Improved Thermal, Structural and Electrical Properties of Elastic-Epoxy Blends System

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Abstract - In this paper, epoxy elasticity factors were investigated by TMA (Thermomechanical Analysis), DMTA (Dynamic Mechanical Thermal Analysis) and FESEM (Field Emission Scanning Electron Microscope) to improve toughness and reduce brittleness of existing epoxy resin. Dumbbell shaped specimens were made and tested at rates of 0, 20 and 35phr (part per hundred resins). TMA temperatures ranged from -20℃ to 200℃. Tg (glass transition temperature) of elastic epoxy was measured by thermal analysis. Also investigated were thermal expansion coefficient (α), modulus and Tanδ (loss factor). And we analyzed structure through FESEM, could find elastic-factors of elastic epoxy that is not existing-epoxy. In addition, we measured permittivity and Tanδ for investigation of the electrical properties of elastic epoxy. Permittivity and Tanδ depend on elastomer composition. Namely, permittivity and Tanδ increase according to the elastomer contents. For experimental analysis results, 20phr was considered an excellent specimen.

Keywords: Elastic-epoxy, High impact, Tg, Elastic-factor

1. Introduction

Epoxy resin includes cured resins and prepolymer that have more than one epoxide group in a molecule. In representative thermosetting-polymers, the two dimensional linear structure changes into a three-dimensional network structure through a curing reaction. The cured epoxy resin has properties of high-temperature, corrosion-resistance, adhesive-force and electrical insulation. The various usages of epoxy- adhesives, coating, electrical and electronic materials and fiber reinforcement composite materials- have increased demand for the material. Epoxy is a popular polymer composite material because byproducts such as water are not created during curing, shrinkage is low, and epoxy tends not to mold [1].

In spite of its high glass transition temperature (Tg) and excellent properties, cross-linked epoxy resin shatters easily. Brittleness is one of the problems involving thermosetting resin as well as epoxy resin [1, 2]. Crack resistance is one of a material's most important properties when faced with an applied load. If elastomer is added into a brittle polymer, the created elastomer particles induce plastic-deformation of the matrix, and then impact resistance increases. Toughness is changed by adding elastomer, improving interface strength and minimizing stress conditions [2]. Therefore, we completed experiments to improve crack resistance of existing epoxy.

In this study, we improved the properties of elastic epoxy, including improving the thermal and structural properties of impact resistance, modulus and high temperature, and investigated the improvements by TMA, DMTA and FESEM. In addition, we investigated the electrical properties of permittivity and Tanδ to find high voltage and insulating characteristics of elastic epoxy.

2. Experimental

2.1 Materials

We added liquid-elastomer miscible with bisphenol-A type epoxy, a representative epoxy, and then cured the samples as specified in Table 1. We agitated epoxy and elastomer at fractions of 0phr, 20phr and 35phr as indicated in Table 1. We enforced cell-exclusion at 0.05Torr for 30 minutes after adding filler (Silica) and hardener (HexaHydroPhthalic Anhydride, HHPA). After adding a mixture of epoxy and elastomer to the specimen mold, we continued the vacuum cell-exclusion process until the cell ceased to exist. Elaborate cross-linking can usually be caused by curing at low temperatures, instead of the more limited cross linking that takes place at high temperatures. Two curing times were tested to determine the proper curing of the unfinished reactant of mixed-liquor. The first curing was completed for 3 hours at 120℃ the second curing was completed for 12 hours at 130℃.

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Table 1 Composition of different specimens

Elastomer (phr)	Filler (%)	First curing (hr/℃)	Second curing (hr/℃)
0	62	3/120	12/130
20	65	3/120	12/130
35	58	3/120	12/130

※ phr (part per hundred resin)

2.2 Procedures

The thermal analysis equipment used to investigate the rheological properties of the material and its thermal behavior for TMA, DMTA was TA, TMA2940, Polymer Laboratories, and DMTA Mark2 Comb. Temperature ranges for TMA and DMTA were changed from -20℃ to 200℃, and the heating rate was 4℃/min. The applied TMA load was 0.05N, and the applied DMTA frequency was 1Hz. Thermal expansion coefficients and glass transition temperatures were measured by TMA, and modulus and Tanδ were measured by DMTA in these experiments.

We used FESEM (Hitachi, S-4300) to analyze the visual structure of the elastic-factor. If specimens are broken at room temperature, deflection of the breaking section occurs, and so we observe the structure by magnification of 1000 times and 5000 times at a voltage of 15kV after breaking by quenching.

Finally, we investigated the permittivity and Tanδ of the materials. In these experiments, the changes of permittivity and Tanδ at 60Hz and different temperatures were measured with the Tanδ meter (Tettex, type 2194).

3. Results and Discussion

3.1 Thermal properties

3.1.1 TMA analyses

Fig. 1 shows the change in thermal expansion coefficient (α) by specimens in temperature ranges from -20℃ to 200℃. Experimental results at 0.05 N force change least 20phr specimen with a thermal expansion coefficient of 62.8 ㎛/m℃. Usually, the thermal expansion coefficient is shown above and below the glass transition temperature. Table 2 shows glass transition temperatures and thermal expansion coefficients by fraction of elastomer. Thermal expansion coefficient values are below 35phr specimen for all specimens beneath the glass transition temperature and increase dramatically above the glass transition temperature.

The rate of change of the thermal expansion coefficient is least at 20phr specimen and greatest for 0phr specimen. This suggests that 0phr specimen were the most brittle. Large changes in the thermal expansion coefficients can cause mechanical damage due to thermal stress at the interface of metal and insulation, and may shorten mean-life. The 20phr specimen formed into a closed matrix with better impact resistance than other specimens. From these results, we found that 20phr specimen had lower thermal stress than other samples [3-7].

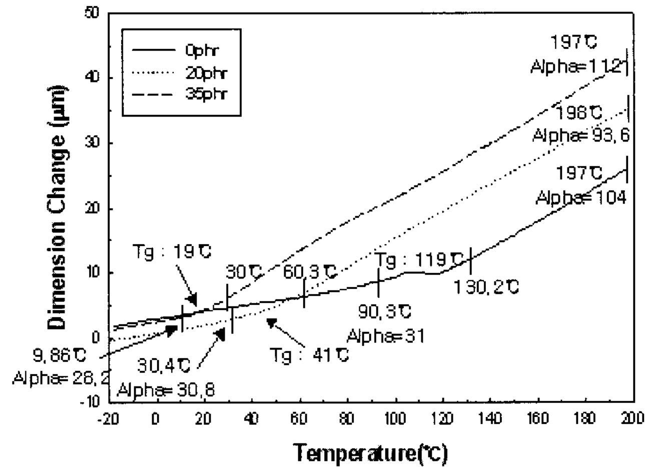


Fig. 1 Length changes according to the temperature of different specimens

Table 2 Thermal expansion coefficient and Tg values by different specimens.

Elastomer (phr)	Tg (℃)	α (㎛/m℃)	
		Before Tg	After Tg
0	119	31	104
20	41	30.8	93.6
35	19	28.2	112

3.1.2 DMTA analyses

Fig. 2 shows the modulus of each specimen when the temperature rises 4℃/min in temperature ranges from -20℃ to 200℃ at 1Hz. In Fig 2, the initial modulus of 35phr specimen is highest, and 0phr specimen is lowest. These properties occur due to the effect of glass transition temperature on elastomer added to epoxy. For glass transition temperatures of specimens consult Table 2.

Usually, materials have high elasticity below the glass transition temperature, and have high viscosity above the glass transition temperature. At 35phr specimen, the initial modulus is the highest at 11.45GPa. At 20phr specimen with 11.4GPa, the initial modulus is less than for 35phr, but is higher than 0phr specimen at 11.34GPa. The changes of initial modulus are inversely proportional to temperature [8].

The reason that the modulus of specimens decreases suddenly in Fig. 2 is that the specimens are not glassy-state but rubber-state with high-energy damage above the glass transition temperature. This modulus is called the damage

or viscosity modulus.

The modulus of 35phr specimen, with a great deal of energy damage, decreases rapidly. The modulus of 20phr specimen, with less energy damage than 35phr specimen, decreases later. The existing 0phr epoxy has a very high glass transition temperature. Therefore, the modulus is decreased near 100℃. The reason that the modulus of the existing epoxy decreases at high temperatures is very high cross-link density and molecular weight. From these results, we know that the modulus of elastic epoxy with 20phr added is higher than elastic epoxy with 35phr added, meaning that 20phr specimen is thermally and mechanically superior.

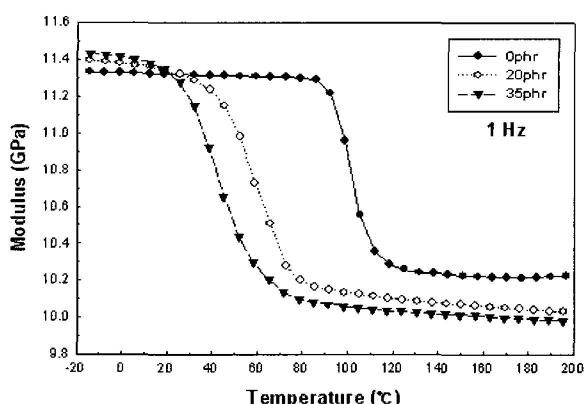


Fig. 2 Modulus changes of different specimens by 1Hz

Fig. 3 shows Tanδ of each specimen when temperature rises 4℃/min from -20℃ to 200℃ at 1Hz. In Fig. 3, Tanδ of 0phr specimen is highest at 0.56 near 100℃, and Tanδ of 35phr specimen with 0.46 comes out than 20phr specimen with 0.43.

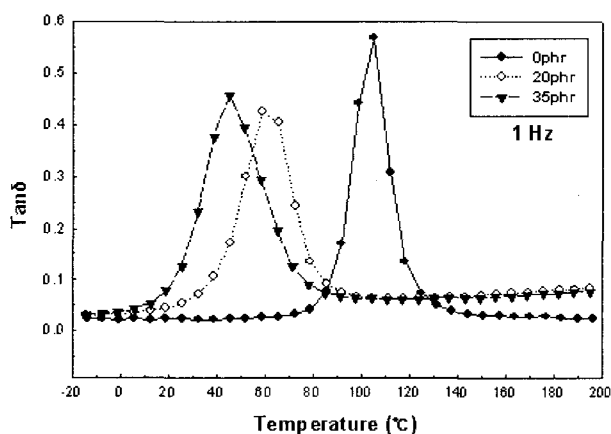


Fig. 3 Tanδ changes of different specimens by 1Hz

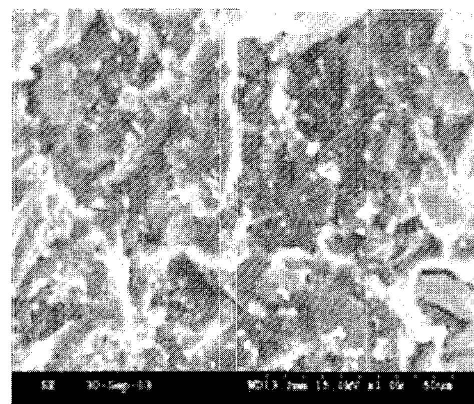
Usually, Tanδ, ratio of loss modulus and storage modulus, appears the highest above the glass transition temperature, and loss modulus is highest between the loss modulus and the storage modulus. When material viscosity increases, elasticity decreases. If Tanδ increases, energy loss will increase due to the increasing loss modulus. Therefore, we should regulate low Tanδ to improve the elasticity of the material. We wished to get excellent material thermally and mechanically by finding the damping behavior of material through Tanδ measurements in these experiments. The 20phr specimen again has the best thermal and mechanical properties [8-10].

In the DMTA experiment, if the modulus of the elastic epoxy decreased at low temperatures more than the 0phr specimen, then Tanδ (loss factor) of the elastic epoxy was less than Tanδ for the 0phr specimen.

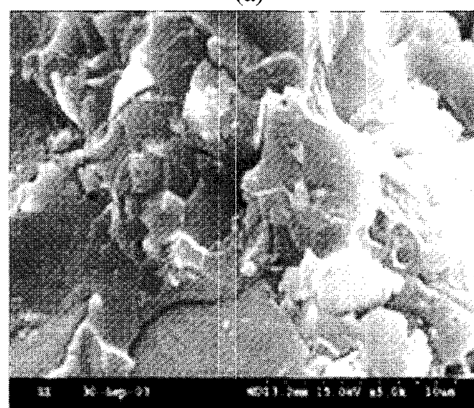
3.2 Structural properties

The elastomer particles dispersed in the epoxy network play definite roles to increase the toughness-effect by increasing the adhesive-force at the interface. Therefore, we wished to observe the distribution forms and growth process of dispersed elastomer particles. We used FESEM, field-emission mode, because SEM, in thermo-electron detection mode, would damage the specimens. [11].

Fig. 4 (a) and (b) show the fracture-surface of the 0phr specimen, which has the highest crosslink density among



(a)



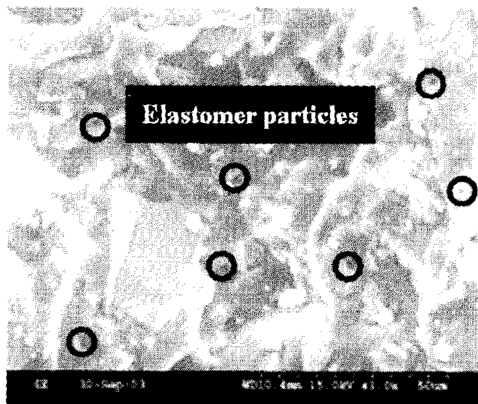
(b)

Fig. 4 FESEM images for the fracture surfaces of the 0phr specimen by (a) 1000 times and (b) 5000 times.

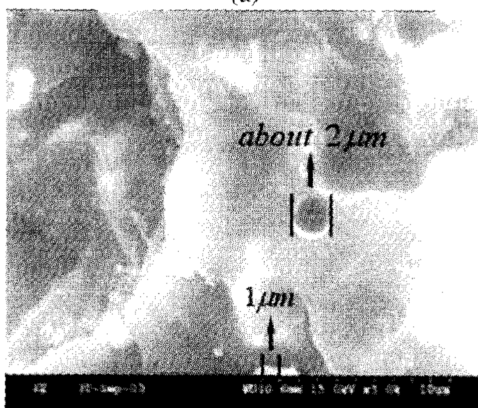
specimens. The high crosslink-density shown at the fracture-surface explains why the epoxy is brittle and easily broken on impact. Fig. 5 (a) and (b) show the fracture-surface of the 20phr specimen.. Elastomer particles are partially formed in the epoxy network between the center and side. The ductility of these fracture-surfaces is higher than the ductility of the 0phr specimen. The dispersed elastomer particles improve the toughness of epoxy resin by absorbing external-force. When the dispersed elastomer-particles were magnified by 5000 times, the diameter of a sample particle was about 2mm.

Fig. 6 (a) and (b) show the fracture-surface of the 35phr specimen. Elastomer particles had amassed in the center, and formed partially on the side. The ductility of fracture-surfaces was much higher than the ductility of other surfaces because of the different particle dispersion. The 35phr and 20phr specimens have different compatibil- ity and phase conversion between the epoxy network and the elastomer.

If each specimen is reacted, phase separation increased the molecular weight of epoxy resin and elastomer. In the case of the 35phr specimen, rapid reaction incorporated more elastomer. Therefore, we observed that the 35phr specimen has larger dispersed particles than the 20phr specimen.



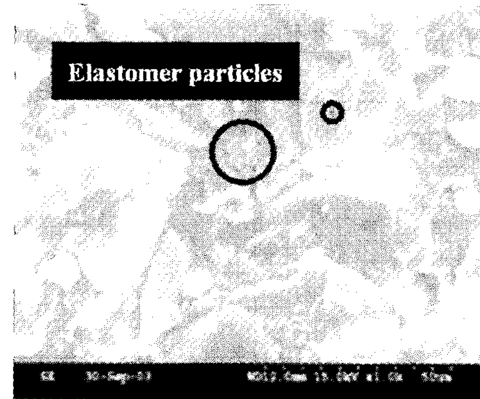
(a)



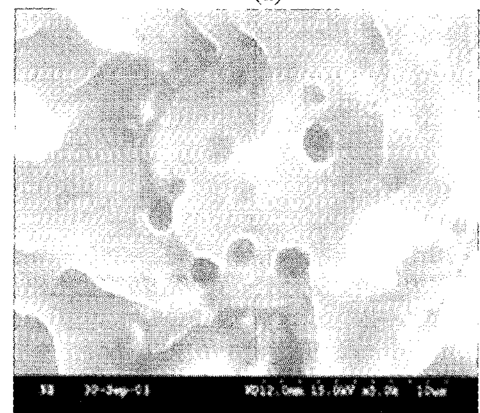
(b)

Fig. 5 FESEM images for the fracture surfaces of the 20phr specimen by (a) 1000 times and (b) 5000 times.

Usually, if size and distribution of dispersed elastomer particles increase, toughness decreases rapidly. If dispersed elastomer particles are evenly distributed in the epoxy network, toughness is increased. In the case of the 20phr specimen, we knew that impact resistance is excellent. The 20phr specimen had the best impact resistance [11, 12].



(a)



(b)

Fig. 6 FESEM images for the fracture surfaces of the 35phr specimen by (a) 1000 times and (b) 5000 times

3.3 Electrical properties

3.3.1 Permittivity

Fig. 7 shows the permittivity of elastic epoxy at 60Hz and different temperatures. Temperatures were changed from -30℃ to 150℃. In Fig. 7, as temperature increases, permittivity increases. These tendencies hit a maximum near the glass transition temperature as measured by thermal analysis. Permittivity of the specimens was uniform below the glass transition temperature, but increased rapidly because of dielectric dispersion above the glass transition temperature. For glass transition temperatures of specimens consult Table 2. Therefore we knew that permittivity had a closed relation with the glass transition temperature of the materials. Also we knew that the rise-width in permittivity increased with temperature

and elastomer fraction. In general, the 20phr specimen was better than the 35phr specimen, but less than 0phr specimen [13, 14].

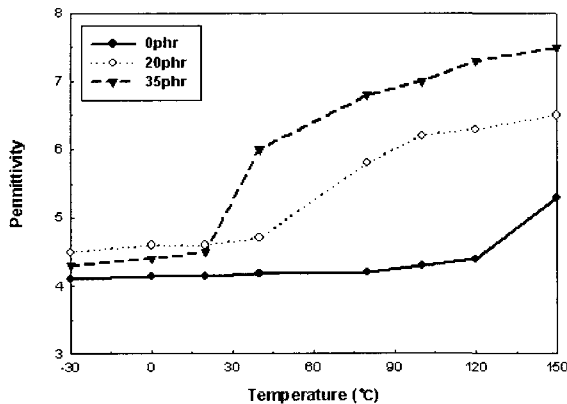


Fig. 7 Permittivity changes by different specimens and temperature in 60Hz.

3.3.2 Tanδ

Fig. 8 shows Tanδ of elastic epoxy at 60Hz and different temperatures. Temperatures were changed from 30℃ to 150℃.

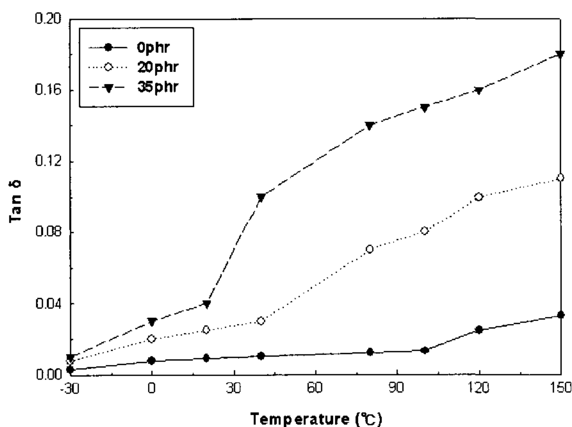


Fig. 8 Tanδ changes for different specimens and temperatures at 60Hz.

Tanδ is not an important factor in DC insulation characteristics, but insulation must have minimal conductivity, temperature dependence, and accumulation of space charge. The AC insulation characteristics required minimal Tanδ to control dielectric losses [13, 14].

We could know that Tanδ of elastic epoxy increases rapidly above the glass transition temperature, as shown in Fig. 8. Tanδ and permittivity showed similar tendencies. Again, the 20phr specimen was better than the 35phr specimen, but less than 0phr specimen.

The experimental results on dielectric properties show that permittivity and Tanδ increase with elastomer fraction but further study on epoxy without elastomer is required.

4. Conclusions

We conclude from thermal, structural and electrical measurements of epoxy for high voltage that addition of elastomer reduces brittleness.

From TMA thermal analysis, we knew that the 20phr specimen had excellent thermal and mechanical among specimens because the thermal expansion coefficient of the 20phr specimen was the least at 62.8 ㎛/m℃.

From DMTA thermal analysis, the initial modulus of the 35phr specimen was the highest 11.34GPa, but changes of modulus were reversed below 28℃. Therefore, the 20phr specimen had better thermal and mechanical properties than the 35phr specimen because of the decrease in high-temperature. In Tanδ experiments of each specimen, energy loss of the 20phr specimen with 0.43 was less than other specimens. In general, thermal and mechanical properties of the 20phr specimen were best.

Structural analysis results by FESEM, 20phr specimen had better impact resistance than other specimens because it formed a close matrix.

Dielectric properties increased with elastomer fraction. High change-width of permittivity and Tanδ occurred above the glass transition temperature by dielectric dispersion.

From thermal, structural and electrical results, the 20phr specimen was best. Future research will focus on which elastomer best improves the brittleness and dielectric properties of the epoxy.

Acknowledgment

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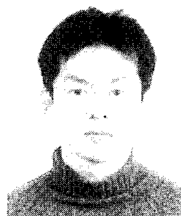

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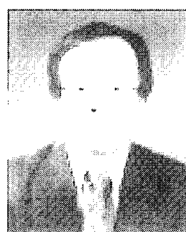

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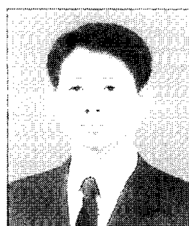

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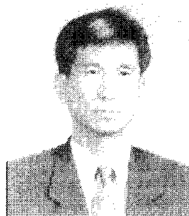

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