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Effects of Postcure Conditions on Mechanical and Dielectrical Properties of DGEBA/MDA/GN System

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DGEBA/MDA/GN 계의 기계적 및 절연성질에 미치는 후기경화 조건의 영향

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초 록 DGEBA/MDA/GN 계의 기계적 및 절연성질에 미치는후기경화 조건의 영향을 연구하였다. 시편은 80℃에서 1.5시간 동안 경화한 후 150℃에서의 후기 경화시간과 후기 경화온도를 다르게 하였다. 후기 경화온도가 증가함에 따라 인장강도, 절연파괴 강도 그리고 유리전이온도는 약간 증가하였으나 충격강도는 감소하였다. 4시간까지 후기경화되었을 때 인장강도와 유리전이온도는 증가하였으나 충격강도는 감소하였다. 그러나 4시간 후에는 거의 일정한 값을 나타내었다. 절연파괴 강도는 후기경화 시간에 관계없이 거의 일정한 값을 나타내었다.

Abstract The effects of postcure conditions on mechanical and dielectrical properties of DGEBA/MDA/GN system were investigated. The epoxy specimens were cured at different temperatures and at 150℃ for different times after curing at 80℃ for 1.5 hr. As cure temperature increased, tensile strength, dielectric breakdown strength and T_g increased slightly but impact strength decreased slightly. As postcure time increased up to 4.0 hrs, impact strength decreased but tensile strength and T_g increased. However, the values were constant above 4.0 hrs. Dielectric breakdown strength was almost constant without dependence with postcure time.

1. Introduction

Epoxy resins have been used in many applications since epoxy resins, whose shrinkage is lower during the cure than those of other thermosetting resins such as unsaturated polyester and phenol resin, have good properties such as thermal resistance, chemical resistance and abrasion resistance, etc.. Epoxy resins have also a good property of electrical insulation so that they have been used in the forms of coatings, castings, sealants and so forth[1,2].

Epoxy resins react with curing agents and transform into three dimensional network[3]. Thus, the selection of proper curing agent and cure conditions is very important[4]. The epoxy systems with aliphatic amines are easily cured at room temperature and offer good chemical resistance to aqueous acids and alkalis. The systems with aromatic amines give higher glass temperature, longer pot lives and greater chemical resistance than the systems with aliphatic amines do. The systems with anhydrides are low cost and have excellent heat stability. In general, the acid anhydride has been used in the demands of long and high temperature in order to obtain optimum properties[5].

In this study, the effects of postcure temperature and postcure time on the mechanical and dielectric properties of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA)/glutaronitrile(GN) system were investigated.

2. Experiment

Materials were DGEBA type epoxy resin(Epon 828, Shell Co.), MDA as a curing agent and GN as a reactive additive. The role of GN was to modify the toughness of DGEBA/MDA system which was too brittle[6,7].

Well mixed DGEBA/MDA(30 phr)/GN(10 phr) system was cured at 80℃ for 1.0 hr and it was continuously cured at 150℃ for different times or at different temperatures. To estimate impact strength, specimens were prepared by recommendation of ASTM D256 at the size of 63.5×13×4(mm) and were tested by Izod impact tester and to study tensile properties, specimens pre-

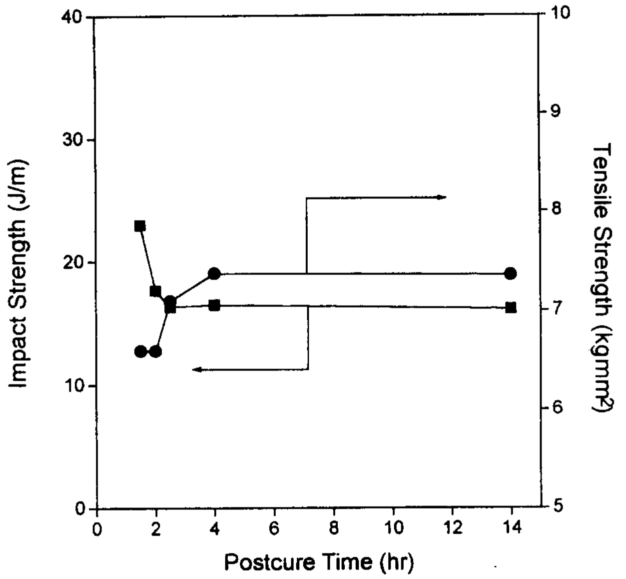

Fig. 1. Impact strength and tensile strength of DGEBA/MDA/GN system with different postcure time at 150℃.

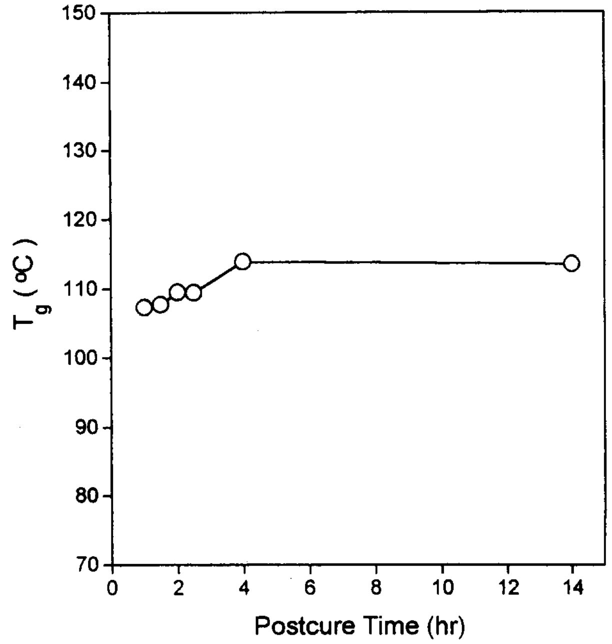

Fig. 2. Glass transition temperature of DGEBA/MDA/GN system cured at 150℃ for different times after curing at 80℃ for 1.5 hr.

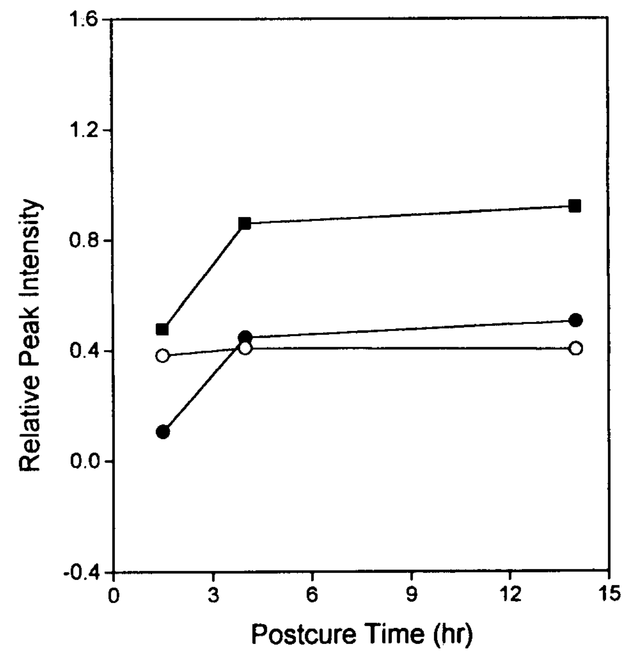

Fig. 3. Relative peak intensities of DGEBA/MDA/GN system with different post cure times. ■ : hydroxyl group, ● : ether linkage and ○ : imino group

pared by ASTM D638 were tested by universal testing machine at the cross-head speed of 10 mm/min. T_g was measured by DSC at 10 ℃/min of heating rate[6] and the relative peak intensities of functional groups were obtained from the data of FT-IR analysis[3].

Specimens used in the investigation of dielectric breakdown strength were needle/plane type. The radius of steel needle was 5 ㎛ and the distance between needle and plane electrodes was 1 mm. High voltage (0.5 kV/sec) was applied to the specimens in silicon oil which was used as immersion medium to prevent surface discharge.

3. Results and Discussion

Fig. 1 showed the impact strength and tensile strength of DGEBA/MDA/GN system for different postcure times at 150℃ after curing at 80℃ for 1.5 hr. As postcure time increased, impact strength abruptly decreased from 1.0 hr to 4.0 hrs and are almost constant over 4.0 hrs. At 4.0 hrs of postcure time, impact strength was reduced about 31.5%. Tensile strength, however, reached to maximum value at 4.0hrs of postcure time and then sustained constant value. These were due to the cure reaction of unreacted functional groups until postcure time was 4.0 hrs, but after that time, all unreacted functional groups linked to the network structure. Thus, impact strength decreased and tensile strength increased.

T_g is closely related to the mechanical structure and Tg is influenced by the structure of molecular chain such as the length of molecular chains, the number and size of branches and crosslink density[6, 8]. Therefore, the change of chemical structure can be estimated indirectly by the change of T_g. It can be also confirmed by the relative peak intensities for functional groups such as epoxide group, amine group, hydroxyl group and ether linkage which participated in cure reaction. Fig. 2 displayed the change of T_g as a function of postcure time at 150℃. As it was expected, T_g increased about 6.5℃ until 4.0 hrs and were constant over this time.

With different postcure time at 150℃, the relative peak intensities of functional groups participated in cure reaction were shown in Fig. 3. As cure time passed up to 4.0 hrs, the relative peak intensities of hydroxyl group at 3500 cm^{-1} and ether linkage at 1120 cm^{-1} increased abruptly. However, their relative peak intensities were almost constant from 4.0 hrs to 14.0 hrs of postcure time. Also, the relative peak intesity of imino group at 1650 cm^{-1} was almost constant above 1.5 hr of postcure time. Therefore, it was reconfirmed that cure reaction was nearly completed.

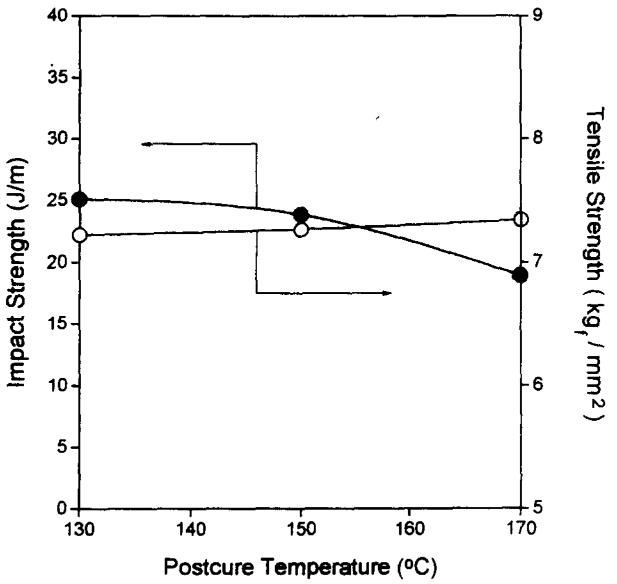

Fig. 4. Impact strength and tensile strength of DGEBA/MDA/GN system with different postcure temperatures.

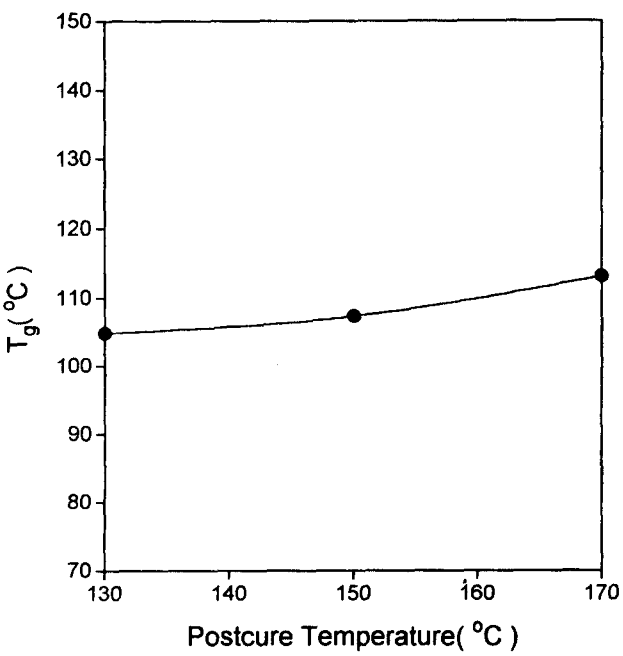

Fig. 5. T_g of DGEBA/MDA/GN system with different postcure temperatures.

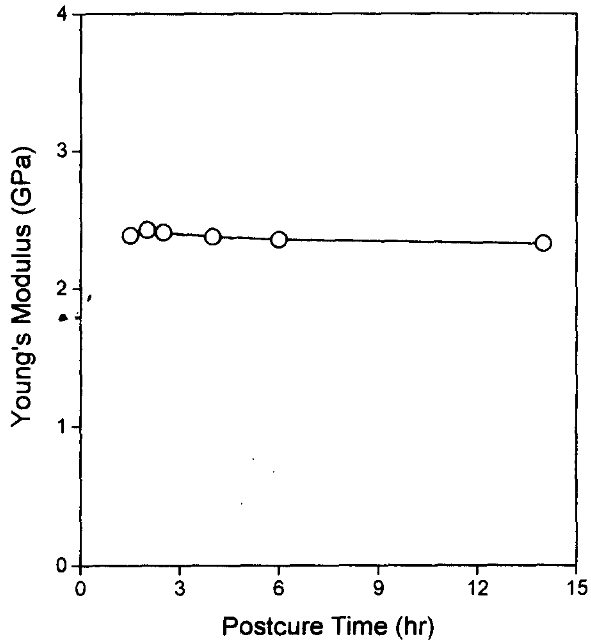

Fig. 6. Young's modulus of DGEBA/MDA/GN system as a function of postcure time at 150℃.

Fig. 4 showed the impact strength and tensile strength of DGEBA/MDA/GN system at different cure temperatures for 1 hr after curing at 80℃ for 1.5 hr. As cure temperatures increased, impact strength decreased about 5.0% at 150℃ but about 24.5% at 170℃. However, tensile strength increased slightly. This meant that cure reaction was well progressed at high temperature and the crosslink density at high tempeature was higher than that at low temperature. Therefore, T_g increased with the increment of cure temperature, as shown in Fig. 5.

T_g of the system cured at 130℃ was higher about 8.3℃ than that of the system at 170℃. Since T_g was increased with the increment of cure temperature, it could be known that the crosslink density of DGEBA/MDA/GN system was highest at 170℃.

The Young's modulus was plotted in Fig. 6 as a function of postcure time at 150℃. Modulus was constant regardless of the increment of post cure time. It meant that modulus was not affected by the postcure time.

Fig. 7 showed Young's modulus of DGEBA/MDA/GN(10) system cured at different temperatures. As postcure temperature increased, Young's modulus increased slightly. With the increment of cure temperature, the crosslink density increased, so the mobility of chain was restricted and Young's modulus increased.

Fig. 8 presented the dielectric breakdown strength of epoxy composite as a function of postcure time at 150℃. With the increment of postcure time, the change of the strength didn't appear.

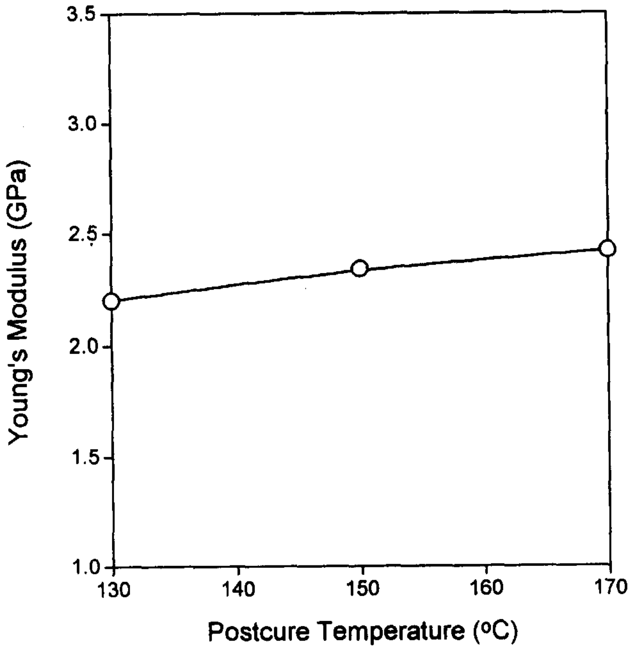

Fig. 7. Young's modulus of DGEBA/MDA/GN system as a function of postcure temperatures.

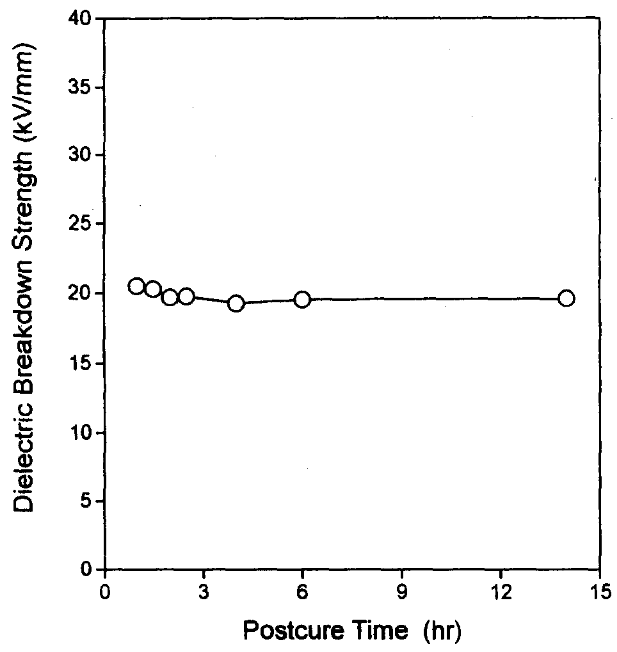

Fig. 8. Dielectric breakdown strength of DGEBA/MDA/GN system with different postcure time at 150℃.

The dielectric breakdown strength of DGEBA/MDA/GN system with different postcure temperature were shown in Fig. 9. There was also no change of dielectric breakdown strength with the increment of postcure temperatures. Electrical tree is one of the main cause of dielectric breakdown. As high voltage applied to the epoxy resin system, electrones were trapped in that system and the space charges were formed. These space charges made electrical field transformed and did insulating materials aged by the form of tree.

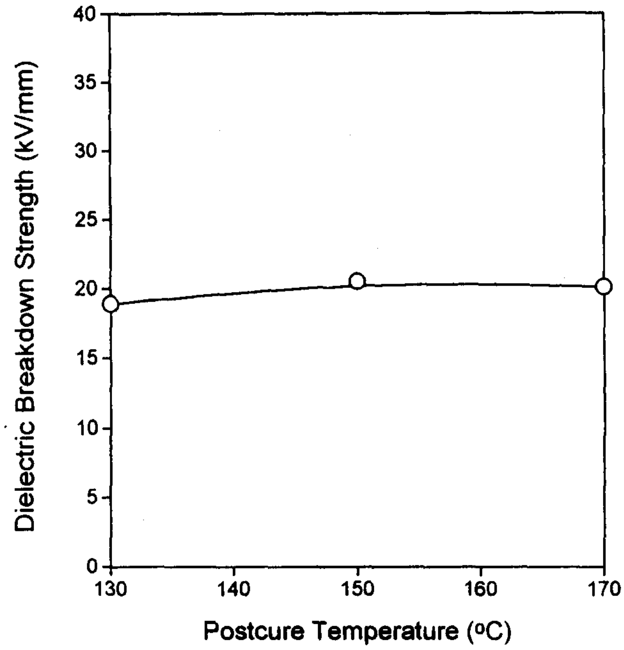

Fig. 9. Dielectric breakdown strength of DGEBA/MDA/GN system with different postcure temperatures.

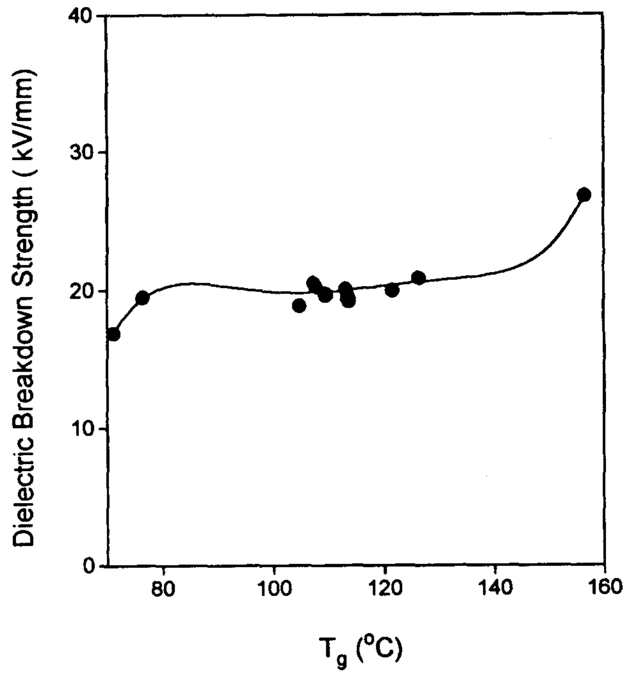

Fig. 10. Dielectric breakdown strength as a function of T_g.

So, these aging phenomena of the system is called as electrical tree.

Electrical trees were initiated and were propagated. Finally, dielectric breakdown occurred. These space charges and mechanical structure had a close relationship. However, there was no change of dielectric breakdown strength despite of the change of T_g with the various postcure conditions[4, 9].

To study the relationship between dielectric breakdown strength of epoxy system and T_g, Fig. 10 was replotted. With the increment of T_g, dielectric breakdown strength turned up as a sigmoid curve. In the range from 80℃ to 140℃, the variation of dielectric breakdown strength was little. It may be that the structure change in this range makes no effect on the formation and propagation of electrical tree. Thus, dielectrical breakdown strength has little change.

4. Conclusions

The effects of postcure conditions on mechanical and dielectric properties of DGEBA/MDA/GN system were studied and the following results were obtained.

1) As postcure time increased, impact strength decreased up to 4.0 hrs and was almost constant above 4.0hrs. On the other hand, tensile strength showed the reverse results of the impact strength. Dielectric breakdown strength preserved nearly constant value in all the range of postcure temperatures.

2) As postcure temperature increased, impact strength decreased but T_g, tensile strength and dielectric breakdown strength increased slightly.

3) In the T_g range from 80℃ to 140℃, dielectric breakdown strength had almost constant values.

References

1. H. Lee and K. Neville, "Handbook of Epoxy Resins", McGraw-Hill, Inc., New York, chap. 1 (1980).
2. 垣内 弘 外, エポキシ樹脂, 昭晃堂, Tokyo, chap. 5 (1990)
3. M. J. Shim and S. W. Kim, Kor. J. of Mater. Res., **3**, 272(1993)
4. Y. S. Cho, M. J. Shim and S. W. Kim, J. of Kor. Ind. & Eng. Chem., **6**, 937(1995)
5. M. T. Goosey, etc., "Plastics and Their Properties for Electronic Applications", Elsevier Applied Science Publishers LTD, London and New York, chap. 4(1986)
6. J. Y. Lee, M. J. Shim and S. W. Kim, J. of Kor. Ind. & Eng. Chem., **6**,288(1995)
7. A. Takaku, T. Hashimoto and T. Miyoshi, J. of Appl. Polym. Sci., **30**, 1565(1985)
8. S. K. Jeoung, J. Y. Lee, H. K. Choi, M. J. Shim and S. W. Kim, J. of Kor. Mater. Res., **4**, 823(1994).
9. L. E. Nielsen and R. F. Landel, "Mechanical Properties of Polymers and Composites", 2nd, Denkker, NewYork, chap. 1(1994)
10. S. Yamini and R. J. Young, J. of Mater. Sci., **15**, 1814(1980)
11. R. E. Whittaker, Polymer, **13**, 169(1972)
12. A. E. Moehlenpah, O. Ishal and A.T. Dibenedetto, J. of Appl. Polym. Sci., **13**, 1231(1969)
13. H. Mitsui, T. Yoshimitsu, Y. Mizutani and K. Umemoto, IEEE Trans. on Electrical Insulation, EI-16, 533(1981).