this study is to investigate the effects of carbon nanotubes to the tribological performance of the epoxy matrix composites with surface modification of CNT by a chemical functionalization.

2. Experiments

2.1 Matrix material

The epoxy resin is Bisphenol-A-based epoxy resin (KER 215) which supplied by Kumho P&B Chemicals and curing agent (Amicure 101) which supplied by Daemyung Chemical Tech. KER 215 has a low viscosity and it gives better wetting with fillers. The viscosity of epoxy resin is 0.7-1.1 Pa-sec and curing agent is 0.2 Pa-sec.

2.2 Reinforcements (Functionalized CNTs)

CNTs used in this study were multiwalled carbon nanotubes (MWNTs) which synthesized by CVD thermal decomposition of hydrocarbons gas. CNTs which used in this study were classified into three types.

- As-produced MWNT which supplied by ILJIN nanotech and used as produced. The purity of AP-MWNTs is reported around 95% by manufacturer. Those MWNTs are mechanically cut by a high speed stirrer (ULTRA T25, 500W) at 19000 rpm for 2 hours and followed with

sonification with ULSSO HI-TECH ULH700S with power of 700W at 14000Hz for 1 hour in methanol.

- Carboxylated MWNTs. Firstly, mechanically cut powder AP MWNTs are surface modified with 3M nitric acid by similar processing method which used by subject^[4].
- Octadecylated MWNTs. AP MWNTs are processed by method (b) and followed by surface modified with ODA (Octadecylamine) which similar processing method which used in subject^[13].

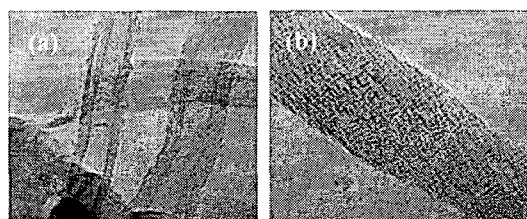


Fig. 1 TEM images (a) AP-MWNTs (b) Octadecylated-MWNTs

Figure 1 shows TEM images of MWNTs. Figure 1 (b) indicates the surface change after surface modification at the outermost wall sides which are covered by ODA through covalent bonding with MWNTs. Variation percentage weight loss of each MWNTs types which measured by TGA (Thermal Gravity Analysis) in nitrogen atmosphere were given in figure 2. This graph shown that weight of octadecylated MWNTs reduce sharply at 200°C and resulted highest weight loss than other MWNTs.

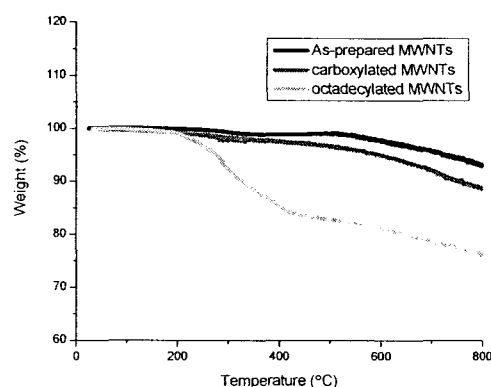


Fig.2 TGA graph of the weight loss of MWNTs in nitrogen atmosphere until 800°C.

2.3 Specimen Fabrication

The CNT reinforced epoxy composites are fabricated by adding desired wt% of MWNTs into epoxy resin. In this study, 0.1, 0.5, 1.0 and 3.0 wt % of MWNTs are used. The MWNTs are added into the epoxy resin and manually mixed for 2 minutes. To enhance the dispersion quality of MWNTs, ultrasonication with the power of 135W is applied for 1 hour. Then, degradation process has been conducted in vacuum oven at 30°C for 1 hour. Curing agent is added to epoxy resin with MWNTs, This solution is manually mixed for 2 minutes and followed ultrasonication for 15 minutes. Another degradation process has been conducted again in vacuum oven at 30°C for 1 hour. After these processes, the epoxy and MWNTs mixture is poured into the Teflon mold and cured in drying oven by two steps. Pre-curing at 80°C for 2 hours and continued by post curing process at 150°C for 3 hours. Bulk MWNTs reinforced epoxy composites for wear test have dimensions of 13 mm (width) x 13 mm (length) x 3 mm (thickness).

2.1.4 Wear test

The tribological property has been evaluated under the sliding condition using linear reciprocal sliding wear tester (ball-on-disc configuration^[9]). The ceramic Zirconia ball with a 10 mm diameter is used as a counterpart. Sliding has been performed under dry and ambient condition with 90N normal load over a period of 20000 cycles for sliding speed of 62.5 mm/s. The relative humidity was about 50- 0%. Before each test, the surfaces of block specimens were cleaned with soap to remove oil layer, and washed with deionized water and tissue. At the end of test, the burrs of specimens are brushed out by a soft brush. The wear amount was determined by weight loss of each specimen. The worn surface morphology is investigated by optical microscope and SEM to examine the wear behavior. The fracture surface morphology also is examined by SEM to study the dispersion quality of CNTs in epoxy matrix and the effects of surface modified to interfacial bonding between CNTs and epoxy matrix.

3. Results and discussion

The variation of the wear loss as a function of MWNTs

types and wt% concentration was shown in figure 3. It can be clearly seen that the incorporation of MWNTs significantly decreases the wear loss of epoxy matrix. Wear loss reduced by increased of concentration MWNTs in epoxy matrix which proves that an enormous aspect ratio of carbon nanotubes surface area give wider load transfer during wear. This graph showed that the wear loss becomes less while the wt% of CNTs is increased. The result also indicates that the wear loss decreases from 28% at 0.1wt% and up to 77% at 3.0wt% of carboxylated-MWNTs reinforced epoxy composite which compare to epoxy polymer.

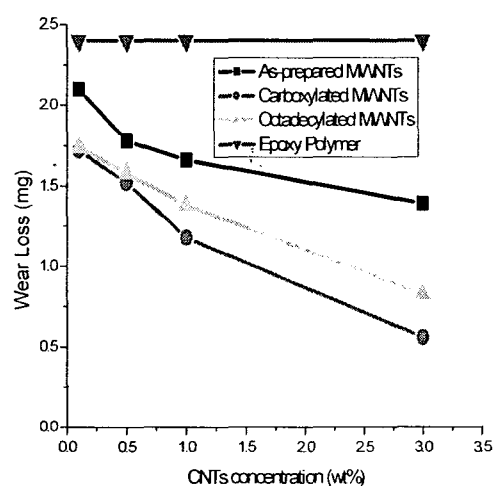


Fig. 3 Variations of the wear loss of MWNTs reinforced epoxy composites with CNTs addition (wt %) and CNTs types.

Also it is shown that the surface modified MWNTs (carboxylated and octadecylated) gives better tribological property than as-produced MWNTs because we assume that the surface modification will increase interfacial bonding. Besides the dispersion state of surface modified MWNTs are better than AP-MWNTs. However, the surface modification with a longer chemical chain, such as octadecylated function gives slightly higher wear loss than the surface modification with shorter chemical chain, namely carboxylated MWNTs at higher wt% of CNTs.

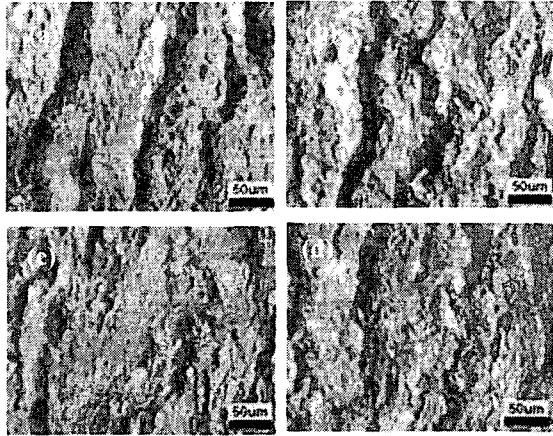


Fig. 4 The optical microscope images of worn surface 3wt% specimen after wear test (a) epoxy polymer (b) As-prepared MWNTs (c) Carboxylated MWNTs (d) Octadecylated MWNTs reinforced epoxy composites

The effect of wt% of CNTs to the tribological property can be explained from the morphology of worn surfaces observed by an optical microscope and SEM. The optical microscope images of the worn surface with 3wt% MWNTs are shown in figure 4. The wear has been initiated by the adhesion peeling micro-cracks wear which is perpendicular to the sliding direction. And the wear amount of this peeling becomes shallow and deep grooves. In epoxy matrix, it is clearly seen the rough surface with deep grooves compared to the surface modified MWNTs which shows relatively smooth, uniform and compact worn surface. From this worn surface optical observation, we can conclude that CNTs in the matrix near the surface are exposed and act like the lubricating thin carbon film on the worn surface, this can reduce the sliding friction, and it results in the smooth wear worn surface morphology. Also we can observe that the burrs for higher wt% of MWNTs reinforced composites have relatively small and soft characteristics than pure epoxy burrs. Figure 5 shows the SEM worn surface images of the epoxy composites with the surfaces modified MWNTs and pure epoxy. It clearly shows that the pure epoxy has deeper grooves than the surface modified MWNTs reinforced composites. The grain boundary size of the pure epoxy bigger than the surface modified MWNTs composite which is a brittle characteristics.

From the observation of the worn surface morphology, we cannot observe any carbon nanotubes.

This agrees with results in the other paper^[8] which states that the Raman spectra of the worn surface shows nearly the same spectra obtained from the pure epoxy surface. That implies that most of CNTs in the surface are swept away due to severe loading condition and/or some of CNTs are changed to the amorphous carbon. Therefore, to observe the CNTs in the epoxy composite specimens, we manually fractured the specimens. Figure 7(a) shows that the surface modified MWNTs are well incorporated with the epoxy matrix and have better dispersion and less agglomeration than AP- MWNTs in fig. 7(b). SEM images of the fracture surfaces in Fig. 8(a) shows that the surface modified MWNTs still remain firmly as embedded in the epoxy matrix However in fig 8(b), AP-MWNTs are pulled out and removed from the epoxy matrix, therefore the longer carbon nanotubes can be observed. This image proves that the surface modification gives stronger interfacial bonding than AP-MWNTs with the epoxy matrix.

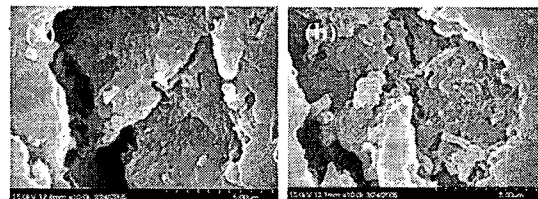


Fig. 5 SEM images of worn surface (a) Pure Epoxy, (b) with Carboxylated MWNTs.

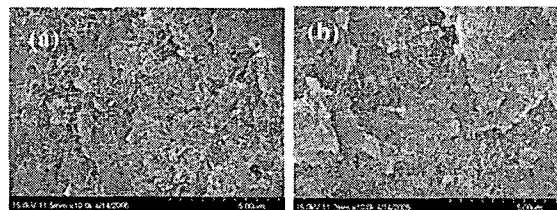


Fig. 6 SEM images of fracture surface (a) As-prepared MWNTs (b) Carboxylated MWNTs reinforced epoxy composites.

The tribological property of the polymer composites is not only dependent on the matrix materials, but also fillers. MWNTs in the matrix have a self lubricating mechanism during wear test, they reduce the wear loss. AP-MWNTs are chemically stable but there are some defects on their surface. Therefore these defects can be chemically combined with other chemical functions through the surface modification process and this leads another application with others solvents matrix by chemical bonding. In this experiment, the surface modified CNTs

with covalent sidewall functionalization gives a uniform dispersion state which exhibits the uniform stress transfer through lubricating CNT film and strengthens the interfacial bonding with the epoxy matrix. Octadecylated MWNTs reinforced epoxy composites also show the same dispersion quality and the interfacial bonding level through the fractured surface. However in figure 2, it shows that it starts to loss its weight at 200°C and other CNTs at 500°C. During the wear test, the temperature of the wear surface is increased certain degrees which leads the degradation of a mechanical properties.

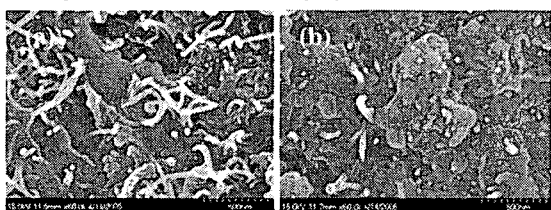


Fig. 7 SEM images of the fracture surfaces (a) AP-MWNTs (b) Carboxylated MWNTs epoxy-composites.

4. Conclusion

Carbon nanotubes reinforced epoxy composites with the different concentration and functional groups are prepared by in situ polymerization process. The tribological property has been investigated by using the wear tester under dry conditions. It has been found that the addition of carbon nanotubes significantly increases the tribological property and shows the less wear loss. Compared to AP-MWNTs, the surface modified MWNTs increases the dispersion quality and the interfacial bonding strength with epoxy matrix.

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