Development of a Model for Predicting the Polymerized Thickness of UV Curable Nanocomposites

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1. Introduction

Nanocomposites (NCs), which are physically or chemically fabricated composites of different materials (e.g., polymer matrix and nanofiller) in the nanoscale, have been applied to various engineering fields as an alternative to conventional single or composite materials[1]. Recently, ultraviolet (UV) curable NCs are emerging as a smart material because they polymerize faster than thermoset NCs and are able to form a fine pattern through photolithography for nano/micro systems. Despite extensive studies on UV curable NCs, little is known about how to model the polymerized thickness of UV curable NCs especially when non-spherical nanofillers which absorb a lot of UV (e.g., graphene, carbon nanotube etc.) are embedded therein.

Here, we develop the theoretical prediction model of UV polymerized thickness for UV curable NCs by modifying the Beer-Lambert law to include both inter-nanofiller distance (DINF) model [2] and nanofiller UV screening. The accuracy of the model is accessed by comparing its prediction with experimental data for graphite nanoflake (GnF)-embedded SU-8 composites having different GnF concentrations of 1 to 25 wt%. The findings of this study will lead to successful and growing development of UV curable NCs.

2. Theory

The process of deriving the polymerization thickness prediction model is divided into three steps (i.e., inter-nanofiller distance, the Beer-Lambert law, and UV screening). First, the DINF concept assumes that the nanofillers are randomly dispersed within the host matrix. Following the model, the nanocomposites can be divided into cubic elements, each containing one nanofiller in the center (Fig. 1). Considering the orientation averaging of the disk-shaped nanofiller, the axis projection length along the x-, y-, z-axes is given by the nanofiller diameter, such as $d_{NF}/3$. Therefore, we can suppose the disk-shaped nanofiller whose diameter is $d_{NF}/3$. It follows then that the length of cubic elements, L, can be expressed as

$$L = \frac{1}{3}(d_{NF} + D_{INF}) = (\pi d_{NF}{}^{2} t_{NF} / 4V_{NF})^{1/3}, \qquad (1)$$

where D_{INF}, t_{NF}, V_{NF} are the DINF, thickness, and volume fraction of the nanofiller, respectively.

Second, the Beer-Lambert law generally describes the transparency (i.e., energy ratio between incident and transparent light) of material exponentially decreases by the thickness of material with exponent of absorption coefficient. For the photolithography, the photoresist polymerizes when the exposed energy is more than a critical exposure energy, E_{cr}. This phenomenon can be simply expressed;

$$E_{cr} = E_0 e^{-\alpha T}, \qquad (2)$$

where E_0, α, and T are the exposure energy of incident light, absorption coefficient, and the polymerized thickness of photoresist, respectively. This expression will be changed to our prediction model including UV screening effect of nanofiller considering their distribution.

Finally, UV screening effect is obtained by projected area with respect to the normal plane of incident UV light direction. The projected area fraction between host matrix and nanofiller in one

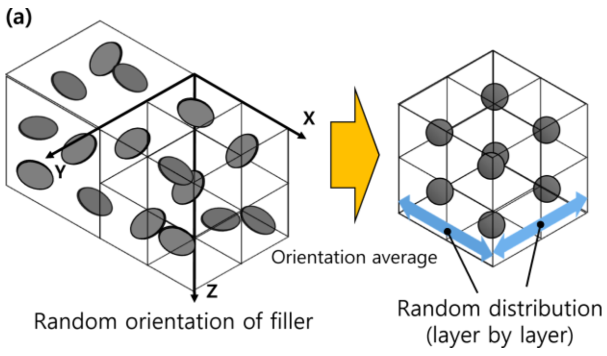

Fig. 1 Schematic draw of average DINF model

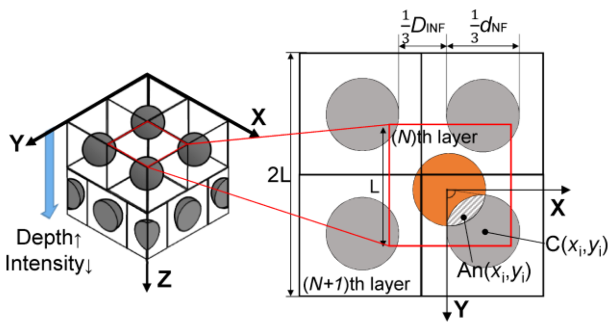

Fig. 2 Schematic draw of the polymerized thickness prediction model.

layer (Fig. 2) can be easily calculated. For the prediction model, it is not enough to reflect total screening effect. When area fraction of two arbitrary layer which are randomly located layer by layer, first of all, is calculated as, averagely, the square of one-layer area fraction. Therefore, total area fraction through first to *N*th layer can be expressed *N* power of one-layer area fraction as

$$f_{PM}\Big|_1^N = f_{PM}{}^N = f_{PM}{}^{\frac{T}{L}}, \qquad f_{NF}\Big|_1^N = 1 - f_{PM}{}^{\frac{T}{L}}. \tag{3}$$

Finally, the Beer-Lambert law is modified as

$$E_{cr} = E_0\{f_{PM}{}^{\frac{T}{L}} e^{-\alpha_{PM}T} + (1 - f_{PM}{}^{\frac{T}{L}}) e^{-\alpha_{NF}T}\}. \tag{4}$$

3. Materials and methods

The fabrication and measurement methods of GnF/SU-8 NCs is described on the previous work[3].

4. Results and discussion

The results of the polymerized thickness of the GnF/SU-8 NCs are shown in Fig. 3 as a function of GnF concentration. The black line is calculated by the prediction model and the red circles are shown the measured thickness. There are two singularities in the prediction model. The two singularities with the $D_{INF} = 0$ concentration and the $f_{PM} = 0$ concentration were analyzed as follows. The UV polymerized thickness predicted by the above model sharply decreases at a low concentration below the $D_{INF} = 0$ concentration at 11.4 wt%. In addition, since there is no real solution wt% at which $f_{PM} = 0$, UV polymerized thickness in the prediction model was to a single cubic element

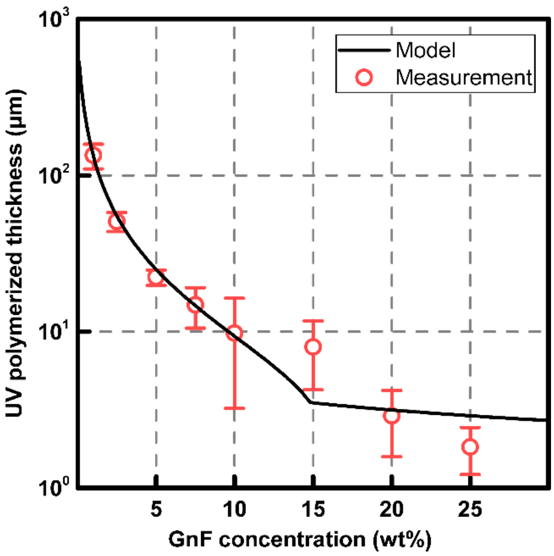

Fig. 3 Predicted UV polymerized thickness of GnF/SU-8 nanocomposites having different GnF concentration of 1.0 to 25.0 at 1,000 mJ/cm^2, compared with the measured one.

length at the previous concentration about 15.0 wt%. The above model has an accuracy of about 11 wt% or less. On the other hand, in order to develop a high-density nanocomposite material, it is difficult for the developer to penetrate into the composite material, so physical stimulation is required. When a physical stimulus is damaged, error is large. For example, when the concentration of GnF is 1 wt%, the predicted value of the model is 133.2 μm, and the measured value through the experiment is 134.2 μm, with a relative error of less than 1%. On the other hand, at 25 wt%, the predicted value is 2.90 μm and the experimental value is 1.83 μm and has a relative error of 37%. The above results show that it is necessary to study and improve the singularity of the model in order to improve the accuracy of the model at high concentration.

5. Conclusions

In this study, the theoretical polymerization thickness prediction model of ultraviolet curable nanocomposites was derived by using the probabilistic model and the Beer-Lambert law and reflecting the ultraviolet blocking effect of the nanofiller. In addition, the accuracy of the model was evaluated by fabricating a GnF / SU-8 composite with a mixture of a plate-type nano-filler GnF and a UV-curable polymer resin SU-8. In order to apply the non-spherical nanofiller to the model, it is necessary to study the additional probability model to replace the spherical nanofiller. If probabilistic models are studied, it is expected that ultraviolet polymerization thickness can be predicted by applying the above model to nanofillers with various shapes and sizes.

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