

# THE MECHANICAL PROPERTY CHANGE OF A NEWLY DEVELOPED EPOXY SYSTEM AT HIGH TEMPERATURE AND OXIDATIVE CONDITIONS

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**SUMMARY:** A newly developed cationic catalyst, *N*-Benzylpyrazinium hexafluoroantimonate (BPH) has been used to cure epoxies. The effect of the catalyst concentrations on the thermal and mechanical properties has been studied. The used catalyst concentrations are 0.5, 1, 2, 3 and 5wt.%. Two given maximum retention times, i.e., 1028 hours at 265°C and 8 hours at 300°C were studied in terms of the mechanical flexural and impact properties in the presence of different concentrations of BPH in air condition. The BPH cured epoxies showed excellent thermo-oxidative resistance. Their mechanical properties nearly remained intact for the short retention times less than 12 hours. The maximum weight losses were about 4.5wt.% at 300°C and 12wt.% at 265°C. At 265°C, the finally retained flexural and impact strengths were respectively more than 30% and 40% on the basis of their initial values after the very long retention time of 1028 hours for the adequate catalyst concentrations of 1 and 2 wt. %.

**KEYWORDS:** *N*-Benzylpyrazinium hexafluoroantimonate, flexural and impact properties, thermo-oxidative resistance.

## INTRODUCTION

Epoxies have satisfactory properties such as excellent adhesion to a variety of substrate, low shrinkage on cure, no cure volatile, outstanding mechanical and electrical properties, suitable weather and chemical resistance, good dimensional stability and fatigue resistance. Epoxy resins becomes one of the most important thermosetting resins

in high performance composite materials [1-3].

Epoxies are cured in two ways: catalysis or polyaddition. In catalytic curing, the epoxy molecules react directly with each other in a reaction started by a catalyst. Such system is said to be homopolymerized. Epoxies cured by polyaddition contain hardeners mixed into the resins. These hardeners contain reactive groups that unite with the epoxy groups and become a vital part of the cured material. The most important classes of curing agents are the aliphatic and aromatic primary amines, polyamides, anhydrides and phenolic resins [2-4]. Thermal stability of cured epoxy resin is affected by the structure of hardener [5-7]. The high temperature atmospheric oxidation of the amine cured epoxy resins can yield amine oxides as decomposition gas, which attack the polymer backbone. Anhydride cured epoxy systems tend to split off the anhydride at the same conditions. The only catalyst curing system has been known to demonstrate high temperature resistance but their curing reactions are generally too vigorous to control. These catalysts have found their proper use as the additive to accelerate the curing reaction of the well-known amine or anhydride curing agents. It has been difficult to obtain a relatively thick laminate with only catalyst curing epoxy resin systems. The wide assortment of metal containing catalytic agent has been studied as initiators for ring opening polymerization of epoxide to control the catalytic curing reaction in epoxy resin systems, firstly in photo-initiating system and the to get the latency in the thermal curing systems [8-14].

A new cationic latent type catalyst has been developed by Korea Research Institute of Chemical Technology (KRICT) which can cure epoxy resins with moderate curing reaction rates [15-19]. The epoxy resins cured with this catalyst showed high temperature oxidation resistance. The aim of this work is to reveal their property changes during their long retention times under the high temperature oxidative conditions by using relatively thick resin casting specimens.

## **EXPERIMENTAL**

### **Materials and Sample preparation**

A cationic latent curing catalyst, *N*-Benzylpyrazinium hexafluoroantimonate (BPH) has been synthesized in KRICT by using benzyl bromide and pyrazine supplied from Aldrich Co. [15]. Epoxy resin used in this study was Diglycidylether of Bisphenol-A, YD-128, supplied from Kukdo Chem. Co. of Korea. The BPH was added into YD-128 such as 0.5, 1, 2, 3, and 5 percent by weight as a catalyst for curing reactions. The chemical structures of these two materials are shown in Fig. 1.

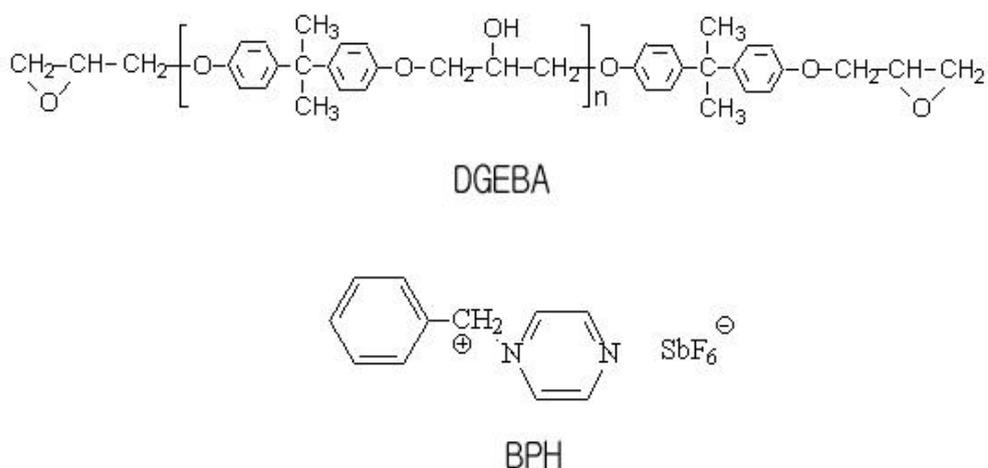


Fig. 1. Chemical Structure of DGEBA and BPH

The degassed resin and catalyst mixtures were cured in convection oven for 1 hour at 120°C and then 2 hours at 150°C, finally 2 hours at 180°C to get the fully cured 3mm thick resin casting specimens for flexural and impact tests.

### Measurements

The curing reaction of cured sample has been studied by Differential Scanning Calorimeter (DSC, du Pont DSC 910). The thermal stability of fully cured samples has been checked by Thermo-gravimetric Analysis (TGA, du Pont TGA 951). The heating rate for the thermal analysis have been always maintained as 10°C/min. Retention time effect on the specimens in terms of the thermo-mechanical property change in the oxidative conditions was tested in air circulating oven at the fixed temperatures of 265°C and 300°C. The maximum retention times were 1,028 hours at 265°C and 8 hours at 300°C. The changes of flexural properties and impact strength were tested with more than 5 specimens for each condition. The flexural test has been done with Instron 1125. The ratio between the thickness of the specimen and the support span was 1:16. The cross-head speed was fixed to 2mm/min by ASTM D790. The impact strength has been measured by using Izod Impact tester. The fracture surface has been analyzed by using Scanning Electron Microscope (SEM, JEOL Model 840A).

## RESULTS AND DISCUSSION

In catalytic curing of epoxy, the content of catalyst is very important. It would be a vital factor to control the inherent properties of the cured epoxy resins. The

concentration effect of catalyst on the curing reactions checked by DSC is presented in Fig. 2.

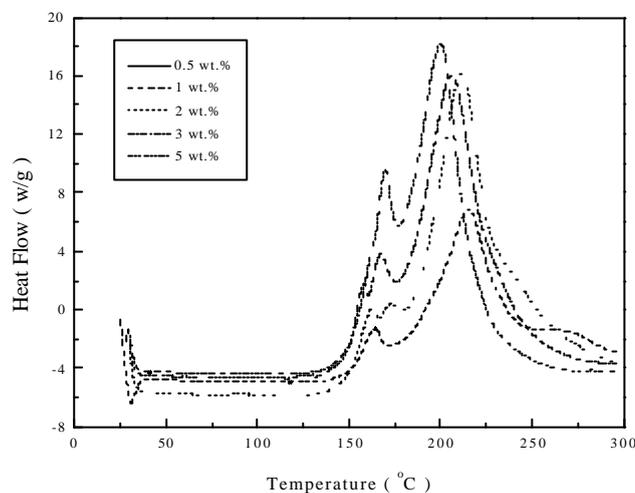


Fig. 2. The concentration effect of catalyst on DGEBA/BPH during curing reactions

There are two peaks for the catalyst contents of 0.5, 1 and 5wt.% on thermograms. But in the cases of 2 and 3wt.% for the catalyst contents, three peaks on thermograms were shown in this work. It means that there are three steps of reaction concerning the curing reactions of this system. The first two reactions are assumed to be activation and initiation stages of the curing reactions, for example, the scission of catalyst and reaction between the resulted catalytic compound and side functional group of epoxies was done. The last reaction is assumed to be a vigorous network formation through final curing reaction. The peak temperature of this final curing reaction has been remarkably lowered by increased catalyst concentration.

The information of only catalytic cured epoxy systems is very few in the monograph and periodicals. The concentration effect of catalyst on thermal decomposition property of fully cured samples prepared in this study has been measured by TGA, as shown in Fig. 3.

The initiation temperatures of thermal decomposition for the catalyst concentration of 0.5wt.% is about 200°C, and for the catalyst concentrations of 1, 2, 3 and 5 wt.% are in the range of 320-330°C. The most interesting phenomena in this system are that there is no weight loss before the initiation of the major decomposition of the system.

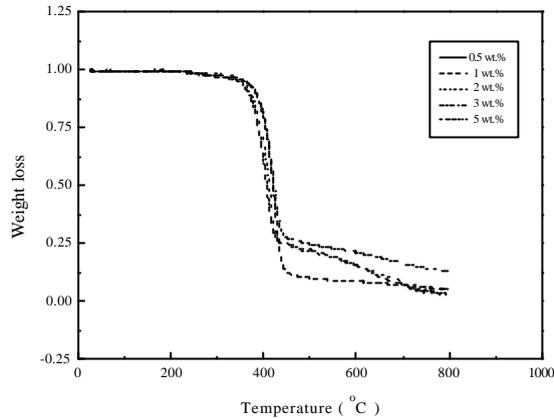


Fig. 3. The concentration effect of catalyst on thermal degradations measured by TGA

It means that the catalyst content of 0.5wt. % is insufficient to fully form the three dimensional networks during the cure reaction of epoxies. The accurate catalyst content in this system has a capability to induce well-connected high temperature stable three-dimensional networks. The results of TGA were obtained in the nitrogen atmosphere. But the real application of the polymeric materials should be considered in the high temperature atmospheric conditions. In these conditions, the oxygen can easily degrade the polymeric materials then deteriorate their properties. Until now the data of catalytically cured epoxies in high temperature air exposure is very few, because of the prejudices for their high temperature resistance assumed to be inferior to some high temperature polymers, for example polyimides.

The flexural properties of the fully resin casting samples were measured at room temperature (RT), as summarized in Table 1.

Table 1. The concentration effect of catalyst on the flexural properties of the fully cured samples at RT

Cat. Conc. (wt.% )	Flexural Modulus (GPa)	Flexural Strength (MPa)
0.5	3.02	67
1	2.98	73
2	2.86	81
3	2.73	84
5	2.71	92

The preliminary test of thermal resistance of this system has been done at 300°C with

selected some concentrations of catalyst, the most poorly cured samples (0.5wt.%) and adequately concentrated samples (1 and 2wt.%).

The weight losses of the fully cured in the oxidative conditions at 300°C have been measured. The results are summarized in Fig. 4.

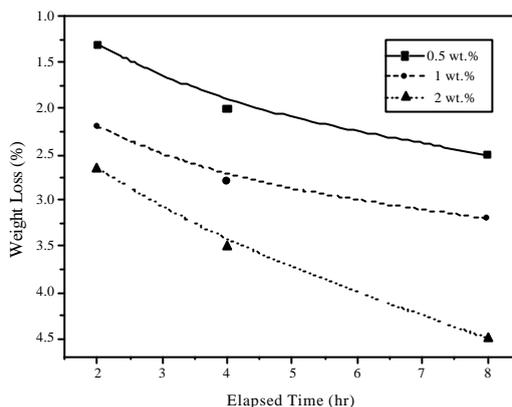


Fig. 4. The effects of retention time and catalyst concentration on weight losses at 300°C in air condition

The weight loss with catalyst concentration of 0.5wt.% is lowest among them. After the retention time of 8 hours in this condition, the final weight losses are 2.5, 3.0, 4.5% for the catalyst concentrations of 0.5, 1, and 2wt.%, respectively. For the catalyst concentration of 2wt.%, the weight loss has been accelerated during the extended retention time. Curiously the weight loss of the cured resin system with lowest catalyst concentration exhibits the lowest in this condition.

While, the mechanical flexural properties of this system due to the retention times at 300°C in air condition have been presented in Figs. 5 and 6.

The flexural modulus with the catalyst concentration of 0.5wt.% increases in increasing the elapsed time until 4 hour and then decreases a little. The flexural modulus with the catalyst concentrations of 1 and 2wt.% remain nearly a constant during the retention time of 8 hours. The poorly developed networks have a tendency to be rearranged due to the applied thermal energy and then degrade a little. The well-developed three-dimensional networks formed in this system remain nearly intact by the applied thermal energy and the presence of the oxygen in the air.

The flexural strength with the catalyst concentration of 0.5wt.% slowly increased and then remains a constant. Also, the flexural strength of 1 and 2wt.% remains nearly a constant during the whole retention time of 8 hours.

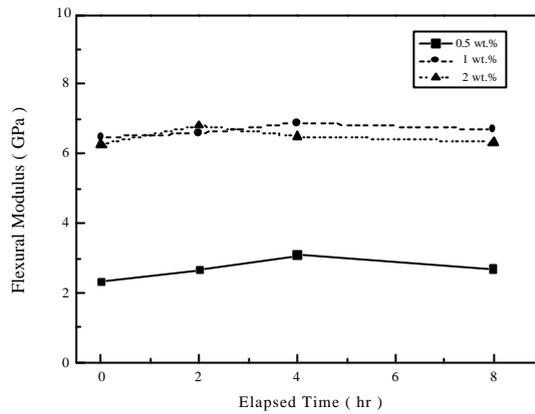


Fig. 5. The effects of retention time and catalyst concentration on flexural modulus

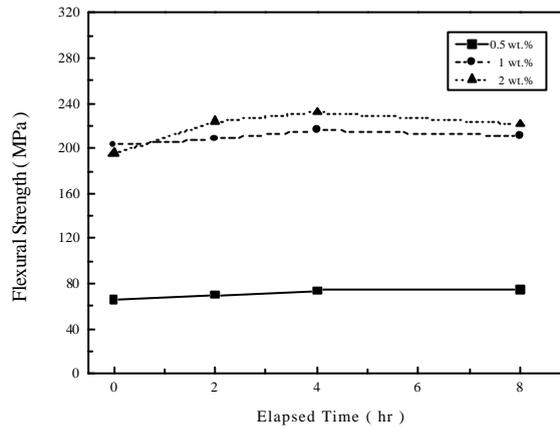


Fig. 6. The effects of retention time and catalyst concentration on flexural strength

The same procedure has been done at 265°C for more extended retention time and the whole catalyst concentrations.

The result of the retention time and the catalyst concentration on weight loss are shown in Fig. 7.

The weight loss is proportional to the catalyst concentrations. The samples with the catalyst contents of 3 and 5wt.% have failed down after retention time of 600 hours. However, the samples with the catalyst contents of 0.5, 1 and 2wt.% retained its initial shape after the retention time of 1028 hours showing the final weight loss of about 11wt.%.

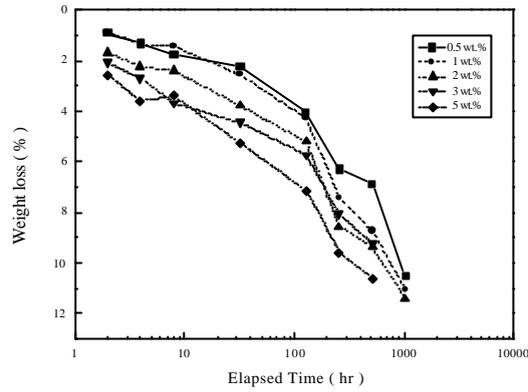


Fig. 7. The effects of retention time and catalyst concentration on the weight loss

The effects of retention time and catalyst concentration on the flexural property changes at 265°C in air condition are shown in Figs. 8 and 9.

The flexural modulus with the catalyst contents of 0.5, 1 and 2wt.% are relatively constant for the retention time shorter than 128 hours. But the results with the catalyst contents of 3 and 5wt.% give a drastic change. It seems that there is some severe change in internal structures due to the rearrangement of the structure and the complex chemical reactions induced by the catalyst.

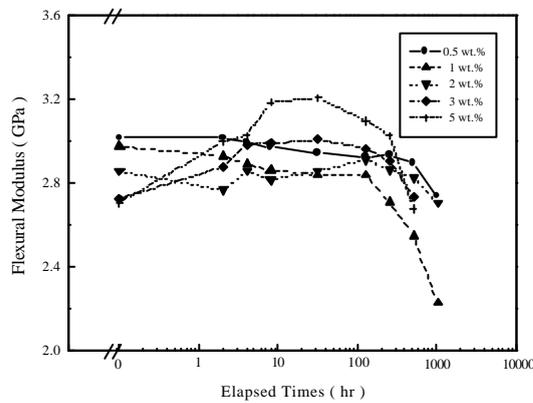


Fig 8: The effects of retention time and catalyst concentration on the flexural modulus

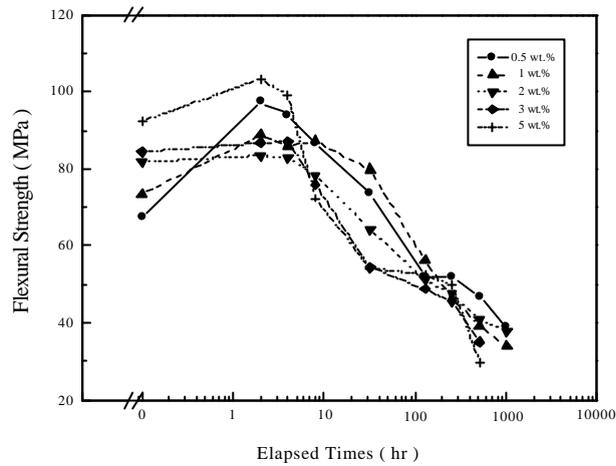


Fig. 9. The effects of retention time and catalyst concentration on the flexural strength

The results of the flexural strength reveal more clearly the facts indicated in the results of Fig. 9. The flexural strength of the samples with the catalyst contents of 2 and 3wt.% remained nearly a constant for the short retention times less than 12 hours. For samples of the other concentrations showed the very sharp increase of the flexural strength and then continuously decrease throughout the retention times. The finally remained flexural strength was about 30% of their initial values.

The impact property changes of the samples studied at 265°C in air condition are shown in Fig. 10.

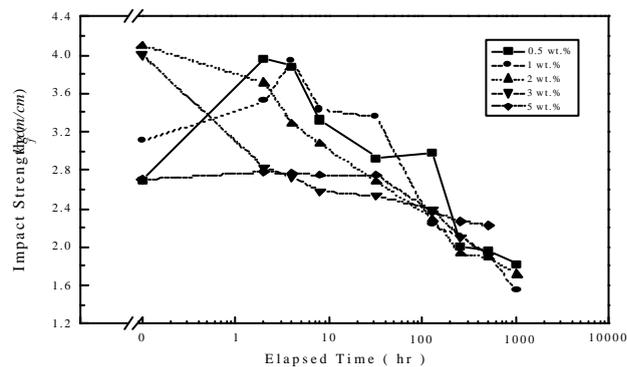


Fig. 10. The effects of retention time and catalyst concentration on the impact strength

The results of the impact strength showed a similar tendency to that with the flexural strength. The finally remained impact strength is about 40 % of their initial values. The decrease of the impact strength is relatively lower for the retention times of 128 hours. This fact means that the obtained three-dimensional networks in this study inherently have very strong toughness. The retention time effect on the fracture surfaces in oxidative high temperature is shown in Fig. 11, in the case of 1wt.% concentration of the sample.

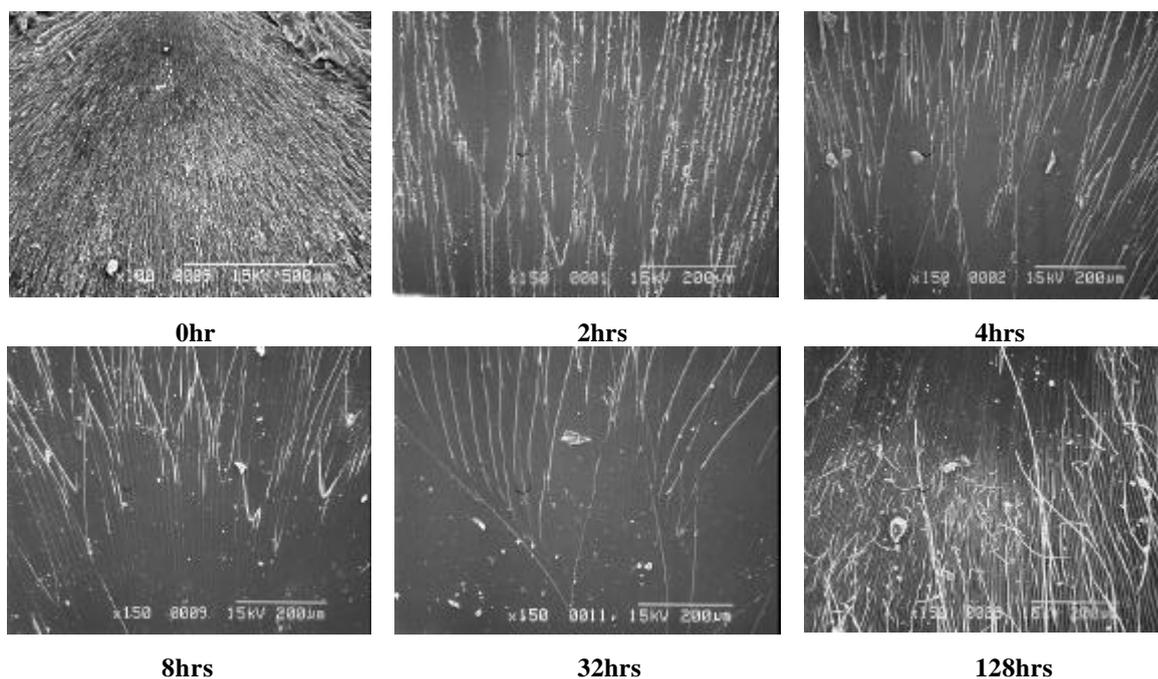


Fig. 11. Some example of the retention time effect on the fracture surfaces induced by impact test

All the samples studied, the impact surfaces showed some hair like pattern. It would be confirmed that the internal structure formed from the final networks has a tendency of linear arrangements.

## CONCLUSIONS

The BPH cured epoxies have inherent high temperature stability that can be also sustained in highly oxidative conditions. They produce no degradation product before

the initial degradation temperature for well-developed three-dimensional network with adequate catalyst concentrations. The mechanical properties of this system remained nearly intact for short retention times of 8 to 12 hours in very severe oxidative conditions such as 265°C and 300°C in air atmosphere. The high catalyst concentration can give some very complex chemical processes and structural rearrangements in internal structures, although the final remained mechanical properties are meaningful for the future development of this BPH cured type epoxies.

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