

High performance epoxy nanocomposites with amine-functionalized graphenes

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요약(영문)

Graphene, consisting of a single layer of carbon in a two-dimensional lattice, has been emerging as a fascinating material with many unique physical, chemical and mechanical properties. In this study, graphenes were prepared by a chemical method. To develop high performance polymer nanocomposites reinforced by graphenes, adequate dispersion of the fillers and strong interfacial bonding between the fillers and the polymer matrix are essential. The purpose of this study was to examine the influence of introducing amine groups on the surfaces of graphenes. FT-IR spectroscopy, SEM were used to confirm the functionalization. Epoxy nanocomposites comprising the graphenes were prepared and their characteristics were investigated by DSC, DMA and TMA. Fracture surfaces of the nanocomposites were investigated by SEM. The functionalized graphenes induced strong interfacial bonding than the pristine graphenes and resulted in considerable improvements in the performance of the nanocomposites.

1. Introduction

A single carbon layer of the graphitic structure can be considered as the final member of the series naphthalene, anthracene, coronene, etc. and the term graphene should therefore be used to designate the individual carbon layers in graphite intercalation compounds.¹ Because it has superior electric and thermal conductivity, stiffness, and high aspect ratio, it can improve those properties of matrix polymers when it is well dispersed. Graphenes exhibit extremely high stiffness and strength, a specific surface area of up to 1800m²/g, and an aspect ratio in the range of several thousands.²⁻³

The incorporation of graphenes into epoxy resin bulk material will surely enhance the thermal and mechanical properties of epoxy resins.⁴ An enhancement of the compatibility between

graphenes and epoxy resins can be achieved by functionalization of graphenes, and the functionalization can also make the graphenes directly bonded to the epoxy matrix through chemical reaction of the functional groups with epoxy groups.⁵ The linkage between the graphenes and the epoxy matrix would lead to strong interfacial bonding. The epoxy nanocomposites comprising graphenes require; (1) good dispersion of fillers in the polymer matrix, (2) a strong interfacial bonding between the polymer matrix and fillers.⁶⁻⁷

So, in this study, mono layered graphenes were prepared, and their surfaces were functionalized by amine groups. The curing behavior and physical properties of pure epoxy and various epoxy nanocomposites comprising 1 phr of carbon nanofillers were investigated to examine the effect of the functionalization.

2. Experimental

Materials. Natural graphite powders (average particle size = 30 μm), sulfuric acid and potassium permanganate were purchased from Sigma-Aldrich Inc., Germany and used as received.

The amine-functionalization was carried out by treating pristine graphites and graphenes with 4-aminobenzoic acid in polyphosphoric acid. To remove residual water after reaction, (Di)phosphorus pentoxide were used. A diglycidyl ether of bisphenol-A (DGEBA) type epoxy resin (YD 128 from Kuk Do Chem., Korea) and an aromatic amine curing agent, 4,4'-methylene dianiline(MDA-150 from Kuk Do Chem., Korea), were used to formulate a basic epoxy resin system. The epoxy equivalent weight of the epoxy resin was about 185 g/mol and the viscosity of the resin was about 12000 cP at 25 $^{\circ}\text{C}$.

Synthesis of graphenes. 1 g of graphite powder was put into 23 ml concentrated H_2SO_4 (in an ice bath). Then 3g of KMnO_4 was gradually added. The mixture was stirred for 1 h and then diluted with 140 ml distilled water at 80 $^{\circ}\text{C}$. After that, 5% H_2O_2 was added into the solution until the colour of the mixture changed to brilliant yellow(10ml), indicating fully oxidised graphite. The as-obtained graphite oxide slurry were washed with dilute HCl solution, acetone and distilled water each several times, and re-dispersed in distilled water and then exfoliated to generate graphene oxide nanosheets by ultrasonication. Then, the mixture was filtered and washed with acetone and distilled water each several times, and then dried using a vacuum oven for 1 day.

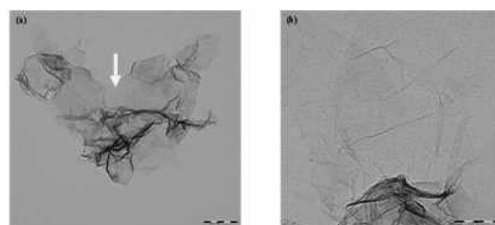
Functionalization of carbon nanofillers. To functionalize the carbon nanofillers by one step,^{17,18} 2.5 g of the graphites or graphenes was treated for 2 h at 130 $^{\circ}\text{C}$ in a solution composed of 4-aminobenzoic acid(1.25g), polyphosphoric acid(84% P_2O_5 assay, 100g), and P_2O_5 (12.5g) in a 500ml flask equipped with a mechanical stirrer.

The resulting functionalized graphites and graphenes were washed with acetone and distilled water each several times, and then dried using a vacuum freeze dryer for 1 day.

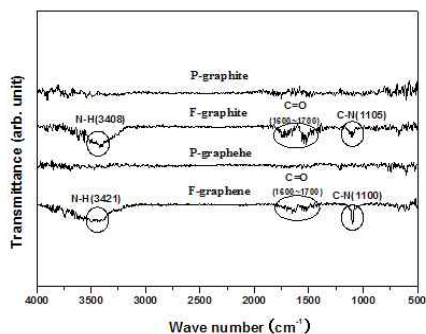
Preparation of epoxy/carbon nanofiller nanocomposites. The pristine or amine-functionalized graphites and graphenes, except for the curing agent to prevent premature curing reaction, were mixed with epoxy resin to achieve epoxy/carbon nanofiller nanocomposites having 1 phr (parts per hundred resins) loading of carbon nanofillers. After dispersion by sonication at room temperature for 1 h, the binary mixture of the epoxy resin and the carbon nanofillers was mixed again with the curing agent by stoichiometry, and sonicated further for 3 min. The mixture were vacuumed to remove the air bubble, followed by curing in an oven at 180 $^{\circ}\text{C}$ for 1 h, and then postcured at 200 $^{\circ}\text{C}$ for 30 min. For comparison purposes, a pure epoxy sample, an epoxy with pristine graphites, an epoxy with amine-functionalized graphites, an epoxy with pristine graphenes, and an epoxy with amine-functionalized graphenes were also prepared.

3. Results and discussion

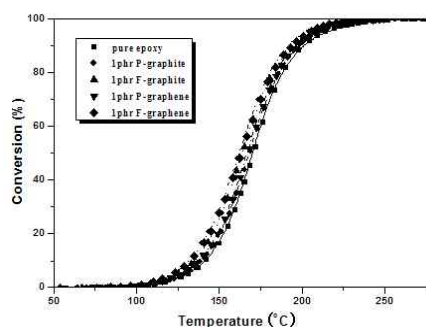
The obtained graphene nanosheets were fully analyzed by TEM observations. [Fig. 1] shows a low magnification TEM image of graphene nanosheets. Large graphene nanosheets (a few hundred square nanometers) were observed to be situated on the top of the copper grid, where they resemble crumpled silk veil waves. Graphene nanosheets were rippled and entangled with each other.



[Fig. 1] TEM images of graphene nanosheets



[Fig. 2] FTIR spectra of pristine and functionalized carbon nanofillers.



[Fig. 3] Comparison between kinetic model (curves) and experimental data (symbols) of each system.

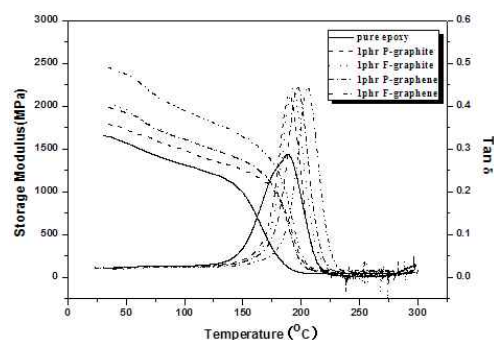
[Fig. 2] shows the FTIR spectra of pristine and functionalized carbon nanofillers. If the functionalization process was successful, the F-graphites and F-graphenes would have amine functional groups on the surface of the graphites, graphenes. As circled in the figure, the absorption peak for the N-H stretching vibrations of amine groups appeared at 3408 cm^{-1} and 3421 cm^{-1} . The other absorption peaks observed at $1600 \sim 1700\text{ cm}^{-1}$ correspond to the stretching vibrations of carboxylic C=O groups of ester linkages, which were formed by chemical reaction between the carboxylic groups of the functional molecules (4-amino benzoic acid) and the oxidized surface of the carbon nanofillers. Moreover, the peaks at 1105 and 1100 cm^{-1} indicated C-N group. From the FTIR analysis, it was considered that the functionalization of the carbon nanofillers was performed successfully.

[Fig. 3] shows that the conversion data obtained from the dynamic DSC thermograms agree well with the conversion curves calculated from the reaction kinetic equation for both pure

epoxy system and epoxy/carbon nanofiller nanocomposite systems. The curing rate of the epoxy/P-graphite nanocomposite system was almost the same as pure epoxy system. But, the curing rate of the epoxy/F-graphene nanocomposite system was considerably faster compared to the other four systems.

[Fig. 4] shows the storage modulus and $\tan \delta$ (E'/E'') of the epoxy/carbon nanofiller nanocomposites and pure epoxy system. The storage moduli of the epoxy/carbon nanofiller nanocomposite systems were higher than that of the pure epoxy and 1 phr P-graphite nanocomposite. One of them, the 1 phr F-graphene nanocomposite, had very large storage modulus. This behavior can be explained in terms of improved interfacial interactions between epoxy and F-graphenes owing to amine-functionalization of graphenes. The glass transition temperature (T_g) corresponds to the temperature of maximum $\tan \delta$. The shifting in T_g showed slightly higher values in the case of the nanocomposite systems. 1 phr F-graphene nanocomposite showed the highest T_g among the samples tested.

The dimension changes of the various nanocomposite systems are listed in [Table 1]. As shown in the table, the dimensional stability of 1 phr F-graphene nanocomposite was higher than those of the other nanocomposite systems because good interaction of well dispersed F-graphene with polymer resin can improve the interfacial adhesion considerably.



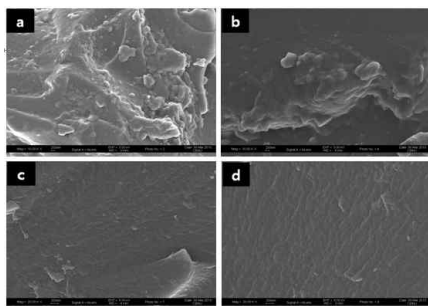
[Fig. 4] DMA thermograms showing storage modulus and $\tan \delta$ of the various nanocomposite systems. (scanning rate: $5\text{ }^{\circ}\text{C}/\text{min}$)

[Table. 1] The dimension changes of the various nanocomposite systems.

	ΔL_{α} [%]
epoxy	1.64
1phr P-graphite	1.52
1phr F-graphite	1.48
1phr P-graphene	1.46
1phr F-graphene	1.34

*Dimension change between 50 ℃ and 250 ℃

To appreciate the influence of the carbon nanofiller on the nanocomposite, the impact fractured nanocomposite samples were scanned after Pt coating and were represented in [Fig. 5] to confirm interfacial adhesion between epoxy and carbon nanofillers. The non-uniform dispersion of 1 phr P-graphite in epoxy resin was evident in [Fig 5(a)]. The P-graphite is dispersed poorly and agglomerated in the epoxy resin. For nanocomposites with poor adhesion between nanofillers and resin, the holes corresponded to where the nanofillers had been pulled out of the resin, and gaps around the base of most nanofillers were observed in the fracture surface. P-graphene and F-graphene are dispersed well in epoxy matrix because of exfoliated structure [Fig. 5(a), (d)]. Also, [Fig. 5(b), (d)] show that carbon nanofillers are torn instead of being pulled out during impact test because of better interfacial bonding between the amine-functionalized carbon nanofillers and the epoxy resin. These indicate that the amine groups formed by the functionalization induces good dispersion and strong interfacial bonding.



[Fig. 5] SEM images of (a) 1 phr P-graphite nanocomposite ; (b) 1phr F-graphite nanocomposite ; (c) 1phr P-graphene nanocomposite ; (d) 1 phr F-graphene nanocomposite.

4. Conclusions

Amine-functionalization of the carbon nanofillers (graphite, graphene) was prepared successfully via treating pristine carbon nanofillers with 4-aminobenzoic acid in polyphosphoric acid. Using the functionalized carbon nanofiller, epoxy/carbon nanofiller nanocomposites were prepared, and their curing behavior and physical properties were investigated. The curing rate increased considerably when the 1 phr F-graphenes were incorporated into the epoxy system. Compared to the Tg of pure epoxy system the Tg of the 1 phr F-graphene nanocomposite was considerably higher. The 1 phr F-graphene nanocomposites showed superior mechanical properties compared to the different nanocomposites and pure epoxy system. SEM images for the nanocomposites showed that the epoxy/F-graphene nanocomposites had stronger interfacial bonding compared to the other nanocomposites.

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