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# Effects of additives on the mechanical and thermal properties of epoxy-based nanocomposites produced using sonication

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**Abstract**−Epoxy nanocomposites were synthesized in the presence of hydroxyapatite with the aid of an ultrasonicator. In general, as the amount of hydroxyapatite increased from 0 wt% to 10 wt%, the mechanical properties of the hydroxyapatite-containing nanocomposite were enhanced. The mechanical properties of the nanocomposite were significantly enhanced by the simple addition of 10 wt% of hydroxyapatite. Specifically, the storage modulus of the 10 wt% hydroxyapatite-containing nanocompsote was 3.2 GPa, which is 46% higher compared to that of the pristine epoxy nanocomposite. The glass transition temperature of hydroxyapatite-containing nanocomposites generally decreased by few degrees in Celsius. To investigate the effect of additives on the mechanical properties of the epoxy-based nanocomposite, nanocomposites were synthesized using both montmorillonite and tellurium dioxide instead of hydroxyapatite. Intrestingly, both additive-based nanocomposite materials resulted in an increase in the storage modulus while the glass transition temperature decreased. These results demonstrate that the addition of few wt% of all three additives (hydroxyapatite, montmorillonite, and tellurium dioxide) can enhance the mechanical properties of epoxy-based nanocomposites.

Keywords: Epoxy, Hydroxyapatite, Montmorillonite, Tellurium Dioxide, Nanocomposite

## INTRODUCTION

Owing to their many outstanding properties, such as their superior mechanical and thermal performance, epoxy resins have been considred for use as a matrix for nanocomposite materials [1]. Various nanoscale fillers, such as clay [2], silica [3], carbon nanotube [4] and aluminum oxide [5], have been applied to improve the mechanical and thermal properties of epoxy-based nanocomposite. Depending on the application, filler materials with different morphologies such as layered structures and spherical particles have been widely applied for the synthesis of various nanocomposites.

To improve the mechanical properties of epoxy-based nanocomposites, layered structures that retain clay have been used as an additive in their synthesis. Hydroxyapatite (HAp) is a naturally occurring mineral form of calcium apatite [6], which has the formula $Ca_5(PO_4)_3(OH)$. The use of both particulate HAp and layered structure that retains HAp as an additive in nanocomposite synthesis has been investigated in detail [7,8]. However, the nanocomposites in the presence of HAp retaining layered structure are deficient in ductility and flaw tolerance property [9]. When montmorillonite, especially K-10, is used as an additive during nanocomposite preparation, it allows for an excellent enhancement in the resulting mechanical properties [10]. Because of the unique platelet-like structure of nanoclays, they have been extensively studied to enhance the mechanical properties of pristine polymers [11].

$TeO_2$ is one of the most attractive additives because its particulate form is on the nanometer scale. Nocke [12] applied $TeO_2$ to prepare polymer composites with a particular focus on its semiconductivity. However, as Pietsch [13] clearly addreassed, the inherent problem associated with nanocomposite synthesis is agglomeration. There are several proposals to overcome this agglomeration issue. In particular, the use of sonication technique is generally considered as a simple and effective solution. In addition, it has advantages such as short reaction time and low cost [14].

The objective of this study was to investigate the effect of using additives as a means of improving the mechanical and thermal properties of nanocomposites. The nanocomposites consisted of epoxy-based resin with various additives and were prepared using an ultrasonication technique. The storage modulus and the glass transition temperature (Tg) of the synthesized nanocomposites are presented for different additives, additive weight percents, and sonication times. Also the thermal properties of the epoxy-based nanocomposite with varying additives are discussed.

## EXPERIMENTAL

### 1. Materials and Methods

The matrix resin used in this study was diglycidyl ether of bisphenol A (DGEBA epoxy resin), and the curing agent was methylene dianiline (MDA-150). Both were provided by Kukdo Chemical Co., Ltd. (Seoul, Korea). HAp (Cat. No. 677418) from Sigma-Aldirch Korea Ltd. (Yongin-city, S. Korea) was chosen as the filler

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material to improve mechanical and thermal properties of the epoxy-based nanocomposite. To explore the effect of fillers on its mechanical and thermal properties, K-10 (Cat. No. 281522) and $TeO_2$ (Cat. No. 435902) were also purchased from Sigma-Aldirch Korea Ltd. All chemicals were used as received without further treatment to purify.

30 g of DGEBA epoxy, 5 g of MDA-150, and a certain weight percent of filler were mixed in a 100 ml beaker at 333 K and dispersed using an ultrasonicator (VCX-750, Sonics & Materials, Inc., Newtown, CT, USA). To investigate the effect of sonication time, the reaction time was varied from 0, 10, to 20 min, while the 5 s pulse on and 5 s pulse off mode was maintained throughout the course of the preparation of nanocomposite. To retain consistency, the weight percent of K-10 and $TeO_2$ was intended to be increased up to 10 wt%. However, the traditional issue of agglomeration, which occurs during the mixng process, prevented the weight percent of K-10 and $TeO_2$ from being increased higher than 5 wt% and 1.6 wt%, resepectively.

**2. Analysis**

Dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) were used to analyze the mechanical and thermal properties, respectively, of the nanocomposites. DMA (DMA 2980, TA Intruments, Inc., New Castle, DE) was used at the frequency of 1 Hz to determine the storage modulus and Tg. The dimensions of the sample were 35 mm (length)×15 mm (width)×3 mm (thickness). The heating rate was 2 °C/min in the temperature range from 25 °C to 160 °C. The thermal analysis involved using a TGA (N-1000, Sinco Co., Seoul, S. Korea). The temperature was programmed to increase from 25 °C to 900 °C with a heating rate of 10 °C/min.

## RESULTS AND DISCUSSION

To explore the effect of additives on the mechanical and thermal properties of the nanocomposite, pristine epoxy (run 1) was used as a reference material. When up to 10 wt% HAp was applied as an additive (runs 2-5), there was no difficulty in synthesizing the nanocomposite. However, when K-10 and $TeO_2$ were used as additives, their miscibility was a severe barrier that had to be overcome, which made it impossible to increase the amount of additives to 10 wt%. Instead, 5 wt% (run 6) and 1.6 wt% (run 7) were the highest weight percent achieved for K-10 and $TeO_2$, respectively.

The HAps have two different morphologies: spherical particles and layered structures. The HAp applied in this study consisted of spherical particles that were less than 200 nm in diameter, as shown in Table 1. Layered-structure HAp was not chosen because their addition resulted in inferior mechanical properties in previous studies [9]. To investigate the effect of additive on the epoxy-based nanocomposite, the particulate form of $TeO_2$, which was as small as 0.1 nm, was chosen as an additive in the nanocomposite synthesis process. Finally, because the general usage of K-10 has previously been reported in nanocomposite syntheses, K-10 has also been used as an additive.

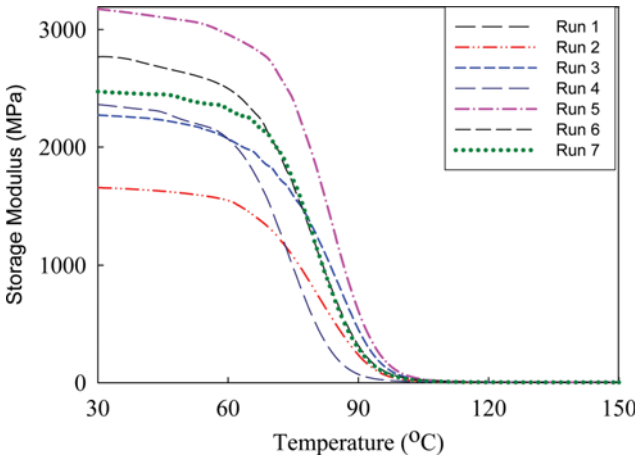


**Fig. 1. Storage moduli of the nanocomposites in the presence of different additives at various temperatures.**

**1. Mechanical Properties**

When 10 wt% of HAp was used as an additive with 20 min of sonication time (run 5), an increase in the storage modulus of almost 50% was achieved when compared with that for neat epoxy (run 1), as shown in Fig. 1. A similar result was observed when K-10 was used an additive with 20 min of sonication time (run 6). However, in the other cases, either a similar storage modulus (runs 3, 4, and 7) or lower value (run 2) was observed. A possible reason for the inferior storage modulus that was observed in run 2 could be that the addition of 5 wt% of HAp in the absence of ultrasonication prohibited the formation of a homogeneous nanocomposite. Depending on the experimental conditions, the presence of a different additive may trigger a similar, improved or unimproved storage modulus. This result indicates that the enhancement of the storage modulus strongly depends on the type of additive, the experimental condition, and the weight percentage of additive applied when producing the composites.

Fig. 2 shows the tan $\delta$ of the nanocomposites as a function of temperature. The $\alpha$-relaxation temperatures obtained from the DMA results allow for the derivation of the Tg of the pristine epoxy resin as well as that of the nanocomposite in the presence of the three different additives. As can be seen in Table 2, the Tg of pristine epoxy resin (run 1) and 5 wt% HAp-containing nanocompos-

**Table 1. Physical properties of the additives**

| | HAp | K-10 | $TeO_2$ |
|---|---|---|---|
| Specific surface area [$m^2$/g] | >9.4 [18] | 220-270 [19] | 10-50 [20] |
| Mean particle size [μm] | <0.2 [18] | 5-10 [19] | ~0.1 nm [20] |
| Basal spacing [nm] | N/A | 1.0 [11] | N/A |

HAp: hydroxyapatite, K-10: montmorillonite, N/A: not applicable

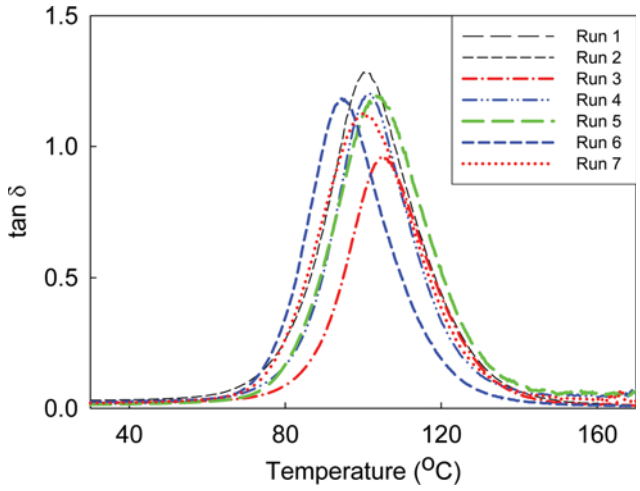


**Fig. 2. Tan $\delta$ of the nanocomposites in the presence of different additives at various temperatures.**

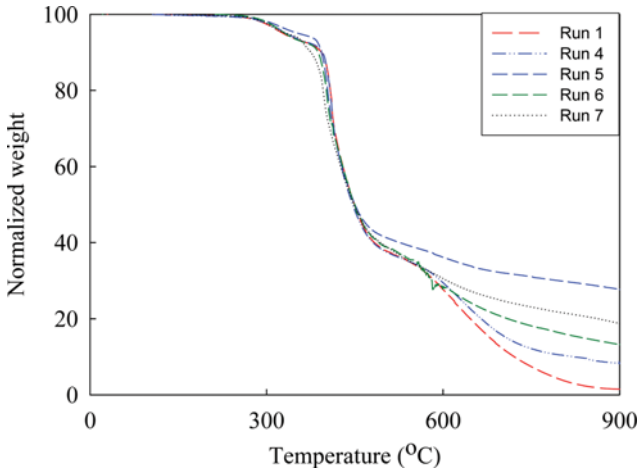


**Fig. 3. TG curves of the nanocomposites.**

ite (run 4) were 106.3 °C and 101.8 °C, respectively. When the weight percent of HAp increased to 10 wt% (run 5), the Tg of the nanocomposite was determined to be 103.9 °C. Furthermore, as long as any weight percent of any type of additive was applied in the synthesis process of the nanocomposite, all cases (runs 2-7) yielded lower Tgs compared to that of the pristine epoxy nanocomposite. This is an intriguing result because the addition of $Al_2O_3$ in the synthesis of epoxy resin results in an increase in the Tg even at 2 wt% [15]. This Tg increase can be explained by the addition of nano-$Al_2O_3$ particles to the epoxy resin, which resulted in a decrease in the amount of free space between macromolecules. As a result, there was a decrease in rotation of movement in the epoxy resins/nano-$Al_2O_3$ system [5]. In this study, Tg decrease was consistently observed, as Wither et al. [16] also reported. As Bozkurt et al. [17] explained, this Tg decrease may be related to the void content and the agglomerated structure of the unmodified silicate layers at higer clay concentrations.

**2. Thermal Properties**

The thermal stability and heat resistance of the pristine epoxy resin and epoxy nanocomposite were analyzed using TGA and are shown in Fig. 3. Table 2 shows the thermal degradation temperature that corresponds to 10, 50, and 70% weight loss and the amount of residual char formed at 900 °C. In general, in terms of the degradation temperatures of the three different weight losses, there was no significant difference between the pristine epoxy resin (run 1) and the additive-containing nanocomposites (runs 2-7). While there was no residual char (1.4%) over 900 °C for the pristine epoxy resin, the 5 wt% (run 4) and 10 wt% (run 5) HAp-containing epoxy nanocomposites exhibited higher residual values of 8.2 and 27.7%, respectively. When 5 wt% of K-10 was applied as an additive to synthesize the nanocomposite (run 6), 11.4% char was formed. In the case of $TeO_2$, 18.8% char was produced when using only 1.6 wt% $TeO_2$ (run 7). This result suggests that weight of char for the additive-containing nanocomposites was as high as a quarter of the starting nanocomposite.

## CONCLUSIONS

This study strongly suggests that the spherical-particulate morphology of HAp can be applied as an effective additive for synthesizing epoxy-based nanocomposites with higher storage moduli. The addition of HAp as an additive during epoxy-based nanocomposite synthesis resulted in a significant increase in the storage modulus in comparison with the pristine epoxy resin. Specifically, 5 wt% and 10 wt% HAp-containing nanocomposites achieved 8% and 46% increase, respectively, in the storage modulus. When K-10 and $TeO_2$ were applied as additives in the nanocomposites, only

**Table 2. Experimental conditions and results**

| No. | Additive | wt% | Sonication time (min) | Storage modulus (MPa) | Tg (°C) | Degradation temperature (°C) | | | Char yield at 900 °C (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 10% | 50% | 70% | |
| Run 1 | Epoxy neat | 0 | 20 | 2187 | 106.3 | 394 | 450 | 589 | 1.4 |
| Run 2 | HAp | 5 | 0 | 1654 | 100.1 | 296 | 443 | 548 | 3.2 |
| Run 3 | HAp | 5 | 10 | 2273 | 104.6 | 296 | 442 | 538 | 7.0 |
| Run 4 | HAp | 5 | 20 | 2362 | 101.8 | 397 | 447 | 599 | 8.2 |
| Run 5 | HAp | 10 | 20 | 3198 | 103.9 | 394 | 451 | 822 | 27.7 |
| Run 6 | K-10 | 5 | 20 | 2767 | 97.1 | 298 | 488 | 586 | 11.4 |
| Run 7 | $TeO_2$ | 1.6 | 20 | 2479 | 100.8 | 375 | 449 | 607 | 18.8 |

HAp: hydroxyapatite, K-10: montmorillonite

5 wt% and 1.6 wt%, respectively, were enough to obtain a similar storage modulus enhancement, compared to 10 wt% of HAp. In terms of char formation, applying any additive in the epoxy-based nanocomposites caused a significant increase in the total amount of char compared to the prisitn epoxy resin. The results illustrate that the addition of three different additives can be used to obtain superior mechanical and thermal properties in epoxy-based nanocomposites.

## ACKNOWLEDGEMENTS

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