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Thermal and Mechanical Properties of DGEBA/MDA/HQ-PGE System

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DGEBA/MDA/HQ-PGE 계의 열적, 기계적 성질

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초 록 반응성 첨가제로 사용된 HQ-PGE가 DGEBA/MDA계의 기계적 성질에 미치는 영향을 살펴보기 위해서 충격강도와 인장강도를 측정하였다. HQ-PGE의 함량이 25phr일 때 충격 강도는 첨가되지 않았을 때보다 40% 증가하고, 인장강도도 약간 증가하였다. 이것은 HQ-PGE가 합성될 때 생성된 수산기가 자촉매 반응을 하면서 에폭시 수지의 미반응된 에폭시기와 반응한 결과로 사료된다. Young's modulus와 신장율은 HQ-PGE의 함량이 증가함에 따라 크게 변화하지 않았다.

Abstract The effect of synthesized hydroquinone-phenyl glycidyl ether(HQ-PGE) as a reactive additive on mechanical properties of diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) system was investigated. The impact strength increased with the increment of HQ-PGE content. Impact strength with 25 phr of HQ-PGE was 45.37 J/m, which was higher about 40% than 32.23 J/m of the system without HQ-PGE. Also, the tensile strength steadily increased with HQ-PGE contents. That results were expected by autocatalytic reaction of hydroxyl group. Young's modulus and elongation had not shifted largely. So those properties, Young's modulus and elongation, are not related to the content of HQ-PGE.

1. Introduction

Epoxy resin which is a typical thermoset, is useful in many industry applications. Because, it has many advantages such as good chemical resistance, excellent adhesion, dimensional stability, and so on[1,2]. But, it has demerit of brittleness, so modification of the demerit has been investigated by many researchers[3~7].

Mechanical properties of epoxy resin are mainly affected by degree of crosslink density. For instance, with the decrement of crosslink density, toughness increased and stiffness decreased. Crosslink density also effects on thermal properties. Generally, high density of crosslink shows high glass transition temperature[7].

In this study, diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline(MDA) system modified by hydroquinone-phenyl glycidyl ether(HQ-PGE) was investigated for the standpoint of mechanical and thermal properties.

2. Experiment

Materials

Commercial epoxy resin DGEBA(Epon 828) with a molecular weight of approximately 350~400 and viscosity of 11,000~14,000 cP at 25℃ was supplied by Shell Co. and curing agent was MDA with a molecular weight of 198 and melting point 90℃ by Fluka Chemie AG. The reactive additives was HQ-PGE which was synthesized with HQ and PGE preliminarily. HQ was obtained from Osaka Hayashi Pure Chemical Ind. and PGE from Fluka Chemie AG. HQ and PGE were mixed with constant ratio and they were reacted at 180℃ for 30 min. Then they were restored in the refrigerator.

Procedure

To prepare the specimens, DGEBA, MDA, and various content of HQ-PGE were completely mixed at 80℃ and the mixture was poured into mold. They were cured at 150℃ for 1 hr after curing at 80℃ for 1.5 hr.

Specimen of impact strength was referred by ASTM D256 and tested by Izod impact tester. In case of tensile strength, specimen was referred by ASTM D638 and test was carried out by universal tester of Autograph series(AGS-1000D) Shimadzu Co. Crosshead speed was 5mm/min. After mechanical test, the fracture surface of specimens was observed by optical microscope.

Also, cured epoxy resin of DGEBA/MDA system

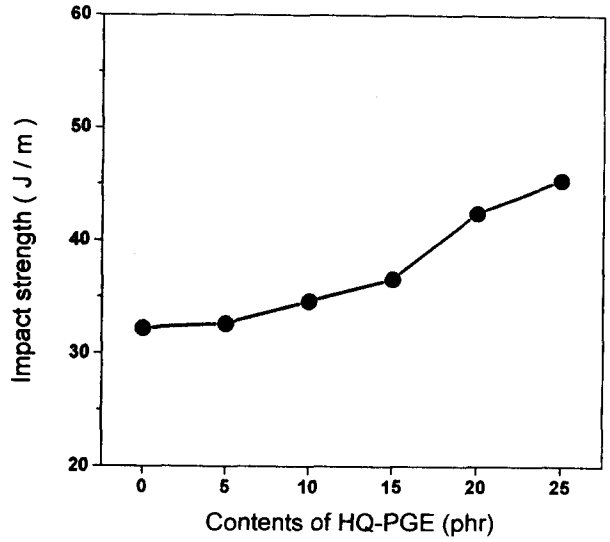

Fig. 1. Impact strength of DGEBA/MDA system with various HQ-PGE contents.

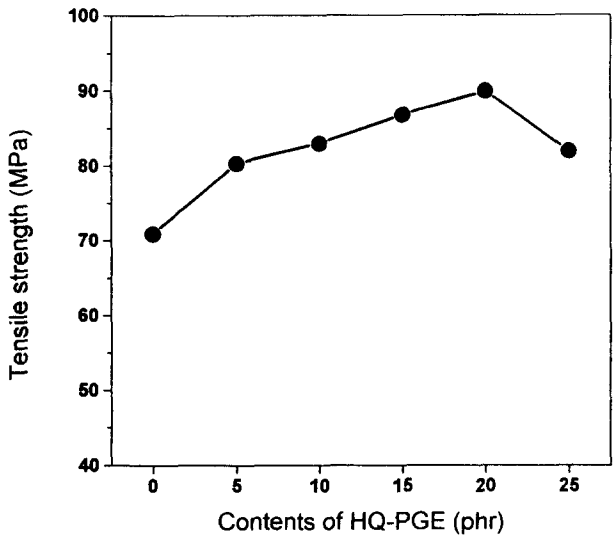

Fig. 2. Tensile strength of DGEBA/MDA system with various HQ-PGE contents.

with various contents of HQ-PGE was analyzed by differential scanning calorimetry(DSC) and thermal gravimetry(TG) to estimate glass transition temperature (T_g) and decomposition temperature(T_d). The heating rate of DSC and TG was 10℃/min.

3. Results and Discussion

Mechanical properties

Mechanical properties of cured epoxy resin with amine were affected by structure, because epoxy resin was cross-linked in the form of three dimensional network[8]. Generally, it has been known that epoxy resin have lower impact strength and higher tensile strength than those of other thermosetting. In order to obtain good mechanical properties, epoxy resin was

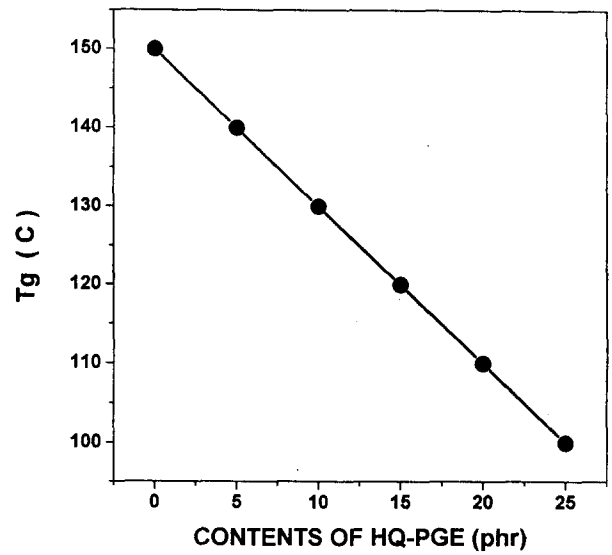

Fig. 3. Tg of DGEBA/MDA system with various HQ-PGE contents.

demanded by means of the improvement of impact strength. However, improvement of impact strength means deterioration of tensile strength[7,9]. By these reasons, both impact and tensile strength should be considered to get optimal mechanical properties.

In this study, preliminarily synthesized HQ-PGE was introduced as a chain extender to modify the impact strength[3~5]. Change of the impact strength of DGEBA/MDA system at various HQ-PGE contents by Izod impact tester was shown in Fig. 1.

As shown in Fig. 1, impact strength was increased with the increment of HQ-PGE content. The value of the system with 25 phr of HQ-PGE was 45.37 J/m, which was higher about 40% than 32.23 J/m of the system without HQ-PGE. This fact indicated the decrement of crosslink density by looseness of the entanglement of polymer chain when HQ-PGE added to the system. In other words, added HQ-PGE made the chain length between segment and segment of epoxy resin longer. Therefore, its resistance force was better than that of the system without HQ-PGE, when some external force impacted the specimen.

In Fig. 2, change of the tensile strength of the system with various contents of HQ-PGE was depicted. We expected that tensile strength of the epoxy system would be decreased with the increment of HQ-PGE content, because of the impact strength. However, the tensile strength of the present system was increased with the increment of HQ-PGE contents. When 20 phr of HQ-PGE added to the system, tensile strength was 89.94 MPa, while the tensile strength of the system without HQ-PGE showed 70.88 MPa. It meant that introduced

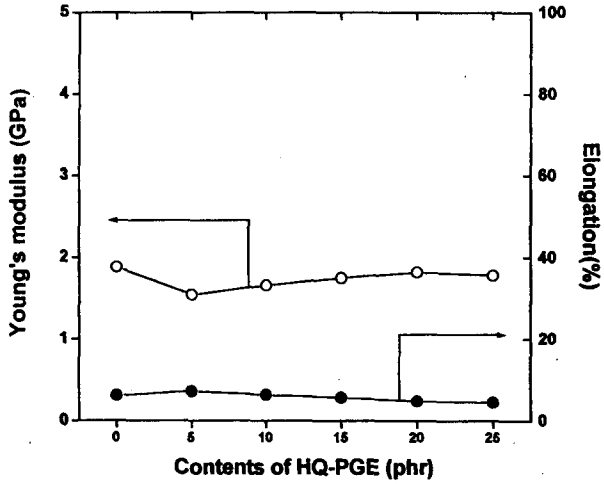

Fig. 4. Young's modulus and elongation of DGEBA/MDA system with various. HQ-PGE contents.

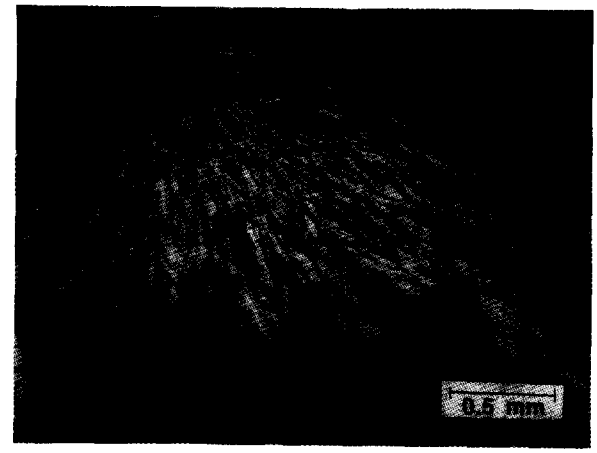

Fig. 5. Fractured surface photograph of DGEBA/MDA/HQ-PGE(10 phr) system.

Table 1. Thermal Properties of DGEBA/MDA System with Various HQ-PGE Contents.

HQ-PGE content(phr)	0	5	10	15	20	25
T_g(℃)	150	140	130	120	110	100
T_d(℃)	357	355	354	352	351	350

hydroxyl groups affected the epoxy structure. However, the effect of hydroxyl group on tensile strength wasn't known to exactly.

In order to confirm the structure change of epoxy system by introduction of reactive additives, glass transition temperature(T_g) of the system with various HQ-PGE contents was estimated and depicted in Fig. 3. T_g consecutively decreased with the increment of HQ-PGE content. From the results, HQ-PGE made the main chain length longer and branch number increased, and crosslink density was reduced consequently[3].

Fig. 4 shows the effects of HQ-PGE on the Young's modulus and elongation of DGEBA/MDA system, when specimens were tested by tensile process. As shown in Fig. 4, it seemed that Young's modulus and elongation are not related to the content of HQ-PGE.

When external stress forced to specimen, it concentrated on weak points such as microcracks so that fracture propagated. As stress consecutively concentrated on those weak points, it reached the critical point specimen and specimen fractured consequently. To confirm this fact, the fractured surface of specimen was photographed by optical microscope in Fig. 5, and we can see the crack propagation from the weak point to other area.

Thermal properties

T_g is the representative property of thermal properties in polymers. When polymers are heated, fixed polymer chains move, and their chemical structures changed. Then, T_g of the polymer shifted to low range[11,12]. Strictly speaking, T_g should not represent only thermal characteristics. Because it is used to confirmation of other properties such as mechanical properties.

T_g and T_d of DGEBA/MDA/HQ-PGE system were listed in Table 1. As presented in Table 1, T_g of DGEBA /MDA/HQ-PGE system was decreased with the increment of HQ-PGE contents. However, T_d was shown independent on HQ-PGE contents. From these results, we learned that reactive additive hardly affected decomposition in this epoxy system.

4. Conclusion

From these results, we can conclude below,

1) Impact strength and tensile strength steadily increased with the increment of HQ-PGE content.

2) Young's modulus and elongation were scarcely affected by HQ-PGE contents.

3) HQ-PGE such as reactive additive made the crosslink density lower in this system and the fact was confirmed by T_g shift.

4) Thermal decomposition of DGEBA/MDA system was independent of HQ-PGE content.

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