Mechanical properties of TiO$_2$/epoxy resin nanocomposites

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Abstract : The purpose of this study is to improve the properties of epoxy resin using the big-sized titanium oxide nanoparticles. The effects of particle weight fraction and shape of sample on the thermal and mechanical properties in titanium oxide reinforced epoxy resin has been investigated. In addition, the effect of particle dispersion situation on the mechanical properties of nanocomposites has been studied.

As a result, the Tg was almost same regardless of the content of nanoparticles. Storage modulus increased up to the content of 3wt% particles and then decreased. Tensile strength and modulus of film-shaped sample with 1wt% was higher than the one of pure epoxy, while other composites were not. The tensile strength of dogbone-shaped sample with 1wt% was only higher than the one of pure epoxy, while other composites were lower than the one of pure epoxy. Tensile modulus of dogbone-shaped samples increased with the content of particles.

Key Words : Nanocomposites, cluster, dispersion agent, tensile strength, particle weight fraction, curing agent, glass transition temperature (T$_g$)

1. Introduction

Polymers are important matrix for advanced materials. They could be made many valuable composites through adding some reinforcing elements such as continuous or short fibers, whiskers, inorganic particles and platelets.[1] In recent years, various nanoparticles have been used for filler in polymer matrix. Because of their small size, nanoparticles have a high surface-to-volume ratio and provide high-energy surface.[2] Nanocomposites show much better the mechanical, chemical, thermal, electrical even optical properties than the micro-sized composites.

Classical composite theory predicts that good bonding between the polymer matrix and the reinforcing filler leads to improved mechanical properties. For all the particle sizes, the composite modulus increases monotonically with the particle weight fraction.

However, the strength of nanocomposites with high filled weight fraction could be below the strength of neat resin due to the large particle clusters like aggregation or agglomeration [3]. And the mechanical properties of the nanocomposites are not a simple average of the properties of the polymer and particles. Inorganic nanoparticles have been successfully used as additives or reinforcements to increase the strength and hardness of the polymer in nanocomposites.[4,5]

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Although nanocomposites have many advantages in various fields, they could have completely opposite properties as their degree of dispersion or the interaction between particles and matrix. That is, the glass transition temperature (T_g) of nanocomposites could be higher [6,7] or lower[8-11] than those of the pure polymer, and mechanical properties could be higher or lower than those of the pure polymer[12]. Some author reported that the T_g was depended largely on the interaction between particles and matrix.[7] The properties of nanocomposites can be affected such as particles, its size, matrix resin and interface between particles and resin. Therefore it is very important that which kinds of materials are chosen for making nanocomposites.

Nanoparticles can significantly alter the properties of the polymer close to the particle surface due to the change in polymer chain mobility. It can enhance or restrict the chain mobility near the particle surface.[13,14]

One major problem of nanocomposites is how to be uniformed the particles dispersion in the organic matrix without macroscopic phase separation. The non-uniformed dispersions of nanoparticles in matrix could be defects and reduce to the great mechanical properties of nanoparticles in the composites. Therefore, Better dispersion of nanoparticles against their clusters like aggregation and agglomeration is the most important point in the processing of nanocomposites.

Some authors reported that the high improvement of the mechanical properties can be achieved at very low particles content such as 1–5wt%.[15] In particular, several authors proved that ceramic and silica nanoparticles could be effectively reinforced bulk polymers.[15,16]

Many researchers found out that a*s* the fraction of nanoparticles increases above a specific fraction

level, the properties can be declined very sharply.[17-20] Therefore, it is necessary to add the particles up to the specific fraction level. Specific fraction could be different according to the composites system such as particles and its sizes, particle dispersions, matrix resins, interface between particle and matrix resin and making processes.

In the previous study[21], it was investigated to the curing behavior and mechanical properties of nanocomposites added titanium oxide nanoparticles with 20 nm in epoxy resin.

Epoxy resin is a widely used polymer matrix for advanced composites with its good stiffness, dimensional stability and chemical resistance. Also, it is widely used in the industry due to the easy production, light weight, high adhesive property and so on.

The purpose of this study is to improve the properties of epoxy resin using the big-sized nanoparticles. The effects of particle weight fraction and shape of sample on the thermal and mechanical properties in titanium oxide reinforced epoxy resin has been investigated. In addition, the effect of particle dispersion situation on the mechanical properties of nanocomposites has been studied.

2. Experimental

2.1 Materials and sample preparation

The materials used in this study were as follows; the titanium dioxide (TiO₂) nanoparticles used were Rcl9 (Milliennium Co.), which was in approximately 250 nm according to the manufacturer. There was Al₂O₃ and SiO₂ surface treatment for particle Rcl9. The epoxy resin used was the diglycidyl ether of bisphenol A (DGEBA, Epon 828, Hexion co.). Curing agent used was polyoxypropylene diamine (Jeffamine D230), which

was obtained from Huntsman Corporation, TX, U S A.

The film-and dogbone-shaped samples for experimental tests of nanoparticles unfilled and filled composites were prepared as following procedures; First of all, two silicone molds with eight dogbone-shaped cavities and two Teflon plates (100x150x10mm) were placed to preheat in oven at 67°C. The liquid epoxy resin was heated for about 1hr at 67°C to lower the viscosity of resin, and degassed for 30 minutes in vacuum oven at 67°C. Nanoparticles measured by using balance (Metter co., 0.01mg) were added to 1 wt%, 3 wt% and 5 wt%, respectively, and then mixed for 30 minutes using a dispermat (BYK-Gardner) at 2000rpm. After the mixture was degassed for 1.5 hrs in a vacuum oven at 67 ^{o}C, the curing agent was added and mixed by hand for 3.0 minutes using wood stick.

And the mixture was separated into two plastics beakers of 100cc. One beaker was used for dogbone- shaped mold and the other one was used for film forming. The liquid mixture in beakers was again degassed for 20 minutes in a vacuum oven at 67°C. After that, the liquid mixture of one beaker was applied to cast into preheated dogbone-shaped silicone mold on the preheated Teflon plate. The other mixture was waited until becoming proper viscosity to form film in oven at 67°C. The waited time, in the case of unfilled one, was 30 minutes for D230 in oven at 67°C from after mixing the curing agent. In the case of filled particles, it needs to take a little longer time compared to the unfilled.

The waited times were a little different according to weight fraction of the filled nanoparticles and the amount of mixture. And then the films were formed on the release paper on the vacuum plate using the drawdown technique. The formed films were cured at room temperature overnight, and then post-cured at 80°C for 2hrs and 125°C for 3hrs for a full cure in forced air circulating oven (Blue M, General Signal co.). It was allowed the samples to become cool to the room temperature in the oven before removal. The thickness of the formed film and dogbone-shaped samples were approximately 90 μm and 2.0 mm, respectively.

2.2 Dynamic Mechanical Thermal Analysis (DMTA)

The storage modulus (E'), loss modulus (E'') and glass transition temperature (T$_g$) of the film-shaped samples were measured using a dynamic mechanical analyzer (TA Instrument, RSA III). The rectangular specimens (30 mm x 4 mm) were cut out from films using a clean razor blade. The gauge length of specimens was 15 mm. The specimens were tested from -130°C to 130°C using a strain 0.01, frequency of 1 Hz and temperature ramp of 3°C min^{-1}. The T$_g$ was determined from the peak position in tan δ (defined as E''/ E'). Storage modulus at -50 ^{o}C is reported. The reported values for the T$_g$ and E' were the average from the four specimens.

2.3 Tensile test

Tensile tests of film-shaped samples were performed using a dynamic mechanical analyzer in tensile test mode (TA Instrument, RSA III) in accordance with the ASTM D638-08 test standard. Specimens were 63.5 mm long, 9.53 mm wide all over and 3.18 mm wide of narrow section. Strain was measured using grip separation. The apparent Young's modulus was determined from the slope of the linear portion of the engineering stress vs. engineering strain curve. All specimens used tensile test were conducted at a constant cross head speed of 1.0 mm/min with gauge length of 15 mm. The modulus and tensile strength are the

average from 7 specimens.

Before the testing, the upper side of dogbone-shaped samples for tensile test was polished to make flat surface. And the edges of the sample were polished by sand paper with the mesh of #1200. Tensile test of dogbone-shaped samples carried out on tensile tester (Instron co.) with a load cell of 1KN. The cross head speed was 1.0 mm/min with gauge length of about 15 mm. Strain was measured using video strain measure meter. Specimens were 60.92 mm long, 10.65 mm width all over and 4.0 mm wide of narrow section. The reported modulus and tensile strength are the average from 10 specimens.

2.4 Microscope observation

Optical microscope was used to observe nanoparticles dispersion situation in the film- and dogbone-shaped samples. The cover glass and oil with refraction index of approximately 1.50 were used to improve image clarify. Refraction index of the oil was almost the same as that of the matrix resin used in this study. The oil should be flowed to fill all contact area between film and the cover glass. Rotary microtome (RCM. co., AFM 990) was used to make cross section specimens of the dogbone-shaped sample for observing the nanoparticles dispersion. The thickness of cut sample was about 20μm.

3. Results and discussion

3.1 Dynamic Mechanical Thermal Analysis (DMTA)

Fig. 1 shows the relationships between the Tan δ and temperature of the film-shaped pure epoxy and nanocomposites samples respectively. Nanocom-posites were filled with 1wt%, 3wt% and 5wt% particles.
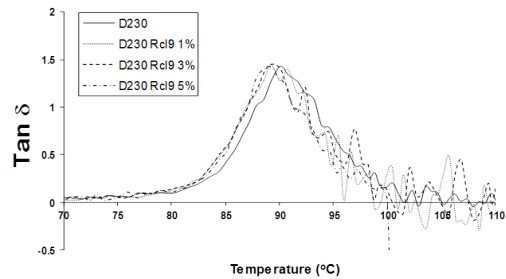

Fig. 1 Tan δ and Temperature of the film-shaped samples

In this study, the peak temperature of the Tan δ is applied to define the glass transition temperature (T_g) and the values were given in Table 1. As shown in Table 1, the T_g were almost same regardless of the content of nanoparticles, but the T_g decreased very slightly with the content of nanoparticles.

Table 1 the T_g of the film-shaped samples

Materials	Tg(℃)
D230	90.54
D230-1wt% TiO₂	89.83
D230-3wt% TiO₂	89.41
D230-5wt% TiO₂	89.28

In previous study[21], nanoparticles have unusual specific surface area and it can restrict the chains mobility of the liquid epoxy resin near the particles, these chains lose some of their mobility. Therefore, nanoparticles interrupted the cross linkage between epoxy resin and curing agent, cross-link density of epoxy became lower and led to decrease the T_g in the nanocomposites. Consequently, the T_g of the titanium oxide/epoxy resin nanocomposites decreased remarkably with the content of nanoparticles. But in this study, the T_g decreased very slightly with the content of nanoparticles. This difference is probably due to the size effect of particles. That is, the particle

used in previous study was 20 nm, while the one used in this study was 250 nm. It is considered that the smaller particles obstructed more seriously the cross linkage in epoxy resin.

Fig. 2 represents the storage modulus of film-shaped pure epoxy and nanocomposites at -50 C° in glassy region. Nanocomposites were filled with 1wt%, 3wt% and 5wt% particles. In this figure, the storage modulus in the glassy region increased up to the content of 3wt% particles and then decreased.
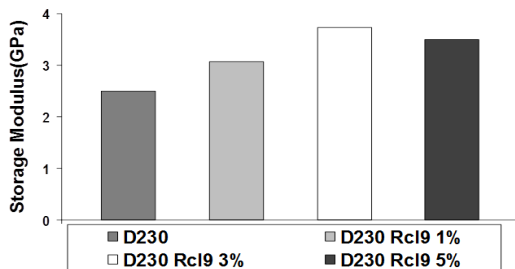

Fig. 2 Storage Modulus of the film-shaped samples

3.2 Tensile strength

In the tensile test, film-shaped and dogbone-shaped samples were used, and the results of tensile test in film-shaped samples were shown in Fig. 3-6.
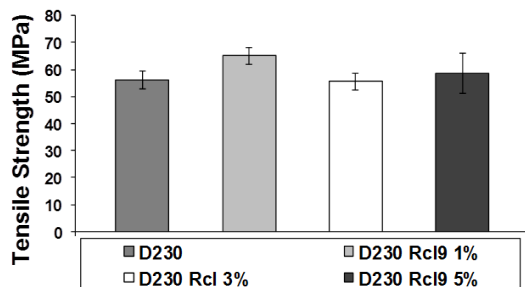

Fig. 3 Tensile strength of the film-shaped samples according to the content of particles

Fig. 3 represents the tensile strength of the

film-shaped pure epoxy and nanocomposites which were filled with 1wt%, 3wt% and 5wt% particles. As seen in this figure, tensile strength of nanocomposites with 1wt% was higher than the one of pure epoxy, while other composites were almost same values.

Fig. 4 reveals the tensile modulus of the film-shaped pure epoxy and nanocomposites which were filled with 1wt%, 3wt% and 5wt% particles. In this figure, tensile modulus of nanocomposites with 1wt% was higher than the one of pure epoxy, while other composites were lower than the one of pure epoxy. This is consistent with the trend of tensile strength as seen in Fig 3. As above mentioned, some researchers found out that as the fraction of particles increases above a specific level in nanocomposites and then the properties can be declined very sharply.[17-20]
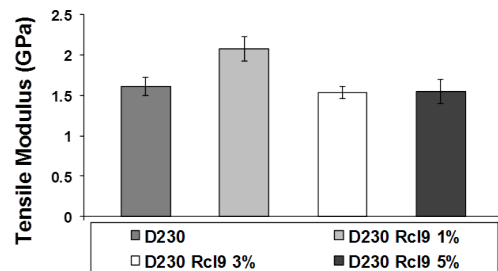

Fig. 4 Tensile modulus of film-shaped samples according to the content of particles

This is probably that better dispersion of nanoparticles in nanocomposites could make improvement on the tensile properties. As can be seen in Fig. 7(a), Fig. 8(a) and 8(b), the dispersion status of 1wt% added composites was better than the ones of 3wt% and 5wt% composites which had large particles clusters.

Fig. 5 shows the tensile strength of the dogbone-shaped pure epoxy and nanocomposites which were filled with 1wt%, 3wt% and 5wt%

particles. In this figure, the tensile strength of nanocomposites with 1wt% was only higher than the one of pure epoxy, while other composites were lower than the one of pure epoxy. This is almost the same trend as the tensile strengths in the film-shaped sample. This meant that the dispersion degree of particles in nanocomposites could influence on the tensile properties, and the specific contents of particles to have the best tensile strength could exist. And it is considered that specific weight fraction for the tensile strength was 1wt% in this composite system.

Fig. 6 presents the tensile modulus of the dogbone-shaped pure epoxy and nanocomposites which were filled with 1wt%, 3wt% and 5wt% particles. As shown in this figure, tensile modulus increased monotonically with the content of particles. It is considered that the modulus of dogbone-shaped sample with big sized particles could be followed with the classical composite theory.
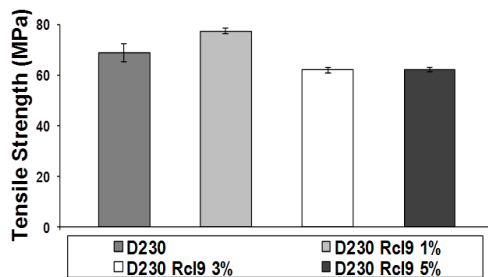

Fig. 5 Tensile strength of the dogbone-shaped samples according to the content of particles

From Fig. 3-6, tensile strengths and modulus of all dogbone-shaped nanocomposites were much higher than the ones of the film-shaped nanocomposites even though the same contents of particles.

This is presumably due to the different thickness dimensions between the film-and dogbone-shaped sample, as described in the

experimental section, each thickness of film- and dogbone-shaped samples was approximately 90 μm and 2.0 mm, respectively. It was found, in case of the presence of large clusters in nanocomposites, the mechanical properties of the film-shaped sample due to the thin thickness were affected worse than those of dogbone-shaped sample.

3.3 Microscope observation

Using the optical microscope, it could be figured out the overall degree of dispersion.

Fig. 7 shows optical microscope photos of the upper side of film-shaped samples which was filled with 1wt% particles.

In this figure, macroscopic dispersion was almost uniform, but microscopic dispersion was non-uniform with many small clusters. There were also resin and particles rich regions.
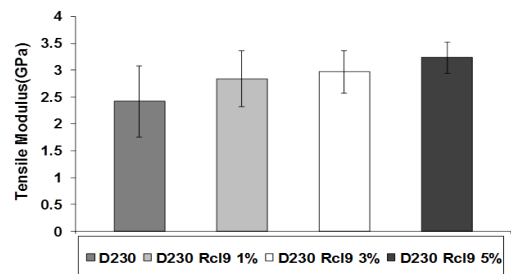

Fig. 6 Tensile modulus of the dogbone-shaped samples according to the content of particles

Fig. 8 represents optical microscope photos of film-shaped samples which were filled with 3wt% and 5wt% particles. Those photos show the dispersion status of nanoparticle on the upper side of film-shaped sample. It is found that the large clusters were formed in film-shaped samples with 3 and 5wt%. This means the content of particles become above 1 wt%, the large clusters were formed. This is probably the reason of the tensile test results of film-shaped sample as shown in Fig. 2-3.
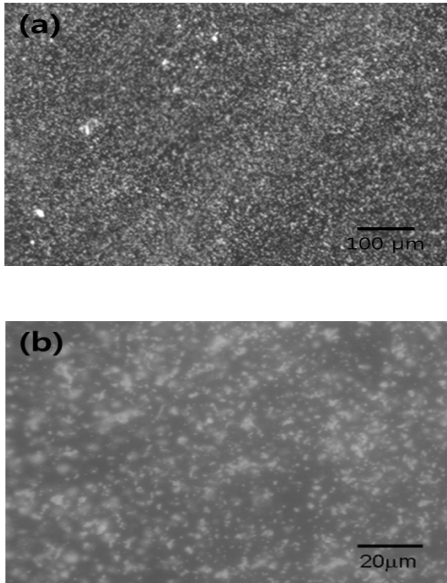
Fig. 7 Optical microscope photos of the upper side of film-shaped samples with 1wt%
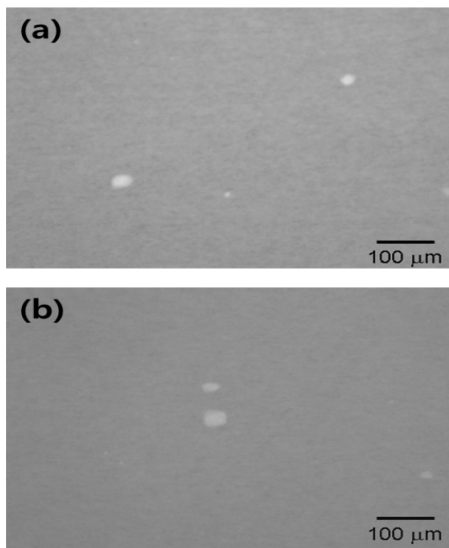(a) Low magnification (b) high magnification

Fig. 8 Optical microscope photos of film-shaped samples, (a) 3wt% (b) 5wt%

Fig. 9 reveals optical microscope photos of cross section of the dogbone-shaped sample with 1wt% particles. Sample was cut by microtome about the thickness of 20μm. In this figure, (a) was low magnification and (b) was high magnification at same sample. As can be seen in this figure, macroscopic particles dispersion was well and almost uniform even though there were a few big clusters, but microscopic particles dispersion was non-uniform with many small clusters. There were also resin and particles rich regions. This trend is the same as the film-shaped sample.

In Fig. 7 and 9, the dispersion situation of nanoparticles in the film- and dogbone-shaped sample with 1wt% was almost same situation. Therefore, both samples were induced the same trend of the tensile strength.
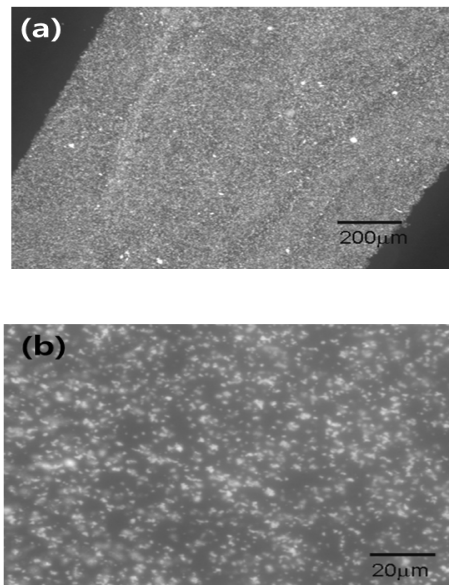

Fig. 9 Optical microscope photos of cross section of dogbone-shaped sample with 1wt% (a) Low magnification (b) high magnification

4. Conclusions

The findings made from this study can be summarized as follows;

1. The T_g is very slightly decreased with the content of nanoparticles.

2. Storage modulus increased up to the content of 3wt% particles and then decreased.

3. Tensile strength and modulus of film-shaped sample with 1wt% was higher than the one of pure epoxy, while other composites were not.

4. The tensile strength of dogbone-shaped sample with 1wt% was only higher than the one of pure epoxy, while other composites were lower than the one of pure epoxy. Tensile modulus of dogbone-shaped samples increased with the content of particles.

Acknowledgement

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