ORGANOCATALYTIC DEPOLYMERIZATION OF ANHYDRIDE CURED EPOXY RESIN AT MILD CONDITIONS

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Abstract

Alkaline catalyst is usually used as catalyst for decomposition of thermoplastic and thermoset polymer containing ester bond. However, inorganic catalyst is difficult to remove from decomposition products. Here, we report an efficient and mild depolymerization method using organic base as catalyst to decompose anhydride cured epoxy resin. The yield of eliminated resin was compared for different organic base in the ethylene glycol. N-methyl-piperidine was an appropriate catalyst because it can be recycled with ethylene glycol by distillation. The approach provides a new potential way to decompose the polymer containing ester bond.

Keywords: Epoxy resin, Depolymerization, Organic base

1. Introduction

Epoxy resins are the most commonly used thermosets in producing fiber reinforced polymer composites and printed circuit boards because of their combination of chemical resistance, heat resistance and good mechanical properties. Currently, waste epoxy resin materials are decomposed mainly using thermal processing and solvolysis [1, 2]. Solvolysis process recovers not only inorganic reinforced materials but also useful organic products by breaking of chemical bonds of epoxy resins [3-5]. However, the high pressure nature of many solvents at high temperatures brings a lot of trouble for processing speed and cost control. On the other hand, the inorganic catalyst can increase the depolymerization efficiency but is difficult to remove from decomposition products. Here, we describe an efficient and mild depolymerization method using ethylene glycol (EG) and organic catalysts, which can be simultaneously recycled by distillation after depolymerization.

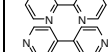
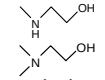
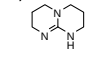
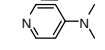
2. Materials and Methods

The matrix resin used in this study was diglycidyl ether of bisphenol A (DGEBA) with the average epoxide value of 0.53 purchased from Sigma-Aldrich. Anhydride cured samples were prepared by mixing the DGEBA, methyl tetrahydrophthalic anhydride (MeTHPA) and curing accelerator N, N'-dimethyl benzyl amine (BDMA) at room temperature and then heating at 100 ^{o}C for 2 h, 150 ^{o}C for 5 h. The weight ratio of DGEBA/MeTHPA/BDMA is 100/78/1. The epoxy resin chips, EG and catalyst were introduced into a glass flask equipped with a reflux condenser. The system was kept in an inert atmosphere at designated temperature. EG was distillated after the reaction is over. The distillated solvent and catalyst were characterized by H^1-NMR.

3. Results and Discussion

Table 1 shows the results of experiments conducted to compare the degradation efficiency of eight different organic catalysts in EG. Reaction temperature was fixed at 180 ^{o}C and the reaction time was 4 h. 2, 2'-dipyridyl shows no activity in decomposition of anhydride cured epoxy resin. The yield of eliminated resin for 2-(Methylamino)ethanol and piperidine was 29.1% and 42.5%, respectively. And the yield of eliminated resin for N, N-dimethylethanolamine and N-methyl-piperidine was 39.1% and 100%, respectively. This result indicated that tertiary amine shows better activity than secondary amine. DMAP also shows high activity in decomposition of epoxy resin. However, the boiling point of DMAP is 162 ^{o}C at 50 mmHg. So it is difficult to remove it from the decomposition products. The boiling point of N-methyl-piperidine is 106 ^{o}C and is lower than that of EG. We distillated EG and N-methyl-piperidine at 180 ^{o}C to recycle solvent and catalyst at the same time.

Table 1. Degradation efficiency of different organic base in EG.

Organic base	Molecular formula	Yield of eliminated resin (%)
2,2'-dipyridyl		0
4,4'-dipyridyl		8.0
2-(Methylamino)ethanol		29.1
N,N-dimethylethanolamine		39.1
1,5,7-triazabicyclo[4.4.0] dec-5-ene (TBD)		84.5
Piperidine		42.5
N-methyl-piperidine		100
4-Dimethylaminopyridine		100

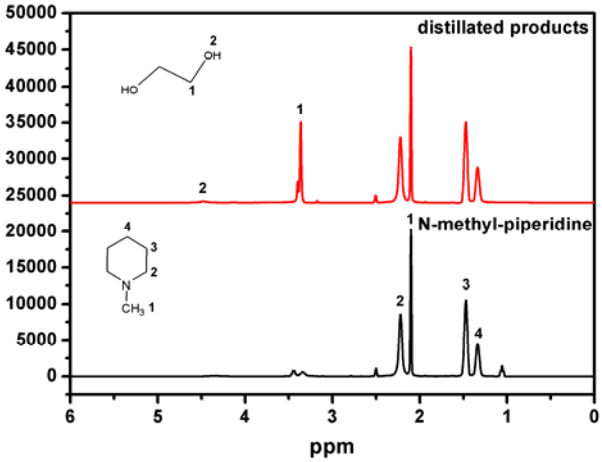


Fig. 2. H[1]-NMR of N-methyl-piperidine and distillated products.

Fig. 3 shows H[1]-NMR of N-methyl-piperidine and distillated products. It can be seen that EG and N-methyl-piperidine were found in the distillation products.

4. Conclusions

In summary, the depolymerization of anhydride cured epoxy resin by the organic base catalyst in the ethylene glycol in good decomposition efficiency at 180 °C. N-methyl-piperidine shows high yield of eliminated resin. Most importantly, the solvent and catalyst can be recycled simultaneously by distillation to save separation step. This method provides an attractive option for chemical recycling comparable to inorganic-based approaches.

References

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