[논　문] 한국재료학회지
Korean Journal of Materials Research
Vol. 7, No. 6 (1997)

Effects of PGE-AcAm on the Tensile and Impact Properties of DGEBA/MDA System

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DGEBA/MDA 계의 인장 및 충격 특성에 미치는 PGE-AcAm의 영향

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(1996년 12월 30일 받음, 1997년 4월 8일 최종수정본 받음)

초　록　에폭시 수지 계의 경화반응 속도를 증가시키고 기계적 물성을 향상시키기 위해 합성 phenyl glycidyl ether(PGE)-acetamide(AcAm)를 diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) 계에 도입하였다. PGE와 AcAm을 2 : 1의 몰비로 혼합한 후 180℃에서 1시간 반응시켜서 PGE-AcAm을 합성하였다. 5phr의 PGE-AcAm이 첨가되었을 때 인장강도가 15% 개선되었으며, 그 이후로는 PGE-AcAm의 함량에 관계없이 거의 비슷한 값을 나타내었다. 반면에 유리전이 온도(Tg)와 충격강도는 PGE-AcAm의 함량이 증가함에 따라 감소하였다. 파단면은 PGE-AcAm이 첨가됨으로써 더 복잡한 형상을 나타내었다.

Abstract To increase the cure rate and to improve the mechanical properties of diglycidyl ether of bisphenol A (DGEBA)/4,4'- methylene dianiline(MDA) system, synthetic phenyl glycidyl ether(PGE)-acetamide(AcAm) was introduced. The PGE-AcAm was prepared by the reaction of PGE : AcAm = 2 : 1(molar ratio) at 180℃ for 1hr. When 5 phr of PGE-AcAm was added, tensile strength was improved about 15% and after that phr, the value was almost constant, while glass transition temperature(Tg) and impact strength decreased with the increment of PGE-AcAm content. The morphology of the fracture surface was more complex when PGE-AcAm was added.

1. Introduction

With the increasing demands of epoxy composites for load-bearing structural applications, many researchers have investigated the modification methods of epoxy resins and reported many good results[1~9]. The well-known methods are the modification of epoxy resins or/and curing agents[1,2], the addition of reactive additives[3~6] and the incorporation with reactive liquid rubbers[7~9]. Mechanical properties of the cured epoxy resins are closely related to the crosslink structure. If crosslink density decreases or if the structure contains soft segments[3,4], tensile strength decreases, while impact strength is improved. If rubber particles form domains in continuous epoxy phase, these domains make the systems tougher by energy dissipation mechanism, while tensile properties decrease[9].

In this study, synthetic phenyl glycidyl ether(PGE)-acetamide(AcAm) as a reactive additive was introduced to diglycidyl ether of bisphenol A(DGEBA)/4,4'-methylene dianiline(MDA) system to make the crosslink density increase and the effects of PGE-AcAm on the tensile and impact properties were studied.

2. Experiment

The epoxy resin was DGEBA type(Epon 828, Shell Co.), MDA was used as a curing agent and PGE-AcAm was as an additive[4,10,11].

To estimate the impact and tensile properties, the specimens were prepared by the following procedure. Well-mixed DGEBA/MDA system with various contents of PGE-AcAm was cured at 150℃ for 1hr after curing at 85℃ for 1.5hr. The size of the specimen for impact test was 63.5×13×4(mm) with a notch at the center. The depth of notch was 2.54 mm and the angle was 45°. For tensile test, the size of the specimen was recommended by ASTM D638.

Impact test was performed by Izod impact tester and tensile test was carried out by Autograph AGS-D (Shimadzu, Japan) at 10 mm/min of cross-head speed. After the mechanical test, the fracture surface was ob-

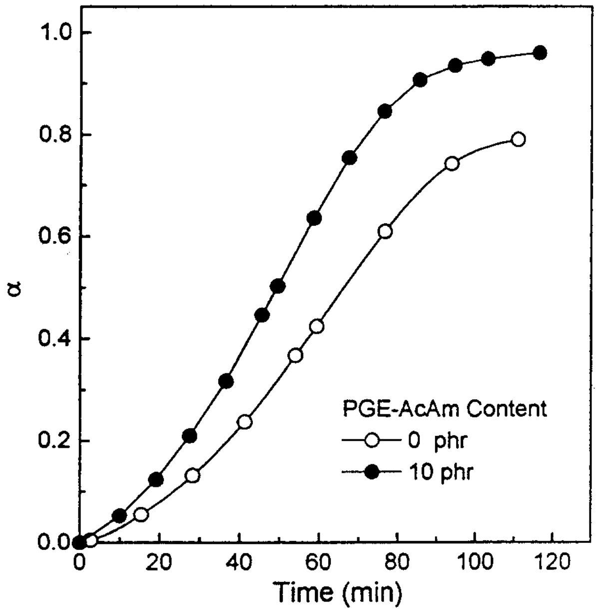

Fig. 1 Comparison of cure rate for DGEBA/MDA/PGE-AcAm system at 80℃.

served by optical microscope and Tg was estimated by DSC at 10 ℃/min of heating rate.

3. Results and Discussion

The typical s-curves for autocatalytic cure reaction of DGEBA/MDA system with and without PGE-AcAm are shown in Fig.1, and the acceleration effect of PGE-AcAm on the cure rate is also shown. When conversion α became 0.6, the reaction time for DGEBA/MDA system was 74.2 min and that for DGEBA/MDA/PGE-AcAm system was 55.8 min. Therefore, the cure rate of the system with PGE-AcAm was 1.3 times faster than that of the system without PGE-AcAm. The acceleration effect was explained by the role of hydroxyl group generated from the reaction between epoxide group in PGE and amine group in AcAm. The hydroxyl group acted as a catalyst on the reaction between epoxide group and amine group, and from the opening of an epoxide ring, another hydroxyl group was generated[12,13]. Therefore, the cure rate was accelerated and it has been reported that the cure rate increased with the increment of PGE-AcAm content.

The increment of cure rate at low temperature reduced the cost to produce an epoxy thermoset for the high strength applications. However, excessive PGE-AcAm contents may affect the properties of the system. So, the mechanical properties of the system with various contents of PGE-AcAm should be investigated.

Fig.2 shows the tensile strength of DGEBA/MDA system with various contents of PGE-AcAm at 10 mm/min of cross-head speed. When 5 phr of PGE-AcAm was added, tensile strength was improved about 15% and after that phr, the value was almost constant with various PGE-AcAm contents. However, Young's modulus(Fig.3) was lowest at 5 phr of PGE-AcAm and after that phr, the value was increased slightly. These meant that the backbone chain of DGEBA/MDA system might be linked tightly by the addition of PGE-

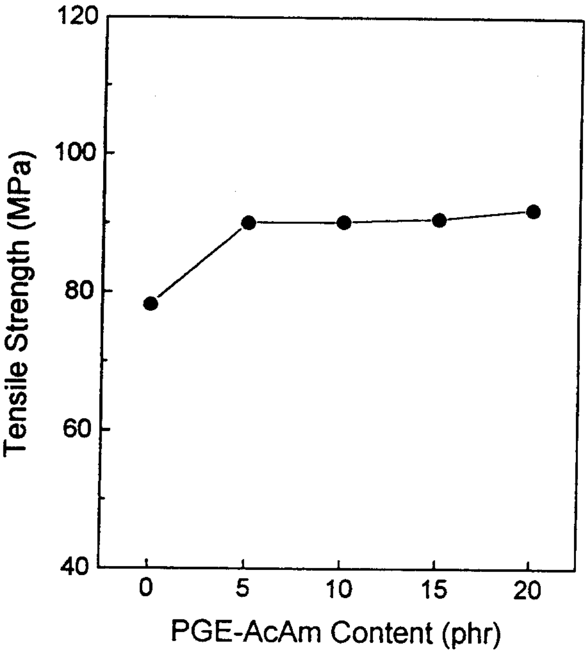

Fig. 2 Tensile strength of DGEBA/MDA/PGE-AcAm system.

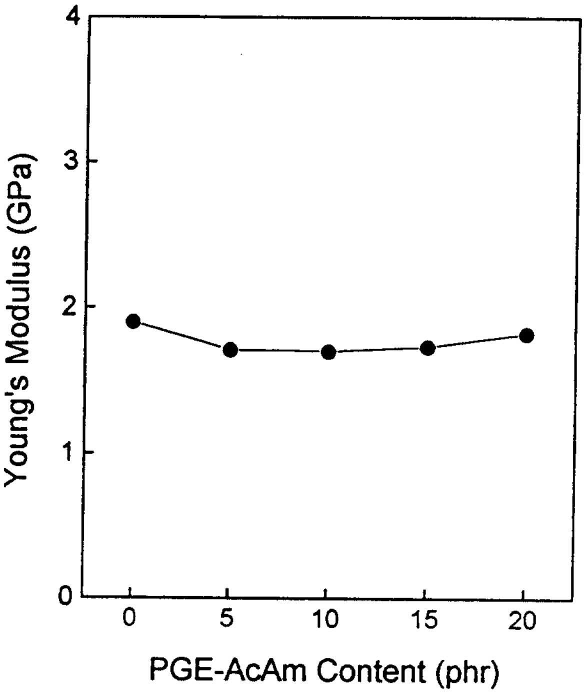

Fig. 3 Young's modulus of DGEBA/MDA/PGE-AcAm system.

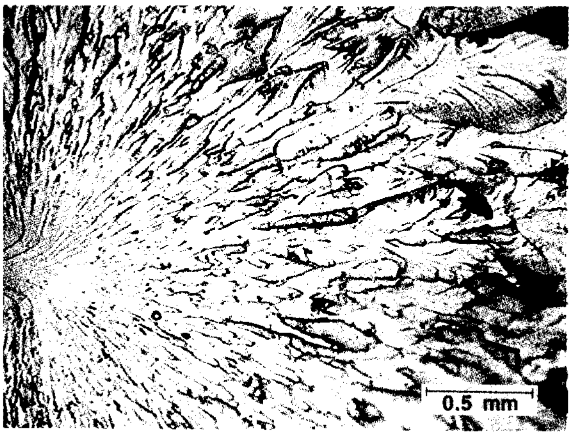

Fig. 4 Morphology of the fracture surface of DGEBA/MDA specimen after undergoing tensile test.

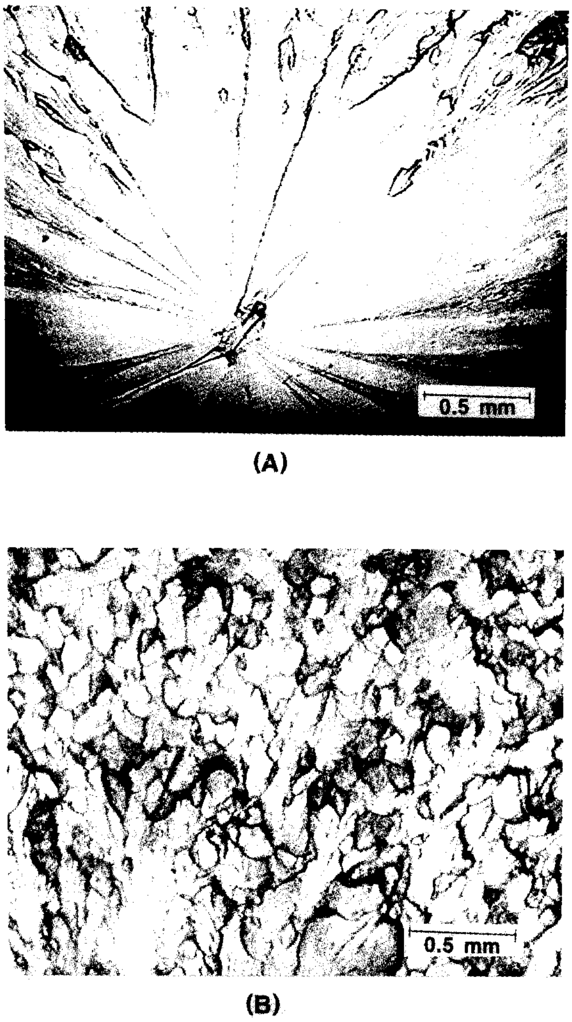

Fig. 5 Morphology of the fracture surface of DGEBA/MDA/PGE-AcAm(20 phr) specimen after undergoing tensile test.
(A) : mirror zone, (B) parabolic marking

AcAm due to the reaction of ether linkage between epoxide group of DGEBA and hydroxyl group of PGE-AcAm.

Fig.4 shows the morphology of the fracture surface of the DGEBA/MDA specimen that was failed in tension and in this figure, the crack propagated from left to right. Microscopically, the fracture morphology has a clearly distinguishable mirror zone, where the fracture initiated and which was surrounded by parabolic markings. The extension of mirror zone corresponded to the increment of the energy done during the fracture and in the parabolic marking region, crack-growth rate was very fast due to the interference of the main crack with new cracks nucleating ahead of it[14,15]. Therefore, the fracture surface of DGEBA/MDA system was so complex and rough.

Fig.5 shows (A) mirror zone and (B) parabolic marking of the fracture surface for the DGEBA/MDA/PGE-AcAm(20 phr) specimen that was failed in tension and in this figure, the crack propagated upward. In the crack initiation region, mirror zone which was much larger than that of DGEBA/MDA system in Fig.4 also was observed and parabolic marking which was more rough and complex than that of DGEBA/MDA system was showed in the region far distant from the crack initiation point. With the addition of PGE-AcAm, mirror zone became wider and this meant that the more energy was needed to fracture. So, tensile strength of the system with PGE-AcAm(20 phr) was larger than that of the system without PGE-AcAm. However, in the parabolic marking region, crack-growth rate abruptly increased and the specimen fractured.

Fig.6 shows the impact strength of DGEBA/MDA system with different content of PGE-AcAm. As was expected, impact strength decrease slightly with the in-

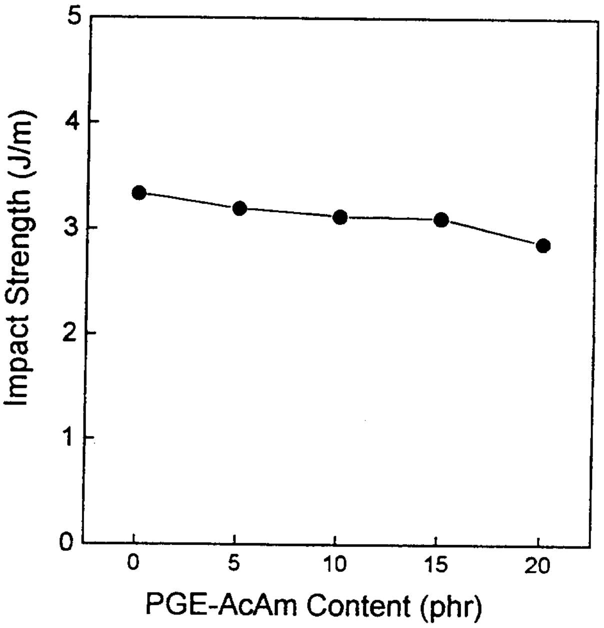

Fig. 6. Impact strength of DGEBA/MDA/PGE-AcAm system.

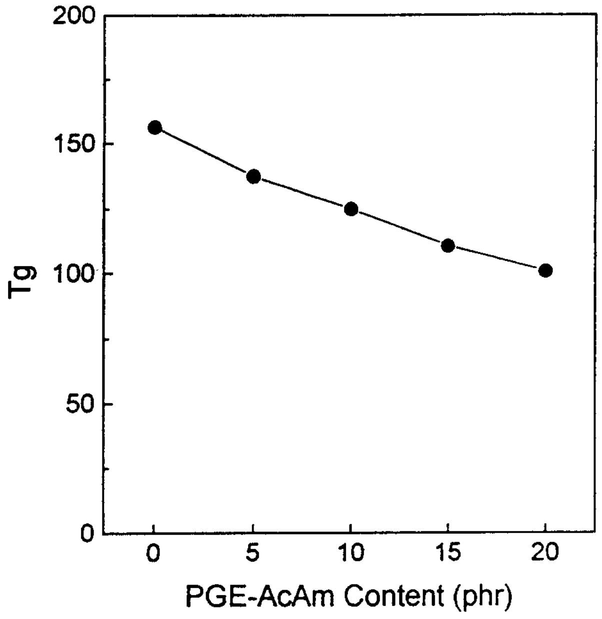

Fig. 7. Tg of DGEBA/MDA/PGE-AcAm system.

crement of PGE-AcAm content. These results are well agreed with the general relationship between impact strength and tensile strength that the improvement of tensile strength is obtained by sacrificing the impact strength. When stress loaded on the tightly crosslinked polymers, the stress propagated rapidly to the adjacent chains without the adsorption and dissipation of the impact, so the material followed the more brittle failure.

Glass transition temperature(Tg) of the system with different content of PGE-AcAm is shown in Fig.7. With the increment of PGE-AcAm content, Tg value decreased and this result is different from the relationship of tensile and impact strength. In the general thermosetts, if tensile strength increased, impact strength decreased and Tg value increased due to the high crosslink density. But this system was not and it can be explained by the increasing number of side chains. For, Tg is the temperature at which the end chains of the polymer can be movable.

4. Conclusions

From these results, the following conclusions were obtained.

1. Cure rate of the system increased with the addition of PGE-AcAm. The acceleration effect of PGE-AcAm was explained by the role of hydroxyl group.
2. When 5 phr of PGE-AcAm was added, tensile strength was improved about 15% and after that phr, the value was almost constant without dependence of PGE-AcAm content. However, impact strength decreased with the increment of PGE-AcAm.
3. With the addition of PGE-AcAm, the fracture surface had wider mirror zone and more brittle parabolic marking region.

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