

The Effects of Poly(tetramethylene ether glycol) on the Physical Properties of Epoxy Resin

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1. INTRODUCTION

Epoxy resins are currently one of the most widely used thermoset polymers. Applications of epoxy-based materials range from common to structural adhesives as well as to matrix materials for high performance composites¹. The outstanding versatility of this resin can be related to the reactivity of the epoxy group, which can be opened by a large number of different chemical compounds, such as aliphatic and aromatic amines, anhydrides and poly-amides². Moreover, the carbon atoms in the epoxy ring are partially positively charged due to the greater electronic affinity of the oxygen atom³. The combined characteristics are responsible for the instability of the epoxy ring and favor its opening. Therefore, a variety of epoxy systems may be produced by selecting distinct types of hardeners and diluents. As a consequence, a wide range of mechanical, physical and chemical properties may be obtained with the same epoxy monomer and are the basis for the many commercial uses of the material. Besides the type of diluents, it is worth mentioning that the properties of specific epoxy are also dependent on the amount of diluents and its molecular weight⁴⁻⁶. The low molecular weight reactive diluents for the epoxy resins can be considered as chain extenders acting as elasticizing agent after resin curing. While the plasticizing effect of non-reactive diluents results in decreased tensile and shear properties, but improves the adhesive performance and offers proper viscosity and good stability in processing. Also, in case of the high molecular weight non-reactive diluents, they might form the domains separated from epoxy resins in which they behave as toughening agents.

In this work, therefore, an evaluation of the thermal and mechanical behavior of epoxy system that occur as a function of the variation of content and molecular weight of diluent will be of interest, in order to understand the resulting changes in the final properties of the epoxy-based materials. As a non-reactive diluent, Poly(tetramethylene ether glycol)(PTMG), a kind of polyol, was used in this study and its effects on the cure reaction and physical properties were investigated.

2. EXPERIMENTALS

2.1 Materials

The epoxy resin used was YD-127 (Kukdo Chemical co.) which has molecular structure of diglycidyl ether of bisphenol A(DGEBA) as depicted in Fig.1. The resin was cured with 24phr of K-H-100 (Kukdo Chemical co.) which is diethyltoluenediamine (DETDA) as shown in Fig.1. As a

diluent, Poly(tetramethylene ether glycol) (PTMG) from DuPont co. in Fig.1 was used in variation of the number-average molecular weight as 650, 1400 and 2900 without any purification.

2.2 Resin preparation

Since the DGEBA monomer used has an equivalent weight of around 189, the stoichiometric

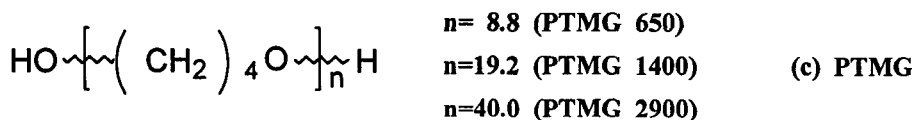
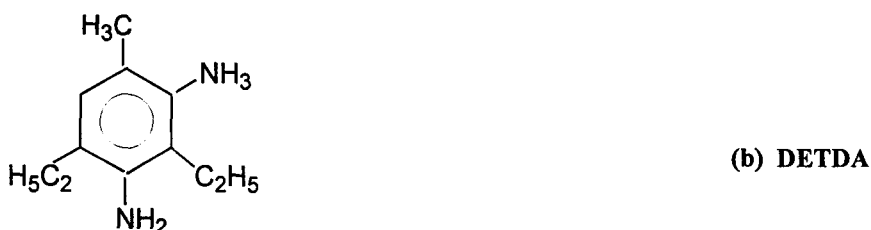
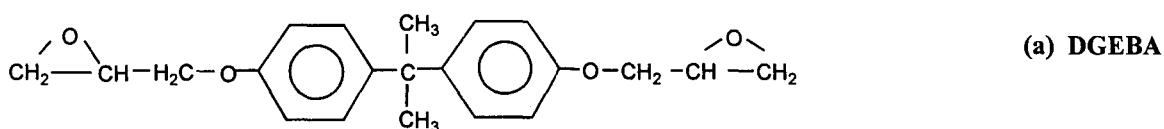


Fig.1 Schemes of (a) epoxy resin, (b) hardner and (c) diluent used in this study

ratio of the DGEBA/DETDA system corresponds, on a weight basis, to 24parts of hardener per a hundred part of resin. In order to investigate the effect of non-reactive diluent content on this epoxy system, the content of PTMG was varied as 10, 20 and 30phr at each PTMG molecular weight (650, 1400 and 2900).

2.3 Measurements of thermal and mechanical properties

The cure behavior and T_g were measured by Modulated DSC Program in DSC-2910 cell (TA Instruments) under N₂ atmosphere. An oscillation amplitude and period were fixed at 1 °C and 60sec, respectively throughout the measurement, and a heating rate also fixed at 3 °C/min. Mechanical properties were measured by Instron 4467 Tester with a clip-on type extensometer..

3. RESULTS AND DISCUSSION

Fig. 2 shows the changes in the heat of cure during the dynamic heating in DSC. The values of

heat of cure in Fig. 2 were the compensated values by the fractions of epoxy resin and hardener only. Obviously, a certain trend is found that the higher molecular weight of PTMG leads to the higher heat of cure as well as the higher content of PTMG does to the lower heat of cure. These cure behavior seemed to be related to the dispersion state of PTMG molecules in the resin. The decrease of heat of cure with increasing content of PTMG seemed to be due to the separating effect of PTMG molecules distributed in the reaction sites between resin and hardener. In particular, it can be thought that the lower molecular weight PTMG has more influence on the heat of cure than higher molecular weight PTMG via restricting the cure reaction by the well-distributed smaller PTMG molecules.. Thus, at the lowest molecular weight and the largest content of PTMG, the lowest value of heat of cure was obtained.

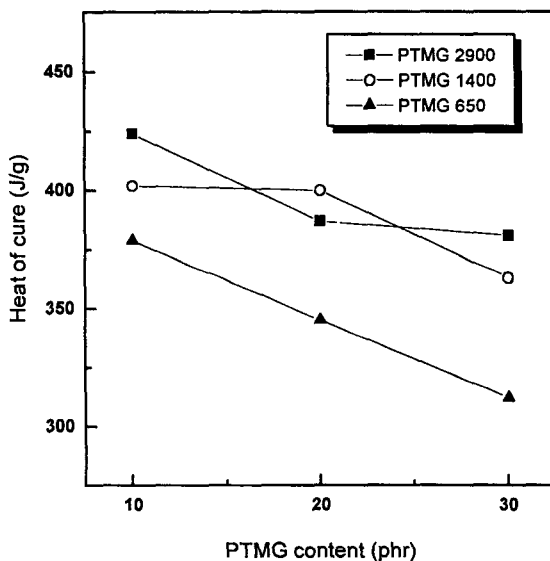


Fig.2 Heat of cure of epoxy resin as the PTMG content

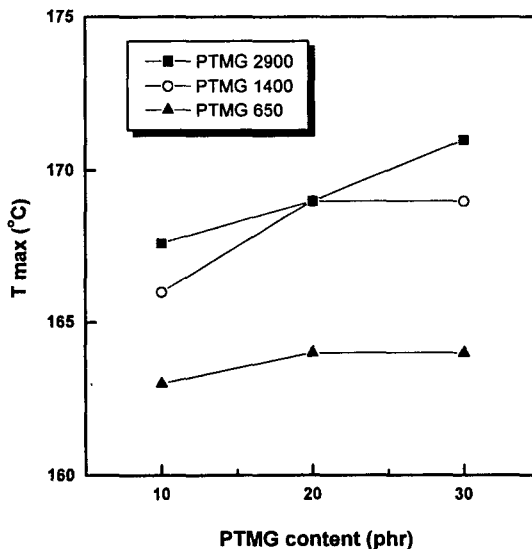


Fig.3 Peak temperature of cure reaction as the PTMG content

The peak temperatures (T_{max}) of cure reaction were shown in Fig.3. As the increase of molecular weight and content of PTMG, T_{max} shifts slightly to the high temperature due to the same reason as the heat of cure behavior. Consequently, the inclusion of PTMG as a diluent has a great influence on the cure behavior of epoxy resin system, although it should not react with the resin. Fig.4 shows the variations of glass transition temperature (T_g) of cured epoxy resin as the content and molecular weight of PTMG. The condition of the lowest molecular weight and highest content of PTMG gives the lowest T_g of the epoxy owing to the largest restricting behavior of the small and well-dispersed molecules of PTMG in the resin, as described before. In the contrary, T_g , in case of 2900 molecular weight of PTMG, is almost unchanged with the PTMG content and is very similar to that of PTMG free epoxy (167°C). This might be originated from the possible formation of PTMG self-domain in the resin which exist separately from the resin and do not affect T_g of the epoxy resin. In this case, PTMG would play as a toughening or flexibilizing agent of the resin. And above results should be mentioned and verified with the viscosity and mechanical properties of epoxy resin.

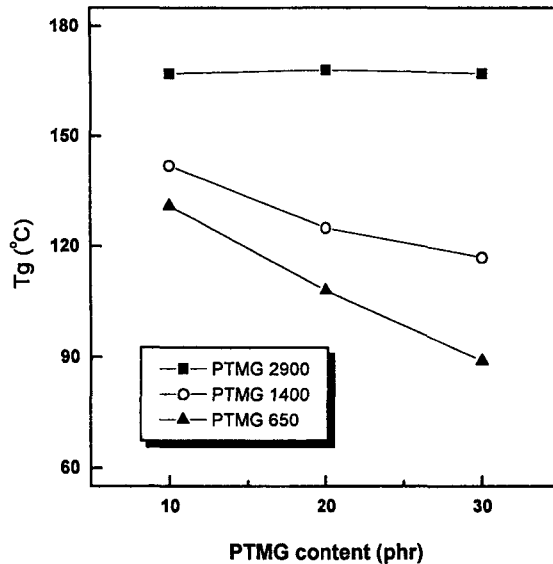


Fig.4 Glass transition temperature of cured epoxy resin as the PTMG content

4. CONCLUSION

The cure behaviors such as heat of cure and cure temperature were investigated to understand the inclusion effect of PTMG as a diluent onto the epoxy resin system. Physical properties of resultant cured resin were also estimated in terms of the content and molecular weight of PTMG. As the result we can obtain following conclusions.

1. The inclusion of PTMG as a diluent has an influence on the cure behavior of epoxy resin system.
2. Heat of cure of epoxy was greatly lowered by the increase of content and decrease of molecular weight of PTMG, due to the less cure reaction from the restricting behavior of well dispersed smaller PTMG molecules onto the reaction between epoxy and hardener.
3. Tg of cured epoxy with PTMG is lowered, except 2900 molecular weight, than that of PTMG free epoxy resin originated from less cure reaction. And in case of 2900 molecular weight PTMG, almost no change in Tg is observed which indicates the possibility of formation of PTMG self-domain separated from the epoxy resin.

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