# IMPROVED DYNAMIC MECHANICAL MECHANICAL PROPERTIES OF E-BEAM-CURED EPOXY COMPOSITE BY MWCNT ADDITIVES

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**Introduction**

Epoxy resin is indispensable due to its desirable properties, such as high strength and stiffness, as well as excellent dimensional, thermal, and environmental stabilities. The well-known disadvantage associated with the application of epoxy-based materials is their inherent brittleness [1-4]. In order to overcome this disadvantage of epoxy-based materials, nanometer-scale reinforcing particles, such as carbon nanotubes (CNTs), have been investigated with the goal of enhancing the mechanical properties of epoxy-based materials[5-6]. In this study, multi-walled carbon nanotubes (MWCNTs) were embedded into an epoxy after a fluorination treatment in order to investigate the effects of surface modification of MWCNTs on the mechanical properties of the treated epoxy.

**Experimental**

Fluorination of the surface of MWCNTs (Aldrich Co.) was carried out by a fluorination apparatus. Fluorination treatment was carried out at 30 $^{o}$C for 5 min at total pressures of 50, 100, and 150 kPa by using mixed gas (fluorine/argon = 1:1, v/v). Approximately 0.02 g of fluorinated MWCNTs was dispersed in 50 ml of ethanol by sonication. The epoxy monomer (20 g, YD128, Kukdo Chemical Co Ltd.) was added into the MWCNT-ethanol mixture and removed the ethanol. Approximately 1 g of the photo-initiator (Triarylsulfonium hexafluoro-phosphate, Aldrich Chemical Co.) was added to the prepared blend and then stirred. The mold was then placed under an e-beam accelerator (ELV-4, EB Tech Co., Korea) (energy: 2.5 MeV, current: 7.5 mA). E-beam irradiation was applied at a dose rate of 300 kGy/h in atmosphere for 10 min. The final products were named EC(P), EC(0.5F), EC(1.0F) and EC(1.5F), according to fluorination pressure.

**Results and Discussion**

The dispersion of the MWCNTs in the investigated epoxy resin blend is presented in Fig. 1, as measured by UV spectra. Under higher fluorination pressures, as used for the CNT(1.5F), further improved dispersion was observed. This result can be explained by the fact that hydrophobic groups functionalized by fluorination treatment resulted in an excellent interface match between the epoxy and fluorinated MWCNTs. Even though the dispersion of CNT(1.5F) is the best, the difference between it and CNT(1.0F) is negligible, showing almost similar dispersion properties. Thus, the CNT(1.0F) was used as a representative fluorinated MWCNT sample for further analysis.

Fig. 2 presents the storage modulus (E′) for the elastic characterization of samples measured at various frequencies. The storage modulus was observed to increase with high frequency in the rubbery region. It was observed that $T_{gs}$ also increases with increasing frequency. In particular, $T_{gs}$ significantly increased for frequencies that exceeded 25 Hz. Thus, from these data, it can be concluded that the stored energy in the epoxy/MWCNT composite is enhanced by higher frequencies. The loss modulus was measured for the viscous characterization of each sample to investigate the effects of loss modulus, which is proportional to the lost or dissipated energy. The measured loss modulus was applied to characterize the viscoelastic properties of samples using a combination of both elastic and viscous behaviors. The ratio of dissipated energy to stored energy is the tangent of the phase angle, δ, called the tan delta, which is given by [7]:

$$\tan(\delta)= E''(\omega) / E'(\omega) \qquad (1)$$

The calculated tan delta is presented in Fig. 3. The each peak height was observed to increase as a function of increasing frequency intensity, indicating that the loss modulus also increased. Thus, it can be concluded that the stored and dissipated energies increased together at higher frequencies. The $T_{gt}$ (transition temperature decided by first infection point of the tan delta curve) was also considered, wherein, by shifting the curve to the right, $T_{gt}$ was observed to increase from 81.8 to 103 $^{o}$C.

The relation between Tg and the applied frequencies with a heating rate of 2 $^{o}$C/min is shown in Fig. 4 to investigate the glass transition relaxation of the fabricated samples. Even though $T_g$ can be calculated using either the first inflection point of the storage modulus curve, the loss modulus, or tan delta, contemporary studies use tan delta [7]. Thus, the obtained $T_{gt}$ is used for estimation of activation energy in Fig. 4. The estimation of the activation energy of the glass transition relaxation is quite useful because it can be used to estimate the temperature shift factors for time-temperature superposition without the construction of complete master curves [7]. The activation energy of the glass transition relaxation is proportional to the slope of a plot of the natural log of frequency vs. the reciprocal of the absolute $T_{gt}$ (K). the calculated activation energies measured at various heating rates using EC(P) and EC(1.0F) were used to investigate the effects of heating rate and MWCNT fluorination. In both cases, the activation energy was observed to increase, indicating that mobility of the polymer chain became more sluggish with increasing heating rate. It is suggested that the external heat could not be efficiently delivered to the sample at high heating rates. When comparing the two samples, the EC(1.0F) sample showed a 13.5±6% higher activation energy than the EC(P) sample. This enhanced activation energy is attributed to the effects of the fluorination treatment of the MWCNTs, resulting in their better dispersion and adhesion in epoxy resin.

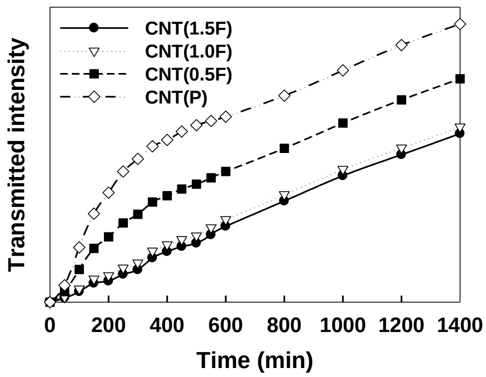


**Fig. 1** Effects of fluorination on MWCNTs based on their dispersion in epoxy resin blend.

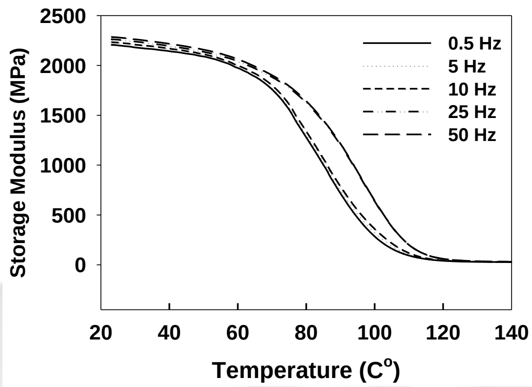


**Fig. 2** Storage modulus of EC(1.0F) at heating rate of 2 $^{o}$C/min and various frequencies.

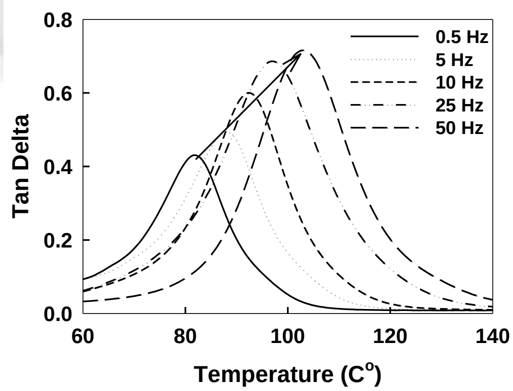


**Fig. 3** Tan delta of EC(1.0F) at a heating rate of 2 $^{o}$C/min and at various frequencies.

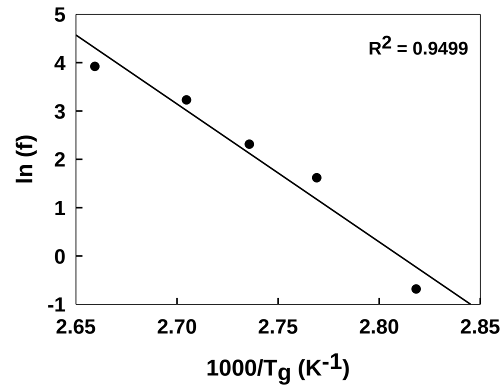


**Fig. 4** Relation between f and $T_{gt}$; f: test frequency, and $T_{gt}$ was measured by tan delta.

## Conclusions

A composite of epoxy/MWCNTs was prepared by an e-beam curing process. The dispersion and adhesion of MWCNTs were observed to be improved by the presence of semi-ionic C-F bonds due to a fluorination treatment. The stored and lost energies increased with increasing applied frequency, as measured by the storage modulus and the tangent of delta. The activation energy was increased by a higher heating rate due to the slow heat transfer in epoxy/MWCNTs composites. In conclusion, it was found that the dynamic mechanical properties of epoxy resin were significantly improved by fluorinated MWCNTs.

## References

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