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An approach to chemical recycling of epoxy resin cured with amine using nitric acid

Weirong Dang*, Masatoshi Kubouchi, Shurou Yamamoto, Hideki Sembokuya, Ken Tsuda

Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan

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Abstract

An approach to chemical recycling of epoxy resin was pursued. Bisphenol F type epoxy resin cured with 1,8-*p*-menthanediamine could be completely decomposed in nitric acid solution resulting from low corrosion resistance to nitric acid. Organic decomposed products of the resin with the highest yield were extracted from neutralized solution. The extract was repolymerized to prepare recycled resin, mixed with bisphenol F type epoxy resin and curing agent of phthalic anhydride. The mechanical properties of virgin resin and recycled resins were compared. It was surprising that the recycled resins were far superior to the virgin resin in strength. The results obtained from differential scanning calorimeter (DSC) showed that the glass transition temperature (T_g) of recycled resins was higher than that of virgin resin. The reason that they formed the better network structure was discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Decomposition; Recycling

1. Introduction

Wastes of thermosetting resins have caused many environmental problems because they were difficult to dispose arising from their network structures [1,2]. Although many approaches to polymer wastes disposal have been already explored, landfill is still a main method of disposal [3,4]. Consequently, technologies of recycling of polymer urgently need to be developed and improved [5]. In recent years, the chemical recycling of polymer wastes has received a great deal of attention [6,7].

Epoxy resin is of great importance for a number of diverse applications including coatings, adhesives, structural materials and electrical insulation, etc. due to its good processability during curing process for forming cross-linking [8–10]. We have been investigating the corrosion resistance of amine cured epoxy resin, finding that it had low resistance to acid solution, and was completely decomposed in high concentration acid and at high temperature [11,12]. The phenomena suggested the possibility of recycling of thermosetting resins by applying their decomposed products. Therefore, epoxy resin attracted interest as a candidate for chemical recycling.

The decomposition of typical bisphenol A type epoxy resin cured with amine in acid solution has been studied [13]. It was initially intended to apply A type for chemical recycling due to its poor corrosion resistance. However, it was found that the main chain of bisphenol A was easily broken, because A type possessed quaternary carbon atom, which was susceptible to be attacked by acid to produce tertiary positive ion. As a result, this paper focused on bisphenol F type epoxy resin (BPF) that possessed methylene group ($-CH_2-$) in the center of main chain.

The objectives of the paper are to pursue an approach to chemical recycling of epoxy resin cured with amine by decomposition and repolymerization. The amine cured epoxy resin was decomposed in nitric acid solution, and then the decomposed products were repolymerized with BPF and curing agent of phthalic anhydride (PA) to prepare recycled resin. The mechanical properties of the recycled resin were reported.

2. Experimental

2.1. Materials

BPF and curing agent, 1,8-*p*-menthanediamine (MDA), were used in the work, which was provided by Dow Chemical Company and Aldrich Chemicals Company, respectively. In addition, PA, which was available from Ciba Specialty Chemicals Company, was used as curing agent when the decomposed products were repolymerized to

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* Corresponding author. Tel./fax: +81-3-5734-2124.
E-mail address: wdang@chemeng.titech.ac.jp (W. Dang).

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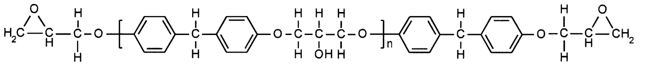
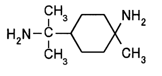
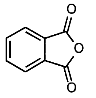


Bisphenol F type epoxy resin



MDA (1,8-*p*-menthanediamine)



PA (phthalic anhydride)

Fig. 1. Chemical structures of epoxy resin and curing agents.

prepare recycled resin. See Fig. 1 for their chemical structures.

2.2. Decomposition experiments

Epoxy resin was cured with MDA (BPF/MDA) in weight ratio of 100:22 at 80 °C for 2 h, and the post curing was conducted at 150 °C for 3 h. The BPF/MDA resin was cast to 2 mm thick plate and cut into 25 mm wide and 60 mm long pieces. Each specimen was put into 30 mm diameter glass tubes, and then immersed in 70 ml of 4 M (=mol/l) nitric acid solution. The immersion temperature was controlled at 80 °C in the water bath.

It was observed that a yellowish brown decomposed compound with high viscosity, namely 'residue', appeared in the upper and bottom of solution. After the residue and remaining specimens were removed from the yellow solution, three extractions with ethyl acetate were carried out. Dried in vacuum under room temperature, the brown high-viscosity extract was obtained.

2.3. Procedure of neutralizing extract

In order to neutralize the nitric acid contained in the extract, it was dissolved in ethyl acetate, and then specified amount of sodium carbonate solution was poured into the solution, with stirring. When pH of the mixture solution reached 7, the ethyl acetate phase was separated from the solution, and then the solvent was removed. The residual product was collected and dried under room temperature at least for one day. Because water can partly dissolve into ethyl acetate, the neutralized product contained some sodium nitrate. To remove the inorganic compounds, the product was redissolved in ethyl acetate. The combined organic solution was then filtered and distillated. Finally, the neutralized extract, referred to as NE, was obtained after being dried in vacuum under room temperature.

2.4. Repolymerization of neutralized extract

Initially, solvent removal and preheating of NE was carried out at 80 °C for about 1 h. And then weighed epoxy resin (BPF), NE, were mixed at 115 °C. Upon completion of the blend, weighed PA was added into the mixture as curing agent at 115 °C. After degassing and solvent removal in vacuum oven at 115 °C, the mixture was cast to 2 mm thick plate. The curing reaction was conducted at 115 °C for 8 h, and post-curing at 130 °C for 10 h. Finally, recycled resin was produced. Additionally, the virgin resin that was prepared with BPF and PA of curing agent was cast under the same curing conditions to make a comparison of properties between the recycled resin and it.

2.5. Analytical methods

Size exclusion chromatograph (SEC) was employed to determine the molecular weight distributions of the residue and the extract. Tetrahydrofuran (THF) was used as mobile phase and the flow rate was maintained at 0.1 ml/min. FT-IR was also applied to analyze their chemical structures.

In addition, mechanical strength of the recycled resins and the virgin resin was measured by the three-point bending test and the tensile test on an Instron Universal Testing Machine at room temperature. The fracture surfaces of the flexural test were observed by scanning electron microscope (SEM). Differential scanning calorimeter (DSC) analysis was also performed at a heating rate of 5 °C/min to investigate network structures of virgin resin and recycled resins. It was also used to determine glass transition temperatures (T_g) of resins.

3. Results and discussion

3.1. Yields of the decomposed products

Fig. 2 gives the change of yield of each decomposed product with increase of immersion time in 4 M nitric acid solution. It can be seen that the resin was rapidly decomposed, and completely disappeared at the immersion time of about 100 h. The residue and the extract appeared at the beginning of immersion, and increased gradually. The yields of the residue and the extract started to reduce after

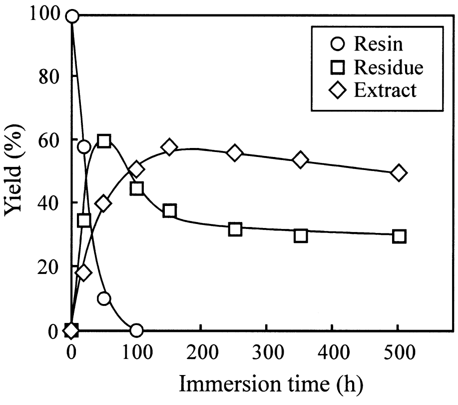


Fig. 2. Change of yields of decomposed products with immersion time (4 M nitric acid solution, 80 °C).

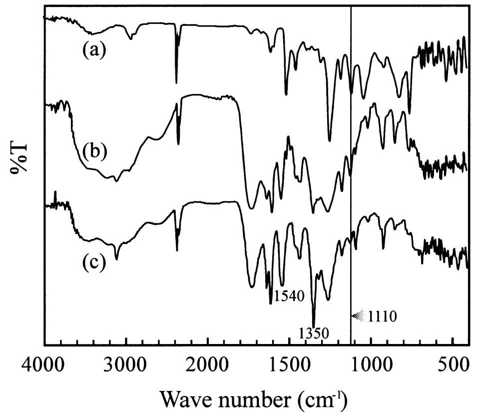


Fig. 3. FT-IR spectra of (a) BPF/MDA resin before immersion; (b) extract (immersion for 150 h); (c) extract (immersion for 500 h).

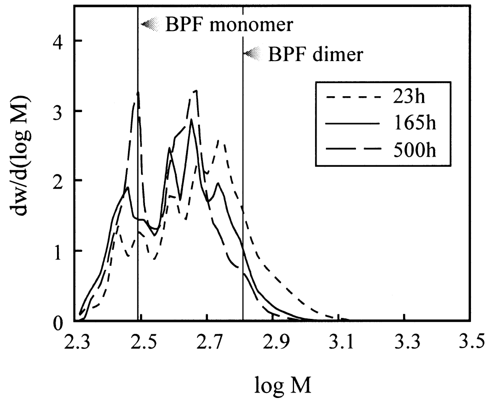


Fig. 4. Change of molecular weight distribution of the extract with immersion time (4 M nitric acid solution, 80 °C).

they reached their highest levels at 50 h for residue and at 150 h for extract, respectively. The extract yielded considerably high level of 60 wt% of initial resin. When the concentration of acid solution was higher (e.g. 6 M), the yield of extract increased; on the other hand, the crystal of picric acid was produced resulting from the breakage of main chain of epoxy resin and subsequent nitration under strong attack of nitric acid [13]. In order to achieve high yield of the extract and avoid producing the crystal, 4 M nitric acid solution was chosen as immersion solution.

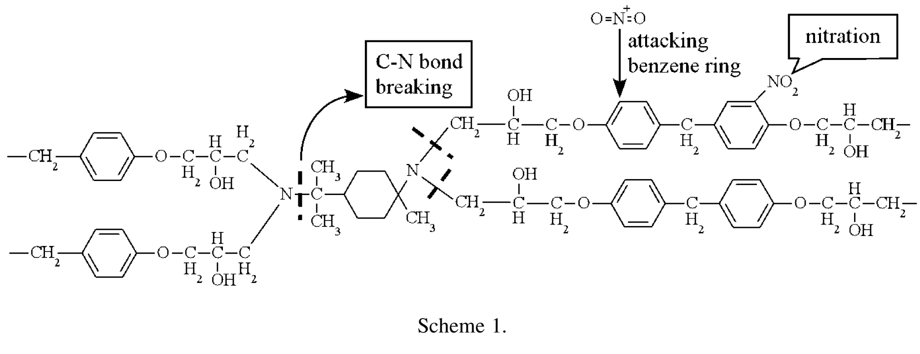
3.2. Analysis of decomposed products

The yield of residue was relatively low after 150 h, and it could continue to be decomposed if initial concentration of nitric acid solution was kept. By analyzing the SEC results of the residue, molecular weight peaks were found to widely distribute in higher region. These results suggested that the residue was mixture of intermediate products with high molecular weight during decomposition process of the cured resin, and, therefore, cannot be easily repolymerized. The following analysis will be dedicated to the extract.

FT-IR spectra of original resin and the extract are compared in Fig. 3. The peak at 1350 cm^{-1} in the IR region of the extract corresponded to nitro group. Aromatic nitro groups absorbing strongly at 1540 cm^{-1} were also found in the IR spectrum of the extract. The results demonstrated that the original resin was nitrated during immersion. Furthermore, the absorption peaks of C–N bonds at 1110 cm^{-1} appearing in spectrum of the original resin became smaller in that of extract with increase of immersion time and almost disappeared at 500 h, implying that the C–N bonds between the molecules were cleaved due to the effect of the nitric acid. Finally, from the molecular weight distribution of extract, shown in Fig. 4, it was found that the peaks appearing in high molecular region shifted to low molecular region with increase of immersion time, and the molecular weight of the extract nearly distributed in region between monomer and dimer of uncured BPF resin. It was supposed that the extract was mixture with lower molecular weight compounds.

Based on these findings, the decomposition reaction was given in Scheme 1. C–N bond was so weak as to be easily broken and benzene ring was nitrated under the attack of nitric acid, confirmed by FT-IR spectra. After breakage of the cross-linking, the decomposed products might mainly be compounds with similar structure as bisphenol F. However, their end groups might change with the immersion time. The longer the immersion time, the shorter the molecular chain of the end groups. That is, the molecular weight of the decomposed products became lower. This agreed with observations from the molecular weight distribution.

Thus, it was concluded that the extract was a mixture with nitrated compounds that retained the structure of main chain of original bisphenol epoxy resin, equivalent to monomer or



Scheme 1.

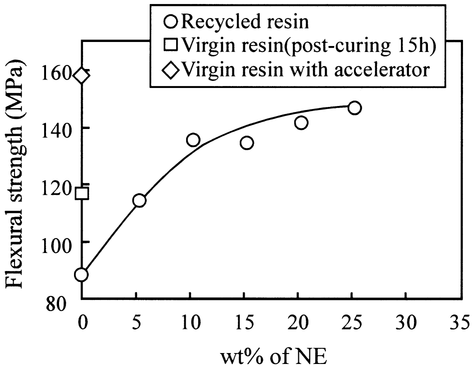


Fig. 5. Flexural strength of virgin resin and recycled resins with the content of NE.

dimer of the resin. It was because the main chain was not broken in the extract that it was considered to reuse as quasi-monomer for chemical recycling of the epoxy resin.

3.3. Properties of recycled resins

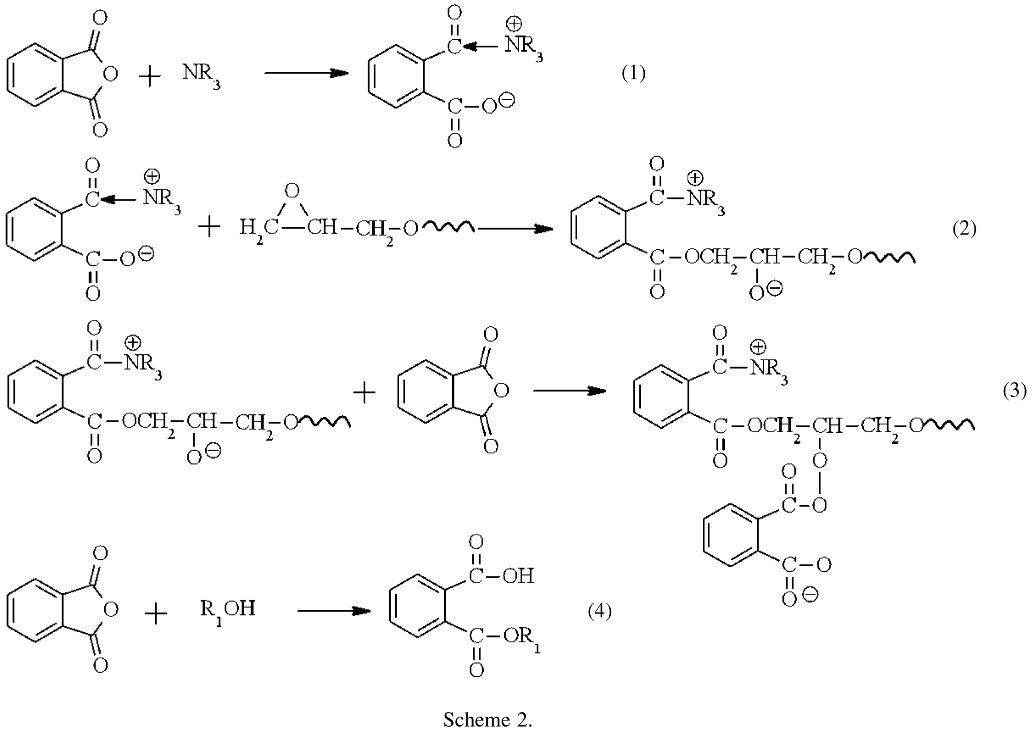
As mentioned above, the quasi-monomer retaining structure of the original resin could be obtained by controlling the immersion condition. After further chemical treatment of neutralization, it was used to repolymerize to prepare recycled resin with original epoxy resin (BPF) and curing agent (PA).

The extract of the decomposed products available at 150 h immersion time was selected as recycling material because its yield was highest (see Fig. 3). The neutralized extract (NE) was added into epoxy resin (BPF) in various weight ratios: 0 (virgin resin, BPF/PA), 5, 10, 15, 20, 25 and 30 wt%. After the mixture was cured with PA, recycled resins were prepared.

At the 30 wt% adding level, cured resin could not be molded because of its high viscosity and short pot life. There were many voids in the molded recycled resin containing 30 wt% of NE, which were formed in the process of degassing under vacuum. The reaction was so rapid that gas was prevented from escaping out of the viscous resin. On the other hand, it was found that the gel time of cured resin was increased with decrease of the content of NE. Below 25 wt%, casting was perfectly done, and 2 mm thick recycled resin plates without void could be produced.

The flexural strength was evaluated from the three-point bending test and the results are shown in Fig. 5. The flexural strength of recycled resins was higher than that of the virgin resin under the same curing conditions. When the content of NE was below 10 wt%, the flexural strength rapidly increased. Meanwhile, the increase of the flexural strength of recycled resins slowed down when it was more than 10 wt%. Although the strength of the virgin resin was increased as post curing time was extended from 10 to 15 h to sufficiently cure the resin, it was still lower than that of recycled resins with high content of NE.

The curing reaction of acid anhydride can be accelerated in presence of the Lewis base, which acts as catalyst in the reaction [14]. The cross-linking reaction of BPF and MDA formed tertiary amine on the base of reaction of the active hydrogen of amine and epoxide during the curing reaction of BPF and MDA. Although BPF/MDA was decomposed in nitric acid solution, NE might contain tertiary amine that acts as the Lewis base. The repolymerization was shown in Scheme 2. With the assistance of the tertiary amine catalyst,



Scheme 2.

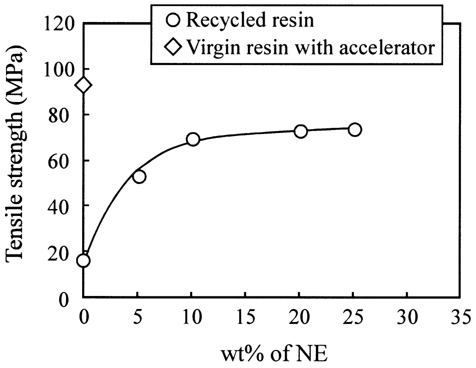


Fig. 6. Tensile strength of virgin resin and recycled resins with the content of NE.

the reaction was initiated by forming carbonium anion by opening some of the cyclic anhydride (Eq. (1)). The carbonium anion opened the epoxide ring (Eq. (2)), regenerating hydroxyl oxygen anion that further reacted with anhydride (Eq. (3)). NE containing hydroxyl group (See Scheme 1) underwent the reaction in Eq. (4) to form polyester chain. After the sequence of these reactions, they were cross-linked to form the network structure of thermosetting. Consequently, the presence of tertiary amine catalyst resulted in the curing reaction of recycled resin was faster than that of virgin resin, and, therefore, the recycled resin formed higher density network than the virgin one under the same reaction conditions. Also, the gel time was shortened and the recycled resin with 30 wt% of NE could not be molded because catalyst increased with the increase of the content of NE.

To confirm the viewpoint stated above, 0.02 wt% of tertiary amine was added into the virgin resin as an accelerator. As shown in Fig. 5, under the same curing conditions, its flexural strength was much higher than that of virgin resin and slightly higher than that of recycled resin containing 25 wt% of NE.

Moreover, the tensile strength was also examined and is shown in Fig. 6. The tensile strength of recycled resins rapidly increased at low content of NE (<10 wt%) and then tended to be stable with the increase of the content of NE. The strength of the recycled resin with over 10 wt% of NE asymptotically approached that of the virgin resin with accelerator. The results well agreed with the conclusion from the bending test.

The fracture surfaces of the three-point bending test specimens were observed by SEM to investigate the relation between morphologies and strength. The fracture surface of BPF/PA, shown in Fig. 7a, was flat and smooth, and the size of initial defect was large, as correlated with its lower flexural strength. The fracture surfaces shown in Fig. 7b and c are for the recycled resin containing 10 and 25 wt% of NE. Fig. 7d gives the fracture surface of the virgin resin with accelerator. These three surfaces, shown in Fig. 7b–d,

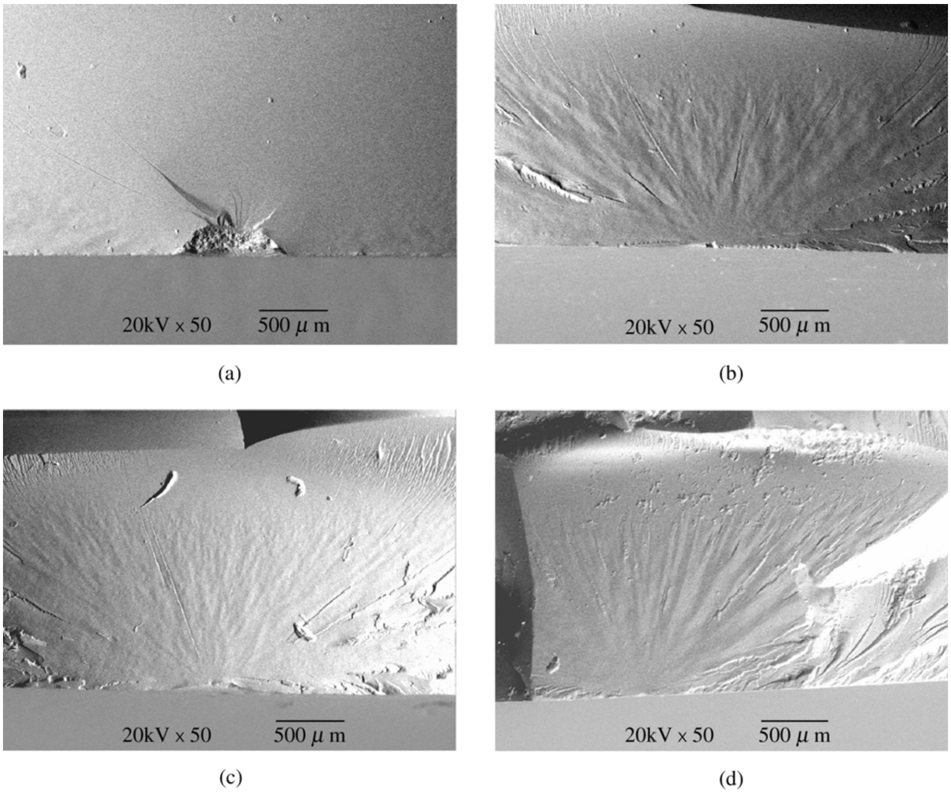


Fig. 7. SEM photographs of fracture surfaces: (a) virgin BPF/PA resin; (b) recycled resin containing 10 wt% of NE; (c) recycled resin containing 25 wt% of NE; (d) virgin BPF/PA resin containing 0.02 wt% of accelerator.

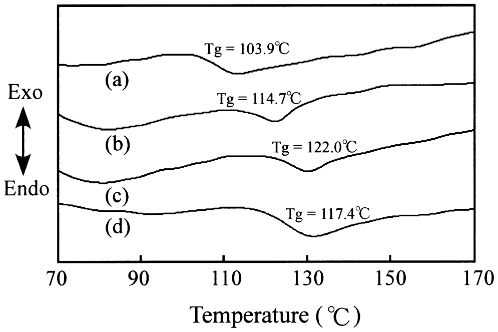


Fig. 8. DSC scans of recycled resins in comparison with virgin resin: (a) virgin BPF/PA resin; (b) recycled resin containing 10 wt% of NE; (c) recycled resin containing 25 wt% of NE; (d) virgin BPF/PA resin containing 0.02 wt% of accelerator.

were relatively rough, and the size of initial defect was smaller than that of virgin resin. This observation could account for its higher flexural strength of recycled resins and also supported the mechanism that tertiary amine accelerated the curing reaction. In addition, it was observed that the fracture of recycled resin was uniform and had no significant defect, implying that epoxy resin, NE, and PA sufficiently reacted and produced the new resin with good network structure.

The recycled resins were compared with the virgin resin by means of DSC analysis. The analytical results are presented in Fig. 8, where each of them showed existence of single glass transition temperature (T_g), providing additional evidence that epoxy resin, NE, and PA reacted each other and formed uniform structure. Also, T_g of recycled resins was higher than that of virgin resin and increased with increase of the content of NE, suggesting that, as expected, the addition of NE did not interfere in epoxy resin–PA reaction but also the density of cross-linking in the recycled resins increased. It was consistent with the analysis of repolymerization that the recycled resins formed better network structure than virgin one. The tendency that the T_g of the virgin resin with 0.02 wt% of accelerator was similar as that of the recycled resins further confirmed the previous discussion.

4. Conclusions

The decomposition behavior of BPF cured with MDA in nitric acid solution was investigated to pursue an approach to chemical recycling of epoxy resin. The decomposed products were obtained including solid residue and extract from liquid phase. The residue was considered to be an intermediate product with high molecular weight, which was produced during the process of the decomposition reaction, and the extract was a mixture with the nitrated compounds retaining the structure of main chain, equivalent to monomer or dimer of bisphenol epoxy resin. And the extract possessed high yield.

A successful approach to chemical recycling of epoxy resin was presented. The decomposed products of the extract were firstly neutralized, and then repolymerized to prepare recycled resin by substituting for a part of epoxy resin to cure with PA. Under the same conditions, recycled resins showed much higher mechanical strength than virgin one. Glass transition temperature of recycled resins was higher than that of virgin resin and increased with increase of the content of NE. These were related to their higher density network structures due to the effect of accelerator contained in the NE.

The decomposition and repolymerization mechanisms will continue to be pursued. In addition, the successful recycling approach presented in this paper provides the potential possibility of recycling of other thermosetting resins, as will be implemented in our follow-up work.

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