RELATIONSHIP BETWEEN DISPERSION AND UV-VISIBLE TRANSMITTANCE IN NANOCARBONS REINFORCED COMPOSITES

Sang-Bok Lee¹, Wonoh Lee¹, Jin-Woo Yi¹, Bo-Hwa Jeong², and Moon-Kwang Um¹*  
¹ Composite Materials Research Group, Korea Institute of Materials Science, Changwon, Korea  
² Nanocarbon Materials Research Group, Korea Electrotechnology Research Institute, Changwon, Korea  
* Corresponding author (umk1693@kims.re.kr)

Keywords: Nanocarbon, Dispersion, Transmittance, UV-Visible, Beer-Lambert, Composite

1 Introduction

Nanocarbons such as carbon nanotubes [1] and graphene [2] due to their excellent structural and functional properties have a lot of attention to improve the performances of nanocomposites. Despite the unique properties of the materials, the properties of the resulting nano-composites do not improve as much as expected due to the difficulties in achieving a uniform dispersion of the carbon nano-particles in highly viscous resin systems. Because the variation in the state of dispersion may play a critical factor of composite performance, substantial research efforts have been devote to ensure uniform dispersion of nanocarbons in the matrix resin through various processing methods [3,4]. Also, it is critical to characterize the state of dispersion as well as to achieve the homogeneous dispersion.

An approach to evaluate the dispersion state of the nanocarbons was developed through a modified Beer-Lambert law and the UV-visible transmittances. A transmittance of CNTs reinforced composites as functions of density of CNT, thickness of specimen, and state of dispersion by various dispersion methods was measured in the wavelength of 300 to 800 nm by UV-visible (UV-vis.) spectroscopy. The change in the transmittance as the dispersion state was confirmed by the simple geometrical simulation considering an screening effect of the distribution of the single nanocarbons and the clusters at the same number of CNTs.

2 Experimental Procedures

CNT (CM95 – Hanwha Nanotech, Korea) was used as the nano-sized carbon additive. An epoxy polymer matrix was utilized for all specimens (YD128 epoxy and KBH 1089 curing agent – Kukdo Chemicals, Korea). Epoxy resin and curing agent with weight ratio of 10:9 were mixed by mechanical stirrer, and then CNTs with weight fraction of 0.01, 0.05, 0.1, and 0.5 %, respectively, were added in the resin. In order to make specimens with various states of CNT dispersion, three different dispersion methods, such as homomixer, gap-mode of three-roll mill (EXAKT 80E, Germany), and force-mode of three-roll mill, were used. Also, the CNT/epoxy resin mixtures through various numbers of cycles (1, 3, 5, 7, 10, 15, 20, 25, and 30) in force-mode of three-roll mill were prepared. Figure 1 shows the schematic diagram of three-roll mill and its operation modes. Specimen for measuring transmittance was prepared by dropping resin mixture between two slide glasses. Metallic gages with thickness of 0.05 mm, 0.1 mm, and 0.15 mm were used to change the thickness of specimen. And then, the CNT/epoxy resin mixtures were cured at 120°C for 2 hrs. A transmittance of CNTs reinforced composites was measured in the wavelength of 300 to 800 nm by UV-vis. Spectroscopy (VARIAN CARY 5000, USA).

3 Modified Beer-Lambert Law

Beer-Lambert law is a fundamental method to analyze qualitatively and quantitatively organic and inorganic-species using data through spectrophotometry. Transmittance and absorbance are expressed as follows [5],
\[ A = \varepsilon \cdot t \cdot c = -\log(T) \quad \text{or} \quad T = e^{-\varepsilon \cdot c} \quad (1) \]

\[ A_n = \sum_{k=1}^{n} c_k \cdot t \cdot c_k \quad (2) \]

where \( T \) is transmittance of light through a substance; \( A \) is Absorbance of light through a substance; \( \varepsilon \) is the absorption coefficient; \( t \) is the thickness of specimen; \( c \) is the density of species; \( n \) is the number of species. There are some conditions that need to be fulfilled in order for Beer-Lambert law to be valid [5]. In particles dispersed composites, the important hypothesis is that the absorbing medium must be homogeneously distributed and/or dispersed in the reaction volume. Therefore, Beer-Lambert law cannot express the difference of the dispersion state of nano-particles.

Figure 1 shows the OM images and schematic diagrams as a state of dispersion by three different dispersion methods. In case of low degree of dispersion by only homomixer in Fig 3(a), several agglomerates are observed and the transmittance is highest of all. As increase in degree of dispersion in Fig. 3(b) and (c), agglomerates were got loose and the transmittance decreased. Based on the results, a new parameter, effective concentration factor (\( \beta \)) for evaluating the degree of dispersion suggested. In this study, because two species (CNT and epoxy resin) were just used, Beer-Lambert law could be modified with effective concentration factor,

\[ A = \varepsilon_e \cdot t \cdot c^*_e + \varepsilon_e \cdot t \cdot c^*_c \quad (3) \]

\[ c^* = \beta \cdot c \quad (4) \]

\[ A = (a + b \cdot \varepsilon_{c_{cnt}}) \cdot t \quad (5) \]

\[ \beta = \frac{A/t - a}{b \cdot c_{cnt}} \quad (6) \]

where \( c^*_e \) and \( c^*_c \) are effective concentrations of epoxy resin and CNT, respectively; \( a \) is cross of the absorption coefficient and the effective concentration of epoxy resin. On the assumption that the effective concentration of epoxy resin as a solvent is constant, \( a \) is also constant. \( b \) is also constant. The value of effective concentration factor (\( \beta \)) is assumed to be from zero to unit. If CNTs was perfectly dispersed, \( \beta \) is defined the value of one.

**4 Results and Discussion**

Figure 2 shows the measured transmittance spectra of 0.1 wt% CNT reinforced composites as a different state of dispersion as well as neat epoxy without CNTs. There are no characteristic absorption peaks of CNT and epoxy resin above the wavelength of 400 nm.

![Fig. 1. Schematic diagram of CNT dispersion states and optical micrographs of UV-vis specimens fabricated using (a) homomixer, (b) three-roll mill: gap mode, and (c) three-roll mill: force mode.](image1)

![Fig. 2. Transmittance spectra of 0.1 wt% CNT reinforced epoxy composites in the wavelength of 300-800nm as a different dispersion state.](image2)
Transmittance of neat epoxy is the highest value of all in whole wavelength range. Also transmittance decreases as an addition of CNTs and a change in state of dispersion.

Figure 3 shows experimental transmittance data of CNT reinforced epoxy composites for various CNT concentrations (0.01, 0.05, 0.1, and 0.5 wt%) at wavelength of 480 nm as a different state of dispersion. Transmittance decreases with increase of weight fraction of CNT, which is in agreement with Beer-Lambert law. For each of the CNT content, transmittance initially decreases abruptly and converges as a change in state of dispersion. The converged value of transmittance is a minimum at each of the CNT content, which also means that CNTs are almost dispersed perfectly in epoxy resin. As stated before, it is assumed that $\beta$ is the value of one in case of the state of maximum dispersion.

Based on the experimental transmittance data and modified Beer-Lambert law, the common constants of $a$ and $b$ and the values of effective concentration factor ($\beta$) at each of the CNT content and the state of dispersion could be calculated. The calculated values of $a$ and $b$ are 0.008 and 60.7, respectively. Also, calculated values of $\beta$ are summarized in Fig. 4. The value of $\beta$ increases with improvement of dispersion state and converges the unit. In case of dispersion using only homomixer, the value of $\beta$ is below 0.2 meaning low degree of dispersion due to a relatively weak shearing force of homomixing process. However, the value of $\beta$ increases steeply through only one cycle gap-mode dispersion of three-roll mill due to its strong shearing force. Also, the value of $\beta$ increases and converges with an increase of the number of cycles at gap-mode of three-roll mill. The representative images in various dispersion states of 0.5 wt% CNT embedded epoxy composites are shown in Fig. 5. In a case of composite using only homomixer, numbers of agglomerations of CNTs are observed. However, the agglomerations were reduced throughout the composites after one time three-roll milling process. As an increment in the number of cycles, CNTs were uniformly distributed in epoxy matrix. After 10 cycles of three-roll milling, agglomerations of CNTs were minimized and separated CNTs were observed throughout the composites. These SEM images verified the enhancement of dispersion state of CNTs by three-roll milling method.
The results indicate that three-roll mill process is one of the most effective methods in order to attain a homogeneous dispersion of carbon nano-particles. In addition, it is concluded that $\beta$ is an effective parameter for a quantitative evaluation of dispersion state.

5 Summary

A quantitative approach that evaluates the degree of dispersion for carbon nanotube (CNT) reinforced epoxy nano-composites was suggested by modification of Beer-Lambert law. Through UV-visible spectroscopy analysis, the transmittance of nano-composites was measured at various dispersion states and it was found that the high degree of CNT dispersion led to reduce the transmittance. Also, an effective concentration factor for quantitative evaluation of dispersion state was newly introduced into the Beer-Lambert transmittance law. From the results and the analysis by the modified Beer-Lambert law, it is confirmed that $\beta$ is an excellent parameter for a quantitative evaluation of dispersion state.

Acknowledgement

This work was supported by the Korea Institute of Materials Science (KIMS).

References