

에폭시/PMR-15 폴리이미드 블렌드계의 경화동력학 및 열안정성에 관한 연구

이재락* · 이화영 · 박수진

Studies on Cure Behavior and Thermal Stability of Epoxy/PMR-15 Polyimide Blend System

Jae-Rock Lee*, Hwa-Young Lee, and Soo-Jin Park

Key Words : Epoxy, PMR-15, Polyimide, Cure behavior, Thermal stability

ABSTRACT

In this work, the blend system of epoxy and PMR-15 polyimide is investigated in terms of the cure behaviors and thermal stabilities. The cure behaviors are studied in DSC measurements and thermal stabilities are also carried out by TGA analysis. DDM (4,4'-diamino diphenyl methane) is used as curing agent for EP and the content of PMR-15 is varied within 0, 5, 10, 15, and 20 phr to neat EP. As a result, the cure activation energy (E_a) is increased at 10 phr of PMR-15, compared with that of neat EP. From the TGA results of EP/PMR-15 blend system, the thermal stabilities based in the initial decomposed temperature (IDT) and integral procedural decomposition temperature (IPDT) are increased with increasing the PMR-15 content. The fracture toughness, measured in the context of critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}), shows a similar behavior with E_a . This result is probably due to the crosslinking developed by the interactions between intermolecules in the polymer chains.

1. INTRODUCTION

In the past few decades, epoxy resins have found extensive use in many industrial applications, including high-strength composite, and printed circuit boards.^{1,2} Epoxy resins are well known for some unique properties, including outstanding adhesion to most surfaces, high mechanical strength, and chemical resistance.^{3,4} They have been used as adhesives, coatings, and resin matrices for advanced composites. However, it is also well known that epoxy resins have rigid, brittle, and poor crack resistance in nature⁵. A large number of epoxy system has been employed to improve their toughness and

currently investigated on the choice of the chemical structures of epoxy prepolymer, hardner, stoichiometric ratio, and thermoset of thermoplastic blending^{5,6}.

Polyimide resins are comprised of one of the most stable and heat resistant polymer system. PMR polyimide (most noticeably PMR-15), prepared by polymerization of monomeric reactants, are high temperature polymers used as the matrix resins in fiber-reinforced composites for a variety of advanced aerospace applications. As composite materials, they posses certain unique characteristics, such as good solvent resistance, high temperature performance, and outstanding mechanical properties.^{7,8}

The objective of this work is to study the effect of different weight percent of PMR-15 polyimide on the cure behaviors, thermal stabilities, and mechanical interfacial properties of an epoxy/PMR-15 blend system.

*Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-600, Korea

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

In the system studied, the epoxy resin was the diglycidyl ether of bisphenol A (YD-128, supplied by Kukdo Chemical Co. of Korea) and PMR-15 polyimide for the present investigation was synthesized through the reaction from BTDA (3,3'-4,4'-benzophenone-tetracarboxylic dianhydride, M_w : 322, m.p : 224~226 °C), NA (5-norbornene-2,3-dicarboxylic anhydride, M_w : 164, m.p : 165~167 °C), and DDM (4,4'-diamino diphenyl methane, M_w : 199, m.p : 90 °C). And the DDM was used as a curing agent for epoxy resin. The chemical structure of epoxy, PMR-15, and DDM are shown in Fig. 1.

The epoxy resin was heated to melt at 50 °C for 30 min in the beaker. After melting of epoxy resin, the PMR-15 was added into the beaker. The content of PMR-15 was varied within 0, 5, 10, 15, and 20 phr to neat epoxy. Samples were then degassed in a vacuum oven at 80 °C. After DDM was added to the mixture, and the reactants were homogenized by a stirrer. The homogenous mixture was poured into a mold and the cure cycle of a fully cured EP/PMR-15 blend system was 120 °C for 30 min, 150 °C for 2 h, and finally postcured at 180 °C for 1 h.

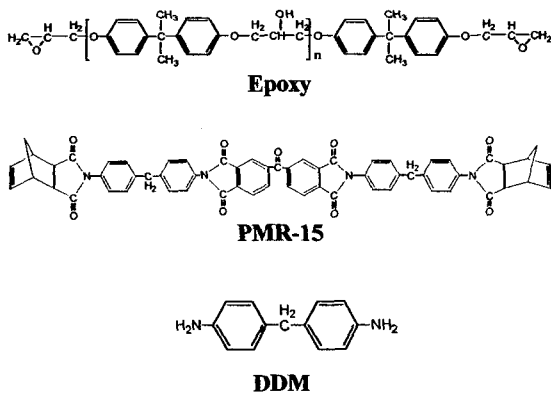


Fig. 1. Chemical structures of EP, PMR-15, and DDM.

2.2 Cure Behavior

The cure kinetics were evaluated by the measurement of the cure activation energies (E_a) with the dynamic DSC (Perkin Elmer DSC-6) method. The samples were placed in aluminum sample pans, and the experiments were performed under a flow of dry nitrogen gas. Temperature scans were performed at different heating rates (5, 10, 15, and 20 °C/min) from room temperature to 350 °C.

2.3 Thermal Stability

The thermal stabilities were performed by a thermogravimetric analyses (TGA 951, Du Pont), at a heating rate of 10 °C/min from 35 to 800 °C to investigate the thermal stability of the cured resins.

2.4 Mechanical Interfacial Property

An Instron tester (Model 1125) was used to measure mechanical properties of the EP/PMR-15 blend system. The critical intensity factor (K_{IC}), which is one of the fracture toughness parameters, can be characterized by a single-edge-notched (SEN) beam fracture toughness test (ASTM E399) in three-point bending flexure. Notches were cut using a diamond saw, approximately half the depth of the specimen. A span-to-depth ratio of 4:1 and cross-head speed of 1 mm/min were used.

3. RESULTS AND DISCUSSION

3.1 Cure Behavior

Fig. 2 shows the dynamic DSC curves for the cure of epoxy with different contents of PMR-15. The DSC scans at different heating rates allow us to determine the cure activation energy (E_a) of the overall process by Kissinger method.⁹

$$-\ln(\phi/T_p^2) = \frac{E_a}{RT_p} - \ln(AR/E_a) \quad (1)$$

where, ϕ is the heating rate, T_p the peak exothermic temperature, A the frequency factor, and R the gas constant.

Table 1 shows the value of cure activation energy obtained by Kissinger method as a function of the PMR-15 content. It is clearly observed that the cure activation energies of EP/PMR-15 blend system show maximum value in 10 phr of PMR-15 content, and decreases slightly with increasing PMR-15 content above 10 phr. From these results, it is expected that the addition of 10 phr PMR-15 in epoxy can lead to a more highly crosslinking in the epoxy/PMR-15 blend system.

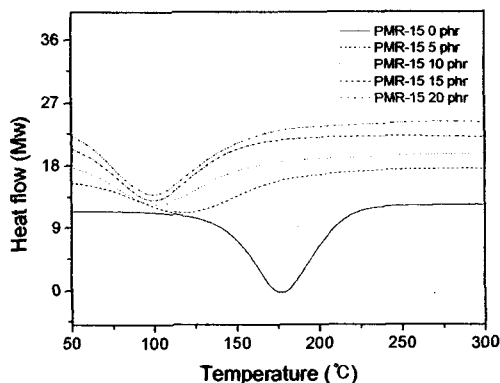


Fig. 2. DSC thermograms of EP/PMR-15 blends.

Table 1. Cure Activation Energies (E_a) Obtained by Kissinger Equation for EP/PMR-15 Blends

Content of PMR-15	E_a (kJ/mol)
0 phr	48.5
5 phr	57.9
10 phr	69.9
15 phr	50.7
20 phr	45.8

3.2 Thermal Stability

It is well known that one of the basic requirements in the multicomponent epoxy system is to have a homogeneous mixture prior to the curing process. Thermograms of epoxy resins prepared from blending different compositions of PMR-15 are superimposed on Fig. 3. As can be seen from these results, the thermal stability of the EP/PMR-15 blend system is largely improved with increasing the PMR-15 content. This enhancement on the thermal properties is due to the strong aromatic/heterocyclic structures presented in PMR-15.

Thermal stability has also given by initial decomposition temperature (IDT) and integral procedural decomposition temperature (IPDT) as shown in Table 2.¹⁰

Fig. 4 shows the schematic diagram of Doyle's proposition for determining the IDT of a major factor on thermal stabilities of the samples and the IPDT is calculated as follows:¹¹

$$IPDT (^\circ C) = A^* \cdot K^* (T_f - T_i) + T_i \quad (2)$$

where, A^* is the area ratio of total experimental curve divided by total TGA thermogram $[(A_1 + A_2)/(A_1 + A_2 + A_3)]$, T_i the initial experimental temperature, and T_f the final experimental temperature.

As a result, we know that thermal properties of nanocomposites are superior to pure epoxy resins due to the increase of crosslinking density between the epoxy resin and PMR-15. It can be also seen that the structure of PMR-15 is attributed to increase the thermal stability of epoxy/PMR-15 blend system.

Table 2. Thermal Stabilities of EP/PMR-15 Blend System from TGA

Content of PMR-15	IDT ($^\circ C$)	IPDT ($^\circ C$)
0 phr	244.8	485
5 phr	269.9	574
10 phr	288.9	611
15 phr	315.6	639
20 phr	321.7	696

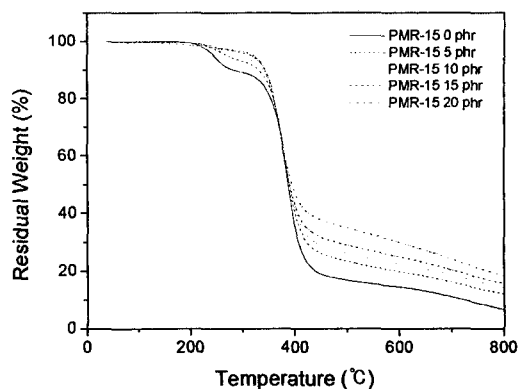


Fig. 3. TGA thermograms of EP/PMR-15 blends.

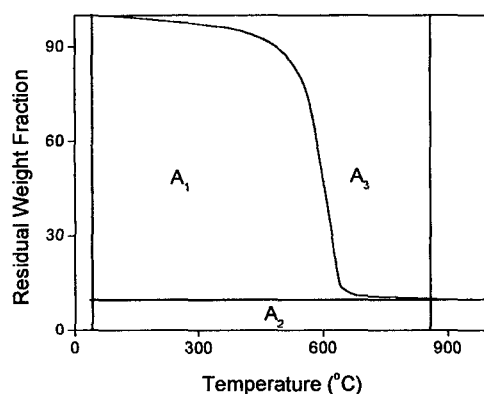


Fig. 4. The schematic diagram of the Doyle's method for determining the IPDT.

3.3 Mechanical Interfacial Property

The degree of adhesion at the interface between PMR-15 and matrix can be investigated by the critical stress intensity factor (K_{IC}). For the single-edge-notched (SEN) beam fracture toughness test, the value of K_{IC} is calculated as follows,^{12,13}

$$K_{IC} = \frac{PL}{bd^{3/2}} Y \quad (3)$$

where, P is the rupture force, L the span between the supports, Y the geometry factor described in ASTM E399, and b and d are the specimen width and thickness, respectively.

In addition, in plane strain, the value for K_{IC} and the critical strain energy release rate (G_{IC}) for the same material and testing conditions, in theory, are related as follows,¹⁴

$$G_{IC} = \frac{(1-\nu^2)K_{IC}^2}{E} \quad (4)$$

where, ν the Poisson's ratio ($\nu = 0.3$ is evaluated in this work) and E the tensile modulus at the same testing conditions as the fracture test.

The K_{IC} and G_{IC} are described by the state of stress in the vicinity of the tip of a crack as functions of the specimen geometry, the crack geometry, and the applied load on the basis of linear elastic fracture mechanics.

Table 3 shows the mechanical interfacial properties of epoxy/PMR-15 blend system to investigate the relationship between the fracture toughness of the material and the interfacial adhesion in blend system. The experimental results show that both K_{IC} and G_{IC} of epoxy/PMR-15 blend system are increased at 10 phr of PMR-15, compared with that of neat epoxy. Mechanical interfacial properties (K_{IC} and G_{IC}) show a similar behavior to E_a , which can be attributed to the crosslinking developed by the interactions between intermolecules in the polymer chains.

Table 3. The K_{IC} and G_{IC} of EP/PMR-15 Blend System

Content of PMR-15	K_{IC} (MPa/m ^{1/2})	G_{IC} (kJ/m ²)
0 phr	2.49	3.87
5 phr	3.29	6.37
10 phr	5.03	12.58
15 phr	3.72	8.27
20 phr	3.16	6.04

4. CONCLUSION

In this work, the cure activation energy (E_a) obtained by dynamic DSC shows maximum value in 10 phr PMR-15 content, and can be correlated with the results of crosslinking activation energy obtained by mechanical interfacial properties. Mechanical interfacial properties (K_{IC} and G_{IC}) also show maximum value in 10 phr PMR-15 content, and systematically decreased with increasing PMR-15 content, which could be resulted from the crosslinking developed by the interactions between intermolecules in the polymer chains. The thermal stabilities based on the initial decomposed temperature (IDT) and integral procedural decomposition temperature (IPDT) are increased with increasing the PMR-15 content, and the maximum value of the IDT is 321.7°C and that of IPDT is 696°C. It can be attributed to the bulk side groups and stable imide ring structure presented in PMR-15 polyimide.

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