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Properties of epoxy nanocomposites filled with carbon nanomaterials

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Abstract: Rheological, mechanical, electrical, and thermal properties of epoxy nanocomposites containing carbon nanomaterials (CNMs) were investigated with different loading. Two kinds of CNMs – multiwalled carbon nanotubes (MWNTs) and carbon blacks (CBs) – were selected to examine the effect of their geometrical structure on various properties. Under sonication, MWNTs and CBs (0.5, 1.0, and 1.5 wt.-%) were mixed with the epoxy resin by using a solvent. Dispersion of the CNMs in the epoxy nanocomposites was characterized by means of transmission electron microscopy and field emission scanning electron microscopy. Carbon nanotubes (CNTs)/epoxy composites show significant differences from the CBs/epoxy composites due to their high aspect ratio. It was found that the CNTs/epoxy composites exhibit non-Newtonian rheological behaviour, while the CBs/epoxy composites with the same weight content show Newtonian behaviour. The CNTs/epoxy composites have better mechanical and thermal properties than the CBs/epoxy composites. In the CNTs nanocomposites, the percolation threshold of electrical conductivity is found to be less than 0.5 wt.-%, which is too low to be obtained by using other carbon materials such as carbon fibre in polymer composites. Effects of CNM content on the various properties were also examined. As loading of the CNMs increased, improved results were obtained.

1. Introduction

Carbon nanomaterials (CNMs) reinforced polymer composites have been studied frequently for several years since carbon nanotubes (CNTs) were discovered by Iijima [1] in 1991 because of the CNTs' unique electronic and mechanical properties such as high tensile strength and modulus. In order to achieve optimal property enhancement in the CNTs/polymer composites, there are several key issues to be resolved, which include improved dispersion and alignment of the CNTs in the polymer resin and functionalization of the CNTs surface to enhance adhesion between CNTs and polymer matrix. Generally, three different methods are used to disperse the CNTs in a polymer matrix: suspension of the CNTs in the dissolved polymer, polymerization of CNTs/polymer mixture, and melt mixing of CNTs with a polymer matrix.

It has been expected that CNTs could play a role as an excellent reinforcement in the polymer composites. For nearly a decade of research, a number of studies have been conducted but their expected potential as reinforcement has not been fully realized [2-12]. Schadler et al. [2] observed the mechanical behaviour of multiwalled carbon nanotubes (MWNTs)/epoxy composites in both tension and compression. It was found that compression modulus was higher than tensile modulus, which indicated that load transfer to CNTs in composites occurred more effectively in compression. Allaoui et al. [3] showed that tensile modulus and yield strength of MWNTs/ epoxy composites were doubled compared with the properties of the pure epoxy resin. Kearns and Shambaugh [4] dispersed single walled carbon nanotubes (SWNTs) in polypropylene (PP) and made fibres out of the nanocomposites via melt-spinning and post-drawing processes. They reported that by adding 1 - 4 wt.-% SWNTs to the polymer, tensile strength of the fibre increased by 40% and tensile modulus increased by 55%. Lau et al. [5] showed that flexural strength decreased by 10% for epoxy nanocomposites with 2 wt.-% of MWNTs, and morphological observation of the fracture surface implied that the CNTs were completely pulled out after the flexural strength test due to weak interfacial bonding between CNTs and polymer matrix. Ruan et al. [6] reported an increase of about 140% in ductility and up to 25% in tensile strength for ultrahigh molecular weight polyethylene (UHMWPE) with loading of 1 wt.-% MWNTs. Wong et al. [7] examined physical interactions between CNTs and polymers. In the absence of chemical bonding between CNT and matrix, it was found that non-bonded interactions, consisting of electrostatic and van der Waals forces, resulted in weak interfacial shear strength of the MWNTs/epoxy and the MWNTs/polystyrene (PS) composites. Based on molecular mechanics simulations and elasticity calculation, the interfacial shear strength was studied in the absence of chemical bonding. Dalton et al. [8] showed that highly concentrated (60 wt.-%) SWNTs/poly(vinyl alcohol) (PVA) fibres displayed very large toughness. In order to detect orientation and deformation of the CNTs in the nanocomposites, the tensile behaviour of both random and aligned MWNTs/PS nanocomposites was investigated by Thostenson and Chou [9]. They found that aligned CNTs resulted in more improved yield and ultimate strengths than random CNTs. It is known that surface treatment of CNTs is needed to obtain more enhanced mechanical properties due to functionalization of the CNTs and grafting with the polymer resin. However, the treatment has not yet been plainly developed for processing these multiphase materials [13-16].

For the purpose of electrostatic discharge (ESD) or electromagnetic interference (EMI) shielding, some level of electrical conductivity is required. It is reported that conductivity above 10^{-6} S/m is needed in order to avoid the electrostatic charging of an insulating matrix. Generally, a highly conductive filler such as a carbon black (CB) is mixed with a polymer matrix and the filler makes a three dimensional network in the matrix. This is known as a percolation and the percolation threshold is characterized as a sharp jump in the conductivity by several orders of magnitude. Sandler et al. [17] dispersed CNTs in an epoxy resin and measured electrical properties of the nanocomposites to relate the filler volume fraction to the electrical conductivity. They showed that the nanocomposites had a conductivity around 10^{-2} S/m with filler volume fractions as low as 0.1 wt.-%. They also found that the conducting properties of the CNTs/epoxy composites resulted from formation of macroscopic aggregates of the CNTs and followed a percolation scaling law. Kymakis et al. [18] investigated the interaction between SWNTs and a soluble polymer, poly(3-octylthiophene) (P3OT), via electrical characterization methods and found a percolation threshold of 11 wt.-%. Ounaies et al. [19] experimentally obtained a relatively low percolation threshold value of 0.07 vol.-% CNT and the results exhibited a non-Ohmic behaviour, indicating a quantum tunnelling conduction mechanism. Thermal conductivity of SWNTs/epoxy composites was studied by Biercuk et al. [20]. Samples loaded with 1 wt.-% unpurified SWNT showed 70% increase in thermal conductivity at 40 K and 125% increase at room temperature. Commonly, nanocomposites filled with CNTs have a higher thermal conductivity, compared with polymer composites filled with carbon fibres of larger diameter such as vapour-grown carbon fibres (VGCF) [21].

There are few reports on the rheological behaviour of CNTs/polymer composites. Pötschke et al. [22] investigated rheological properties of CNT/polycarbonate (PC) composites. It was found that the increase of viscosity of the nanocomposites filled with CNTs was much higher than viscosity changes known for polymer composites filled with carbon fibres or CBs. The viscosity increase was accompanied by an increase of the elastic melt property, storage modulus G', which was much larger than that of the loss modulus G''.

It is necessary to understand the effect of geometrical features on various properties of CNT-filled composites compared with those filled with other carbon fillers. Therefore, in this study, MWNTs and CBs were selected as reinforcement materials in epoxy nanocomposites and experimental results of the nanocomposites are compared with each other. Rheological, mechanical, electrical, and thermal properties of the nanocomposites were examined with different loadings of the CNMs. Differences in various properties between the MWNTs/epoxy and CBs/epoxy composites were observed at the same weight content of the CNMs. The dispersion state of the CNMs in the epoxy nanocomposites was characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

2. Experimental part

2.1 Materials and preparation of CNM/epoxy composites

MWNTs and CBs used were supplied by Iljin Nanotech Co. and Korea Carbon Black Co., Korea, respectively. The CNTs synthesized by chemical vapour deposition (CVD) had an average diameter of 20 nm and a length of 10 - 50 µm. The average diameter of the CBs was 20 nm and they had spherical shape. Epoxy resin (YD 128) and hardener (TH 432) were obtained from Kukdo Chemical, Korea, based on diglycidyl ether of bisphenol-A and modified aromatic amine, respectively. The CNTs prepared were composed of many aggregates of different sizes. Since the aggregates would be obstacles to uniform dispersion of the MWNTs and were hardly broken into individual tubes in the epoxy resin, the CNTs of 0.5, 1.0, and 1.5 wt.-% were first dispersed in ethanol solutions under sonication for 2 h. The CNTs/ethanol solutions with different CNTs weight fractions were then mixed with the epoxy resin. The mixture was also sonicated for 1 h at 80°C and kept in a vacuum oven for 5 days to remove air bubbles and ethyl alcohol. After adding the hardener, the mixture was stirred by using a magnetic bar for 15 min under sonication. The epoxy resin loaded with the CNTs was injected into a mold and cured in the vacuum oven for 3 days. The CBs/epoxy composites were prepared by the same procedure.

2.2 Rheological measurements

Dynamic rheological measurement was carried out by using a C-VOR stress-controlled rotational rheometer from Bohlin instrument Ltd. The measurement was conducted in an oscillatory shear mode using a parallel plate geometry at constant temperature of 25°C. Stress sweep tests were performed to identify the linear viscoelastic regime. Shear stress, 1 Pa, was fixed during all frequency sweep tests and sample thickness was set to be 1 mm.

2.3 Mechanical measurements

Mechanical properties of CNMs/epoxy composites were measured with an Instron 8516. Tensile tests were carried out at ambient temperature and at a constant cross-head speed of 3 mm/min. Specimens were made in dog-bone shape by compression molding.

2.4 Electrical and thermal conductivity measurements

DC Electrical conductivity was measured by the standard four-probe method at ambient conditions. A current was applied to specimens and voltage was generated under 2 V DC. That is, as the current gradually increased, the voltage was measured and the electrical conductivity was obtained as the slope of voltage vs. current. The specimens had 10 mm diameter and 1 mm thickness. Thermal conductivity measurement was carried out according to ASTM E1225-87, which is based on the temperature difference between reference and sample specimens at steady state and room temperature. The sample was a cylinder with 10 mm diameter and 20 mm length.

2.5 Morphological characterization

FESEM images were obtained with a JEOL JSM-6330F operating at 5 kV to examine surfaces of the specimens fractured during tensile test. They were coated with Pt for 5 min prior to the measurement. In addition to FESEM, TEM observation was carried out with a JEOL JEM-2000EXII at 100 kV for more exact characterization of the nanocomposites' morphology. The TEM specimens were microtomed to an ultra-thin section with a thickness of about 80 nm and coated with carbon for 7 min to prevent the specimens from degradation caused by irradiation of electrons.

3. Results and discussion

3.1 Rheological properties

In order to enhance the processibility of CNMs/epoxy composites, the rheological behaviour of the nanocomposites in molten state should be understood in detail. Knowledge of rheological properties of the nanocomposites is also helpful in understanding structure-property relationships. Dynamic oscillatory shear measurements of polymeric materials are generally performed by applying a time-dependent strain, $\gamma(t) = \gamma_o \sin(\omega t)$, and measuring the resultant shear stress, $\sigma(t) = \gamma_o[G' \sin(\omega t) + G'' \cos(\omega t)]$, where G' and G'' are the storage and loss moduli, respectively.

Fig. 1 (a) and (b) represent the storage modulus, G', for CNTs/epoxy and CBs/epoxy composites. The storage modulus of CNTs nanocomposites dramatically increases with increasing CNTs loading compared with that of the pure epoxy resin, while that of the CBs nanocomposites increases slowly with respect to loading. As CNTs loading increases, the storage modulus also exhibits a solid-like behaviour of frequency independence, especially at lower frequencies. It can be explained by the fact that the CNTs form a physical connectivity or percolated structure due to their high aspect ratio of about 1000 and their high surface area. Fibre-reinforced composites show the same result as the CNTs nanocomposites [23]. That is, interaction of fibrous fillers has greater frequency independence than that of other non-fibrous fillers. At the terminal zone in Fig. 1 (a), slopes of the storage modulus for 0.5, 1.0, and 1.5 wt.-% loading are 0.83, 0.66, and 0.61, respectively. It means that there is non-terminal behaviour at the zone. Differences of the slopes at the terminal region are closely related to the internal structure of the nanocomposites, which is affected by particle-particle interaction of the CNTs in the polymer matrix. Such non-terminal behaviour has been also reported for other particulate nanocomposites at high volume fractions and high aspect ratio [24,25]. In the case of the CBs/epoxy composites, the storage modulus has less consistency as shown in Fig. 1 (b).

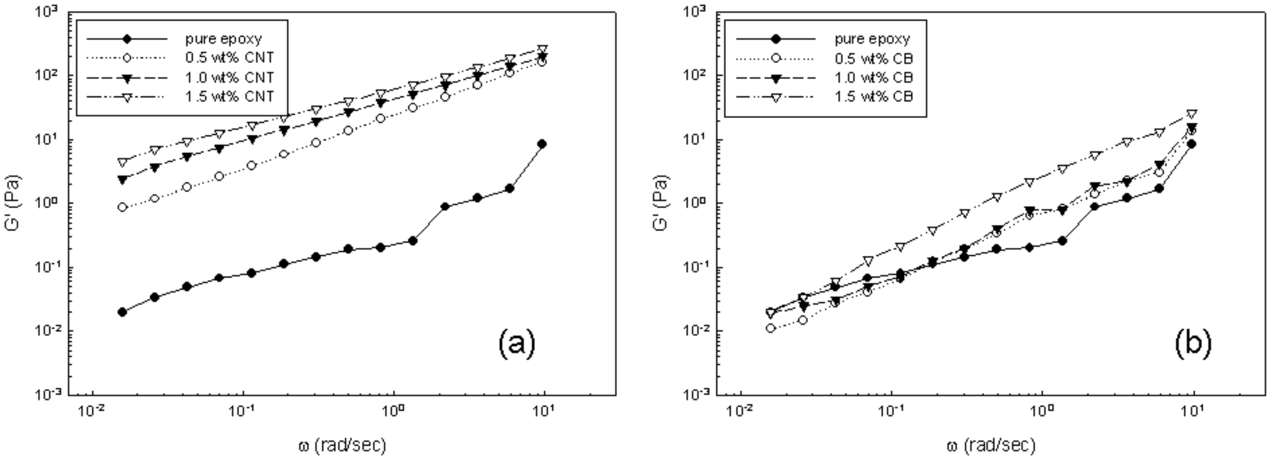

Fig. 1. Storage moduli of epoxy nanocomposites filled with (a) CNTs and (b) CBs, as a function of angular frequency

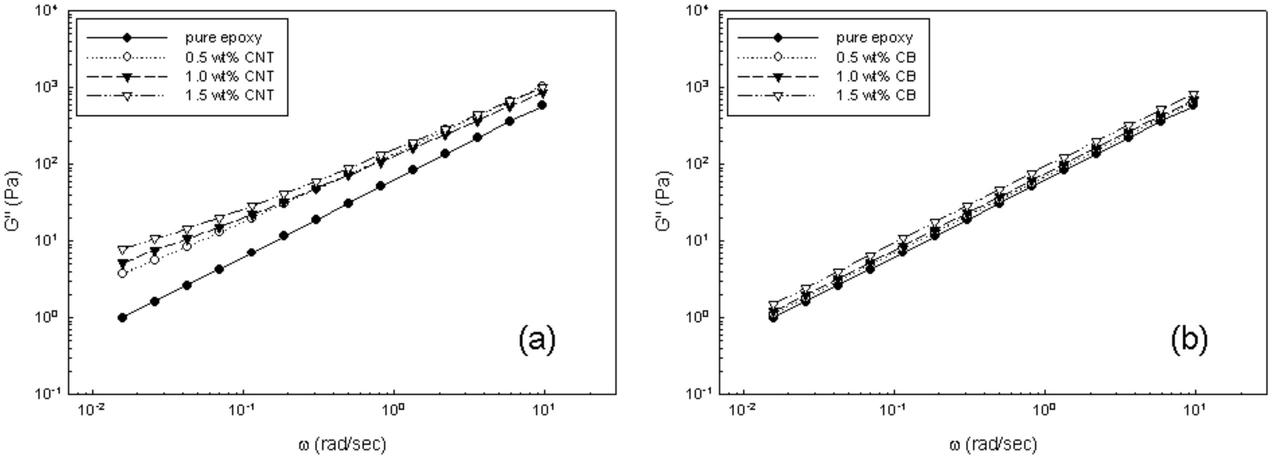

Fig. 2. Loss moduli of (a) CNTs/epoxy and (b) CBs/epoxy composites vs. angular frequency

The dynamic loss modulus, *G*'', of the nanocomposites is represented in Fig. 2 (a) and (b). It is known that *G*' is more sensitive than *G*'' to the morphology of filled particles because the energy between polymer resin and particles is more related to the storage than to the loss modulus. However, the loss modulus of the CNTs/epoxy composites also indicates the different rheological behaviour with respect to loading and the geometrical structure of the CNMs. It is similar to the behaviour of *G*' for the CNTs nanocomposites. Fig. 2 (b) shows the terminal zone behaviour of the loss modulus in the CBs/epoxy composites, i.e., the slope of the loss modulus is equal to one at low frequency.

Complex viscosity, |η*|, of CNMs/epoxy composites is shown in Fig. 3. The CNTs/ epoxy composites rheologically exhibit non-Newtonian behaviour, close to a power law fluid, and the viscosity increases with increase in CNT loading. The reason is that the interaction between the CNTs and the polymer resin becomes larger due to the high aspect ratio as the CNT content increases. On the other hand, the CBs/epoxy composites show Newtonian behaviour and the complex viscosity depends on the weight fraction of the CBs. The increase in complex viscosity with respect to CNT loading is primarily caused by the large increase in the storage modulus, *G*'.

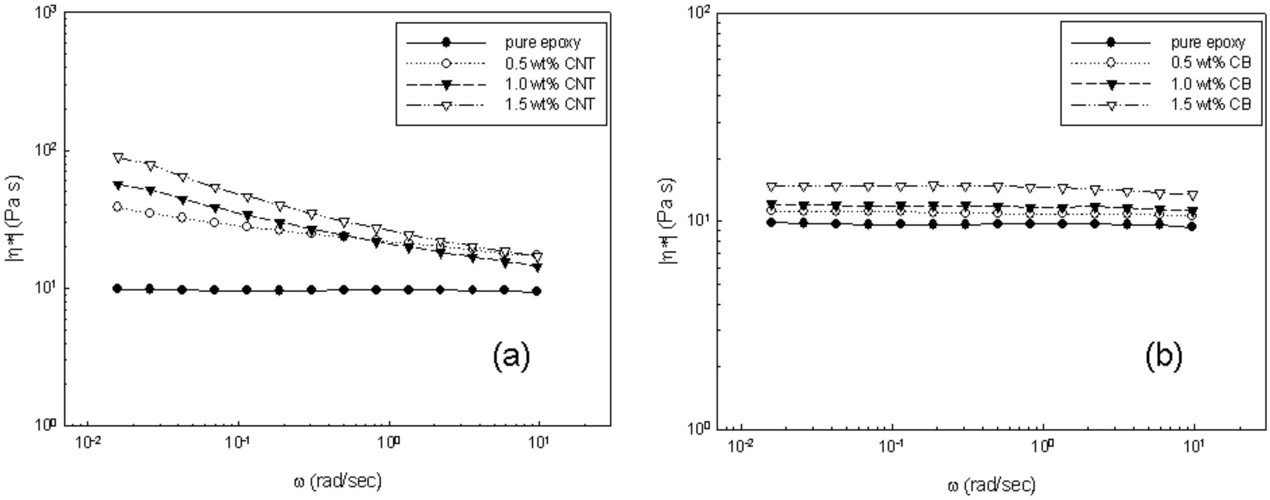

Fig. 3. Complex viscosities of epoxy nanocomposites filled with (a) CNTs and (b) CBs

3.2 Mechanical properties

Tensile modulus and strength of the nanocomposites increase with increasing CNM loading as shown in Fig. 4 (a) and (b). Enhancement of mechanical properties is a general tendency for nanocomposites because the CNMs act as reinforcement in the nanocomposites.

Tensile modulus and strength of the CNTs/epoxy composites are much higher than those of the CBs/epoxy composites because of their different structures. The CNTs with high aspect ratio are more efficient than the CBs in transferring applied load. Elongation at break is plotted as a function of CNT content in Fig. 5.

As the CNM loading increases, the elongation at break of both the CNTs and the CBs nanocomposites is reduced, with larger reduction for the CBs nanocomposites. In the case of CNTs/epoxy composites, mechanical properties are improved but not as much as expected. It can be explained by the following two reasons. The first reason is the weak bonding between the CNTs and the surrounding matrix. It has been reported that the interfacial bonding between the CNTs and the polymer resin is weak and load transfer from the polymer to the CNTs is not large enough to break the CNTs under tensile loading. As a result, the CNTs are frequently pulled out. This phenomenon can be observed by FESEM as shown later. The second reason is related to the structural problem of outer shells of the CNTs. Because weak van der Waals forces act between individual graphene shells in the MWNTs, slipping between the shells will occur.

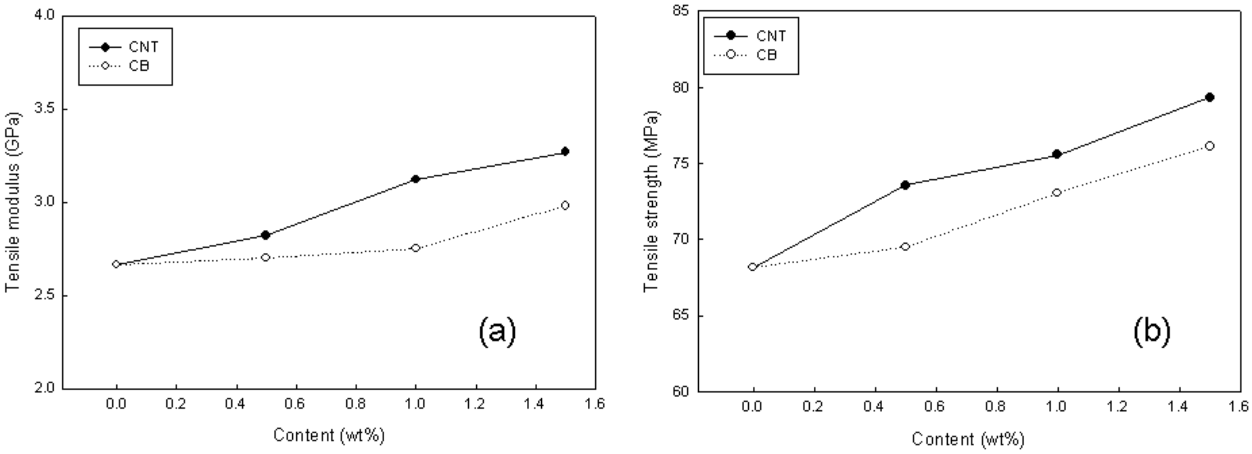

Fig. 4. Effect of geometrical structure on mechanical properties: (a) tensile modulus and (b) tensile strength of CNMs/epoxy composites vs. carbon loading

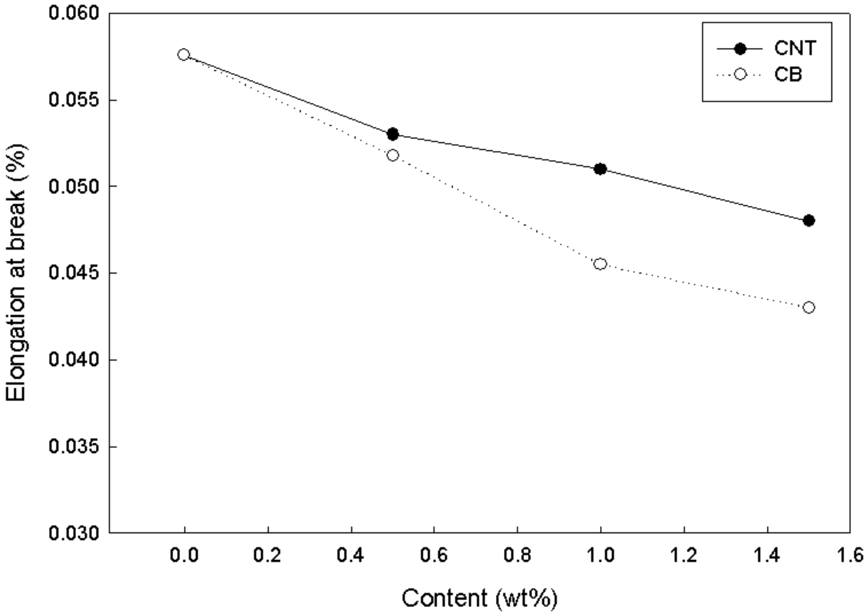

Fig. 5. Elongation at break of CNMs/epoxy nanocomposites as a function of carbon content

3.3 Electrical and thermal conductivities

Fig. 6 shows the effect of CNM content on electrical conductivity. When the CNTs are embedded into epoxy resin with up to 1.5 wt.-%, the electrical conductivity increases by six orders of magnitude. The electrical conductivity is much higher than that of CBs/epoxy composites. To obtain a similar electrical conductivity to that of the CNTs/ epoxy composites by using CBs, much larger amounts of CBs are needed than of CNTs. Therefore, CNTs may replace CBs by using a smaller amount. Generally, an electrical conductivity in the order of 10^{-6} S/m is sufficient for anti-static applications.

In Fig. 6, a low percolation threshold of less than 0.5 wt.-% loading is observed in the CNTs/epoxy composites and the value is much lower than that of the nanocomposites containing the CBs. According to percolation theory, electrical paths are made up of conductive inclusions in the direct-contact structure based on Ohmic behaviour and the percolation threshold values strongly depend on the shape of particles [21]. Above the percolation threshold, the CNTs provide the conductive three-dimensional paths. It is easy for the CNTs to form the paths due to their slender structure compared with the spherical CBs. In thermal conductivity, similar results to the electrical conductivity are obtained as shown in Fig. 7. However, there is no percolation threshold phenomenon for thermal conduction. It is known that the electrical and thermal conductivities of MWNTs are about 10^6 S/m and 10^3 W/mK at room temperature.

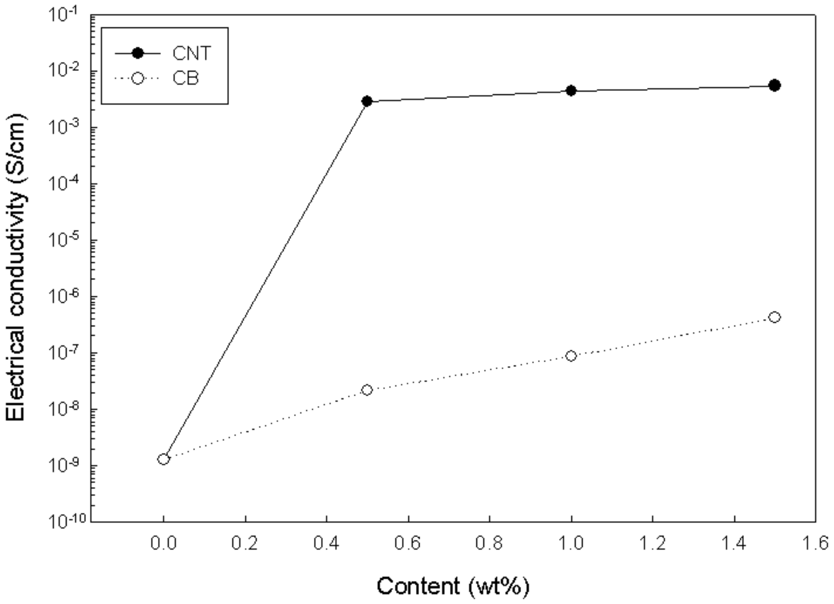

Fig. 6. Electrical conductivity of nanocomposites containing different CNMs, as a function of carbon content

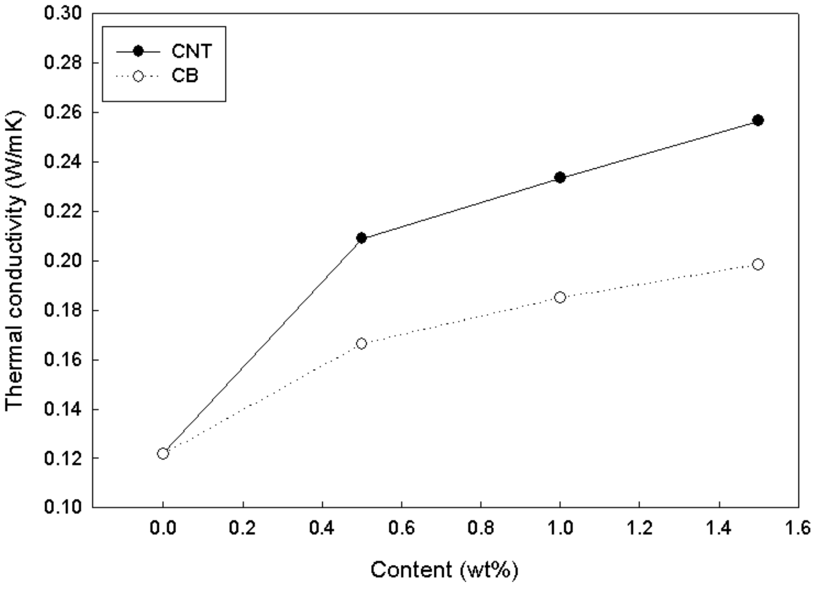

Fig. 7. Thermal conductivity of the nanocomposites vs. carbon loading

No percolation threshold of thermal conductivity is observed because the ratio of thermal conductivities of CNTs and polymer matrix is not higher than 10^4. The electrical conductivity of the CNTs is around 10^{15} times larger compared with the polymer resin.

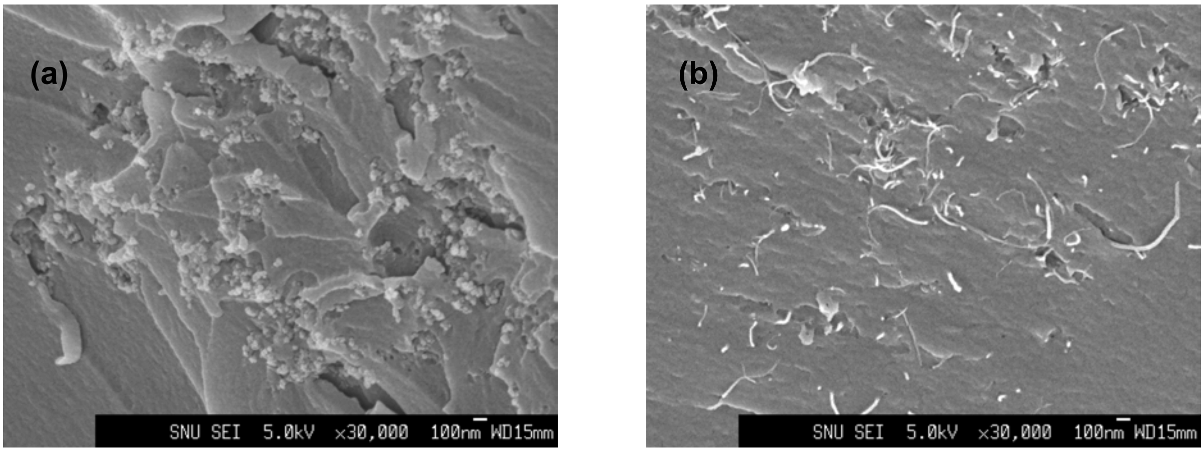

Fig. 8. FESEM images of the fracture surface for nanocomposites with 1.5 wt.-% (a) CNTs and (b) CBs

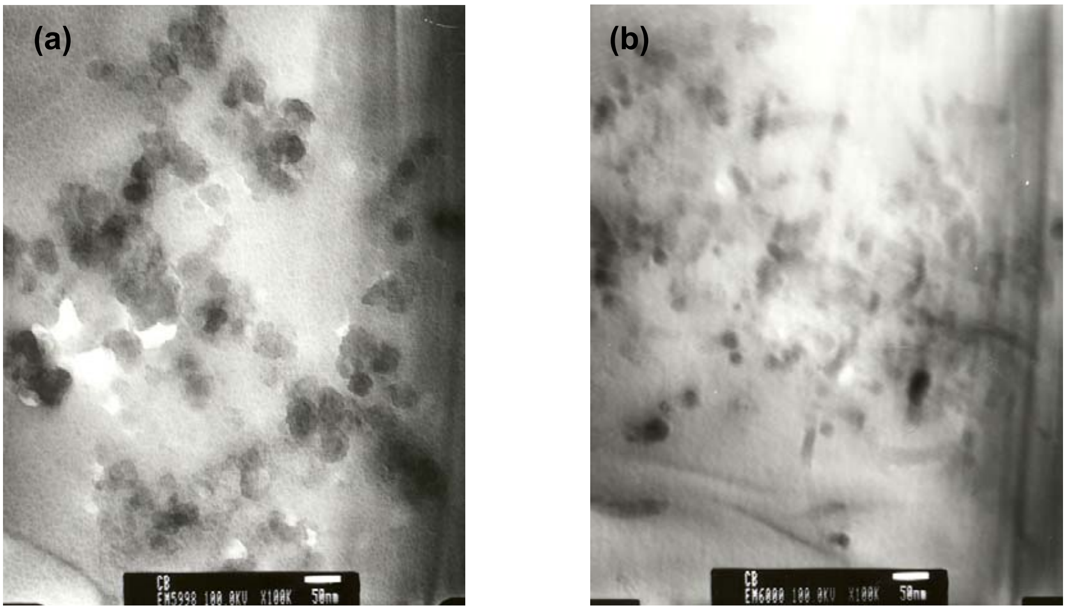

Fig. 9. TEM images of epoxy nanocomposites filled with 1.5 wt.-% (a) CNTs and (b) CBs

3.4 Morphology

After carrying out tensile experiments of CNMs/epoxy composites, FESEM images of the fracture surface of the tensile specimens are taken and exhibited in Fig. 8 (a) and (b). Fig. 8 (a) shows that CNTs are relatively well dispersed in the epoxy resin. The CNTs are not broken but pulled out due to the weak interfacial bonding between the CNTs and the polymer resin. In contrast, CBs exist in the form of agglomerates as shown in Fig. 8 (b). The agglomerates reduce reinforcing effects of the CBs because they are acting as flaws in the resin. This is why the CBs/epoxy composites have worse mechanical properties than the CNTs/epoxy composites.

TEM images of the CNMs embedded in the epoxy resin are shown in Fig. 9 (a) and (b). The CNTs in Fig. 9 (a) have the shape of slender cylinders and the carbon blacks are aggregated in the form of grapes as shown in Fig. 9 (b).

4. Concluding remarks

Rheological, mechanical, electrical, and thermal properties of CNT/epoxy and CB/epoxy composites were experimentally examined as the CNM loading was increased up to 1.5 wt.-%. Morphology of the nanocomposites was characterized by FESEM and TEM images. Differences in the various properties are attributed to the different geometrical structures of CNTs and CBs. Since the CNTs have a much higher aspect ratio than the CBs, a percolation network is formed more easily by the CNTs. The nanocomposites filled with the CNTs show non-Newtonian behaviour and have higher storage and loss moduli than the pure epoxy resin. But there are no significant differences between epoxy and the CBs/epoxy composites. Addition of CNMs increases tensile modulus and strength and lowers elongation at break lower. Especially, the CNTs/epoxy composites show more improved mechanical properties. The CNTs nanocomposites have poor interfacial bonding between the CNTs and the polymer matrix, which is identified in the FESEM images by the pull-out of CNTs. The electrical conductivity of the CNTs composites is increased by six orders of magnitude in the range below 1.5 wt.-%. A percolation threshold less than 0.5 wt.-% is obtained and the threshold is very low compared with conventional composites such as fibre-reinforced composites. The CNTs yield much higher electrical and thermal conductivity than the CBs in the nanocomposites because the CNTs can provide conducting paths in the polymer at even lower loading.

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