EFFECTS OF ADDITIVES ON THE CHEMICAL RECYCLING OF AMINE AND ANHYDRIDE CURED EPOXY RESIN IN SUBCRITICAL WATER

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Abstract

Epoxy resin is most commonly used in producing fiber reinforced polymer composites and printed circuit boards due to its chemical resistance, heat resistance and good mechanical properties, but it is difficult to recycle this kind of materials. Sub- and supercritical water have been an attractive solvent for the chemical recycling of epoxy resin because they are cheap, non-toxic and nonflammable. However, the decomposition efficiency is required further increasing. In this study, different additives were added into subcritical water to increase the decomposition efficiency of amine and anhydride cured epoxy resin. Phenol and KOH were observed to show a synergetic effect in decomposing amine cured epoxy resin. The resin decomposition efficiency reaches a maximum at a weight ratio of KOH/phenol=1/10. KOH is more effective than phenol for decomposing the anhydride cured epoxy resin. Ethanolamine is also an effective additive for decomposing this kind of epoxy resin. Alkaline conditions are found to be favorable to the cleavage of ester linkages. On the above basis, a method is established to recover carbon fibers with no tensile strength loss from a carbon fiber reinforced epoxy resin composite.

Keywords: *Epoxy resin, subcritical water, amine, anhydride.*

1. Introduction

Epoxy resin is most commonly used in producing fiber reinforced polymer composites and printed circuit boards due to its chemical resistance, heat resistance and good mechanical properties, but it is difficult to recycle this kind of materials [1]. In recent years, Sub- and supercritical water has been an attractive solvent for the chemical recycling of epoxy resin materials because it is cheap, non-toxic and nonflammable [2]. However, exploring new reaction system is necessary to improve the decomposition efficiency and lower the cost of facility and operation.

2. Materials and Methods

4, 4'-diaminodiphenylmethane (DDM) and methyl-tetrahydrophthalic anhydride (MeTHPA) cured epoxy resins were prepared by mixing diglycidyl ether of bisphenol A with corresponding curing agent, respectively. The cured resin was decomposed in a non-stirred batch autoclave reactor. The decomposition products were characterized by FTIR and GC-MS.

3. Results and Discussion

Fig. 1 shows the decomposition rate of the DDM cured epoxy resin in subcritical water with different additives. As shown in Fig. 1, 12.6 wt% of DDM cured resin was decomposed in water at 315 °C for 30 min. The decomposed resin percentage increased to 15.2 and 40.3 wt% when phenol and KOH were added into water, respectively. It is noted that adding phenol and KOH simultaneously led to the complete decomposition of the resin under the above conditions. This phenomenon indicates that phenol and KOH have some synergistic effect on the decomposition of DDM cured epoxy resin.

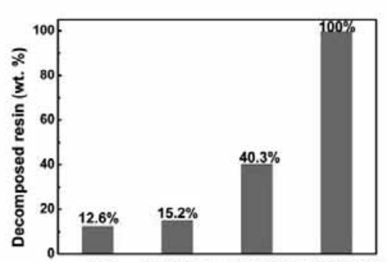

Fig. 1. Decomposition rate of the DDM cured epoxy resin in different reaction system.

Fig. 2 shows the effect of the content of phenol on the decomposition rate of the DDM cured epoxy resin in water at 315 °C for 30 min at a fixed weigh ratio of KOH/H_2O=1/100. It can be observed from Fig. 2 that the presence of a small quantity of phenol (1 g and 2.5 g) decreased the decomposed resin percentage comparing with the case only adding KOH. When the quantity of phenol increased, more cured resins were decomposed. The decomposed resin percentage reached a maximum at a KOH/phenol weight ratio of 1/10.

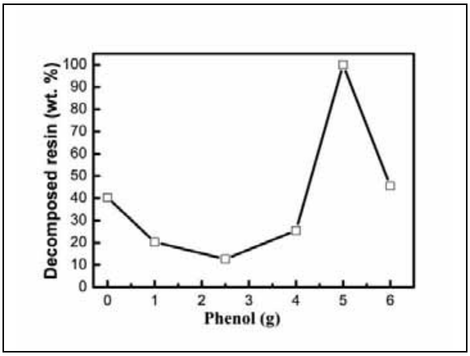

Fig. 2. Effect of the phenol content on the decomposition rate of the DDM cured epoxy resin in subcritical water with fixed KOH.

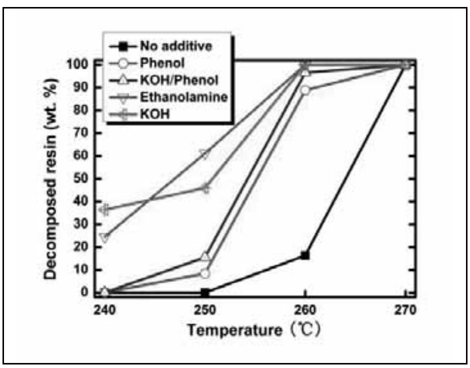

Fig. 3. Effect of the reaction temperature on the decompoition rate of the MeTHPA cured resin with different additives in subcritical water.

Fig. 3 shows the effect of the reaction temperature on the decomposition rate of the MeTHPA cured resin with different additives in subcritical water for 30 min. As can be seen in Fig. 3, higher decomposition rate was observed in the presence of alkaline materials such as KOH and ethanolamine. The combined phenol and KOH did not take the effect similar to DDM cured systems.

Fig. 4 shows the FT-IR spectra of MeTHPA cured epoxy resin and decomposed products in subcritical water with and without ethanolamine. The peak at about 1730 cm^{-1}, which is attributed to ester bond, shifted to 1645 cm^{-1} (attributed to amide group) after subcritical water treatment in the presence of ethanolamine, indicating that amino group of the ethanolamine attacked the ester bond and formed amide.

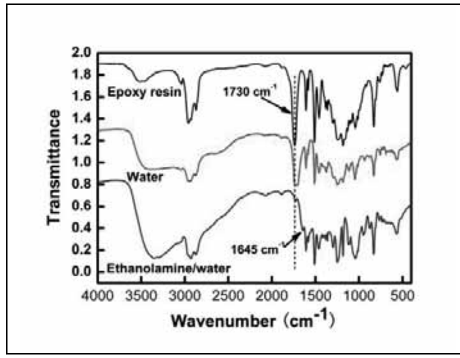

Fig. 4. FT-IR spectra of MeTHPA cured epoxy resin and its decomposed products.

4. Conclusions

Various additives were used in subcritical water to improve the decomposition rate of the amine and anhydride cured epoxy resins. A combined effect of phenol and KOH was found for the decomposition of DDM cured resin. The resin decomposition efficiency reaches a maximum at a weight ratio of KOH/phenol =1/10. Among the additives used in this work, the most efficient one in promoting decomposition of anhydride cured resin was alkaline materials, which in favor of cleaving ester bond in the resin network.

References

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