

Chemical Recycle of Thermosetting Resin in Supercritical Water

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We have evaluated the feasibility of a new method to depolymerize thermosetting resins into monomer with supercritical water(SCW). Cured bisphenol A type epoxy resin decomposed completely at 673K and 10 minutes reaction time to tetrahydrofuran-solubles. For this case, the yield of monomers(phenol, isopropyl phenol and isopropenyl phenol) was around 15wt%, which was probably due to the hydrolysis of bisphenol A units of the resin. On the other hand, for the case of cured phenolic resin, at 753K and 40min reaction time with alkali (0.6 wt% in supercritical water), 70wt% of the loaded resin was decomposed and 40wt% of the monomers (phenol, cresol and xylenol) was recovered. However, above 753K, monomer recovery ratio decreased at higher temperatures, which is thought to be due to dehydration of neighboring hydroxyl groups of the cured phenolic resin.

Introduction

Recycling of waste plastics is an important and urgent problem to be solved from the standpoint of environmental protection and effective reuse of organic compounds. Thermosetting resin products are widely used for parts of electrical appliances and automobile because of their excellent properties but they are practically insoluble in most solvents and do not liquefy with heat treatment. So, recycling of these resins is widely recognized to be difficult.

With chemical recycling, we are developing a new method to depolymerize thermosetting resins into monomer with supercritical water (SCW). There have been many experimental investigations reported of chemical recycling of thermoplastic resin such as Polyethyleneterephthalate (PET)[1]. However, decomposition of cured thermosetting resin in SCW have received little attention[2].

In this research, we compared decomposition reaction of typical thermosetting resin, epoxy resin and phenolic resin, in supercritical water with pyrolysis in argon and evaluated the feasibility of a process based on SCW through batch-type experiments.

Materials and Methods

Cured bisphenol A type epoxy resin and cured phenolic resin, prepared by grinding and

sieving, were used, that had a grain size of 0.5~1.0mm. The compositions of both cured resins are shown in Tables 1, 2. The structures of them are shown in Figures 1, 2.

Table 1. Composition of Cured Bisphenol A type Epoxy Resin

		Weight Ratio
Prepolymer	Bisphenol A type Epoxy* ¹	100
Curing agent	3-Methyltetrahydrophthalic acid anhydrid	70
Curing acceleto	2-Ethyl,4-methylimidazol* ³	0.5

*1 Epikote 828 (Yuka shell epoxy)
 *2 EPICLON B-570(Dainippon Ink & Chemicals Inc.)
 *3 Shikoku Chemicals Corp.
 Curing Condition : 353K/4hr+393K/1hr+423K/4hr

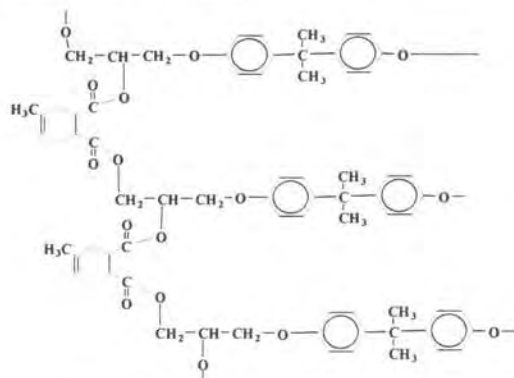


Figure 1. Structure of Cured Bisphenol A type Epoxy resin

Table 2. Composition of Cured Phenolic Resin

		Weight Ratio
Prepolymer	Phenol Novolak* ¹	100
Curing agent	Hexamethylenetetramine	15

*1 PR-50622(Sumitomo Durez Ltd.)
 Curing Condition : 423K/15min (Compression Molding) + 453K/4hr (afte

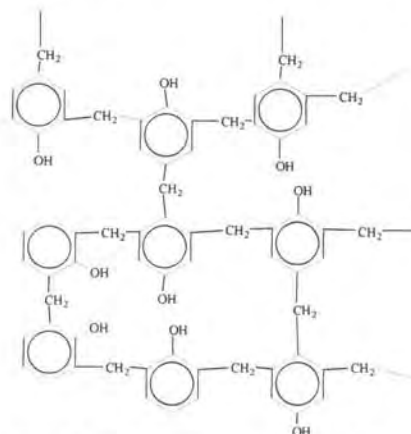


Figure 2. Structure of Cured Phenolic resin

Experiments were conducted with stainless (SUS316) tube bomb reactor(6.0cm³). Around 0.3g of cured resin was loaded with 3.0g of water in the reactor and air of the reactor is displaced with argon. Experiments without water, pyrolysis in argon, were also conducted. The reactor was submerged in a molten salt bath, which was controlled at the reaction temperature. The reactor was quenched by immersion in a cold water bath to terminate the reaction.

Decomposition products were analyzed according to procedures shown in Figure 3.

We defined the decomposition (1) and the yield of phenolic monomers(2) as follows.

$$\text{Decomposition} = \frac{\text{Weight of Cured Thermosetting Resin loaded} - \text{Weight of THF Insolubles}}{\text{Weight of Cured Thermosetting Resin loaded}} \times 100 [\%] \quad (1)$$

$$\text{Yield of phenolic monomers} = \frac{\text{Weight of Phenolic Monomers}}{\text{Weight of Cured Thermosetting Resin loaded}} \times 100 [\%] \quad (2)$$

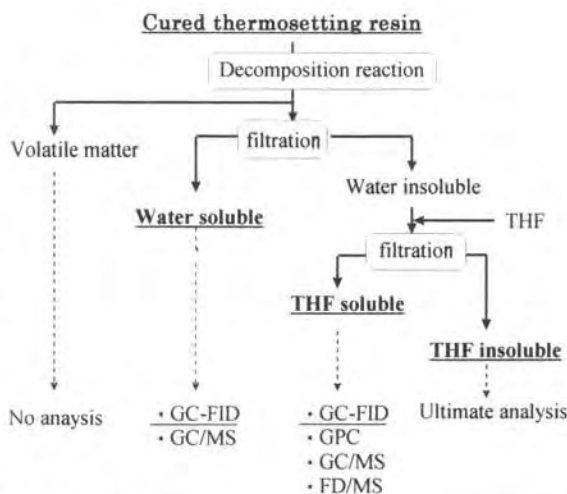


Figure 3. Analytical procedure of decomposition product

In this study, phenolic monomers refer to phenol, cresol, xylenol and other substituted phenols, do not include oligomers that are larger than a phenolic dimer.

Result and Discussions

Cured bisphenol A type epoxy resin

Cured bisphenol A type epoxy resin was completely decomposed to tetrahydrofuran-solubles both in SCW and in argon at 673K and 10 minutes reaction time. The main products, both in SCW and in argon, were phenolic monomers (phenol, 4-isopropylphenol, 4-isopropenylphenol) originating from bisphenol A units, and aromatic carboxylic acids originating from the curing agent. However, 3-phenoxy-1,2-propanediol (a) was produced in SCW, where this compound could not be detected in the argon (pyrolysis) experiments.

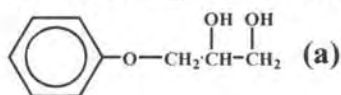


Figure 4 shows the influence of reaction time on the yield of phenolic monomers. The yield in SCW was higher than that in argon. Maximum yield of phenolic monomers was around 15% which corresponded to about 50% recovery, since the content of bisphenol A unit in the parent epoxy resin was 30%.

We consider that yield of phenolic monomers increased in SCW is due to the hydrolysis of ester, ether and isopropylidene linkages of the cured epoxy resin. This hypothesis is supported by the presence of 3-phenoxy-1,2-propanediol, that was only observed in the experiments with SCW.

Cured phenolic resin

Figure 5 shows the influence of reaction time on the decomposition and the yield of phenolic monomers. Here, phenolic monomers consisted of phenol, cresol and xylenol. Both decomposition and yield of phenolic monomers in SCW were higher than that in argon. Especially, the yield of phenolic monomers in SCW reached about 20% at 120min reaction time. We considered that the increase in yield of phenolic monomers was due to hydrolysis,

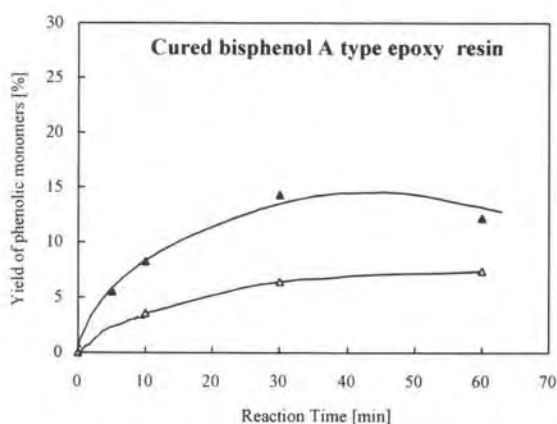


Figure 4. Influence of Reaction Time on Yield of phenolic monomers
Reaction Temp = 673K
▲ in SCW (water density = 0.5g/cm³)
△ in Argon (water density = 0.0g/cm³)

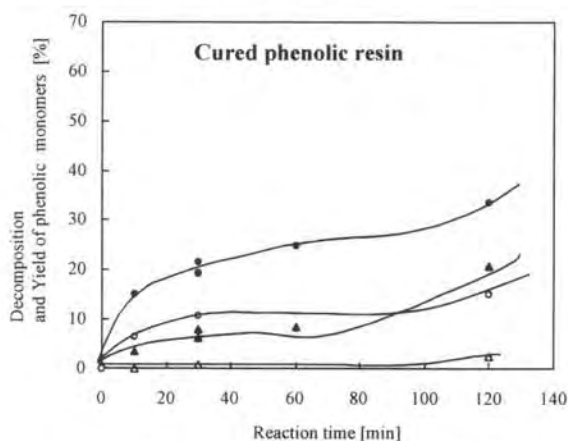


Figure 5. Influence of Reaction time on Decomposition and Yield of phenolic monomers, Reaction Temp = 673K
● ○ Decomposition ▲ △ Yield of phenolic monomers
Filled symbols = in SCW (water density = 0.5g/cm³)
Unfilled symbols = in Argon (water density = 0.0g/cm³)

as well as cured bisphenol A type epoxy resin.

Next, to promote the decomposition reaction, we studied the influence of reaction temperature, from 673K to 773K with alkali. Tagaya et al.[2] reported that alkali salt promote the decomposition of model compounds of phenol resin.

Figure 6 shows influence of the alkali additive, Na_2CO_3 , and reaction temperature on the decomposition and the yield of phenolic monomers. The decomposition of the resin and the yield of phenolic monomers increased together, as reaction temperature increased. At 753K, 70% of the resin was decomposed and a 40% yield of phenolic monomers was achieved. The 40% yield actually corresponds to a 50% yield since the parent phenolic resin contains about 80% of phenol unit.

At temperature higher than 753K, the yield of phenolic monomers decreased, which is probably due to the following. Above 753K, we observed methyl substituted xanthene (b), which may be produced by dehydration of neighboring hydroxyl groups of cured phenolic resin. Methyl substituted xanthene do not decompose to phenolic monomers because of their thermal and chemical stability.

Conclusion

Results show that conversion of thermosetting resins, cured bisphenol A type epoxy phenol resin and cured phenolic resin, to phenolic monomers in SCW is superior to pyrolysis in argon. Especially, bisphenol A type epoxy resin decomposed completely without acid or base catalysts. Although cured phenolic resin was more difficult to decompose, decomposition can be increased by raising reaction temperature and adding alkali.

Research results show that it is technically feasible to recycle thermosetting resins with supercritical water.

References

- 1) Adschiri T., Shibata R., Arai K., *KagakuKougakuRonbunshu*, **23**, 4, 505-511(1997)
- 2) H.Tagaya, Suzuki Y., Kadokawa J., Karasu M., Chiba K., *Chemistry Letters*, 47(1997)

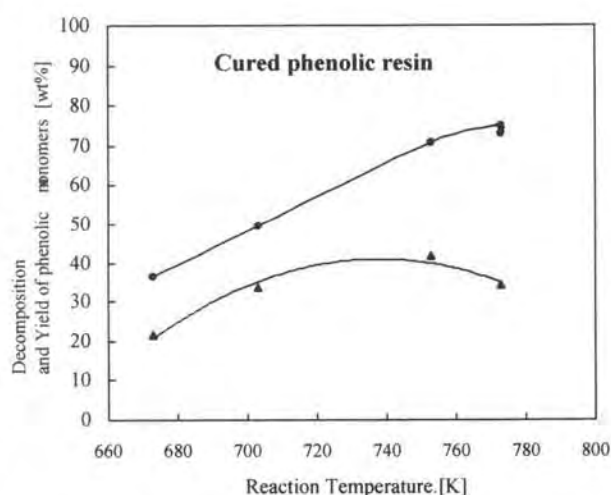
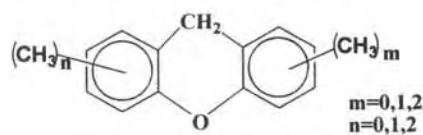


Figure 6. Influence of Reaction Temperature, on Decomposition and Yield of phenolic monomers

Reaction time =40min, Water density=0.35g/cm³

alkali additive (Na_2CO_3) =0.6wt% in SCW

• Decomposition ▲ Yield of phenolic monomers



Methyl substituted Xthene (b)