

Chemical recycling of glass fiber reinforced epoxy resin cured with amine using nitric acid

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Abstract

An approach to chemical recycling of amine cured epoxy resin using nitric acid solution has been proposed [Dang W, Kubouchi M, Yamamoto S, Sembokuya H, Tsuda K. *Polymer* 2002;43:2953–8. [1]]. 1,8-*p*-Menthanediamine cured bisphenol F type (BPF/MDA) epoxy resin was decomposed in nitric acid solution, and then the decomposed product was repolymerized with original resin. In this paper, applicability of the proposed approach to glass fiber reinforced bisphenol F type epoxy resin cured with diamino diphenyl methane (DDM) was investigated. It was concluded that the approach was applicable to BPF/DDM epoxy resin, and potentially to all of amine cured epoxy resin. Flexural strength of the recycled resin was higher than that of virgin resin until the content of the neutralized extract, which was available from degradation of BPF/DDM epoxy resin, was not more than 30 wt% of the original resin. The reinforcement of glass fiber could be separated and recovered. The existence of the reinforcement did not affect decomposition the matrix.

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1. Introduction

With increase of production and application of plastics during the last decades, plastics wastes have caused many environmental problems. In recent years, great efforts have been launched in the field of disposal of plastics, especially thermosetting resin that is difficult to dispose arising from their network structure. Chemical recycling is a new and promising route for converting plastic wastes by returning them back to its original constituents, that is, monomers or petrochemical feedstock, and has received a great deal of attention in recent years [2–4].

On the other hand, research and development on chemical recycling are a long-range effort. Although considerable advances have been seen in this field in the past decades, chemical recycling is still at the development or pilot plant stage [5]. Among the existing technical difficulties, high cost and low quality of products were still main problems [6,7]. To date, few of recycled materials can

satisfy needs from market. Therefore, recycling technology needs to be improved so that it could be used in a wide range of application and would represent an asset rather than an expensive burden for recovery of recourse and diminution of environment stress.

In our past research, a successful approach to chemical recycling of epoxy resin cured with amine using nitric acid solution has been proposed [1]. 1,8-*p*-Menthanediamine (MDA) cured bisphenol F type (BPF) epoxy resin was decomposed in nitric acid solution, and then the decomposed products were repolymerized with original resin and curing agent of phthalic anhydride (PA) for preparing recycling resin. The recycled resin showed excellent mechanical properties.

However, curing agent of MDA is an alicyclic amine which is one of the most traditional curing agents, but not frequently used in recent years, because its physical properties deteriorate when it is kept under 160–200 °C. In practice, 4,4'-diaminodiphenylmethane (DDM) is one of most widely applied curing agents, because DDM cured resin possessed excellent mechanical properties and resistance to heat [8]. In addition, thermosetting resins are usually

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reinforced by reinforcement such as glass fiber to modify their brittleness and increase their strength, to form composite materials with complex structure. From the recycling point of view, unfortunately, it is difficult to separate the matrix and reinforcement since the reinforcement leads to complex structures. In order to investigate the practical applicability of the proposed approach, glass fiber reinforced BPF epoxy resin cured with DDM (GFRP) was selected as experimental material for chemical recycling in this study.

At first, GFRP was decomposed in nitric acid solution, and the decomposed products and the fiber were recovered. Then, the decomposed product was used to prepare recycled resin, together with original BPF epoxy resin and curing agent of phthalic anhydride (PA), and mechanical properties of the recycled resin were examined. Finally, corrosion behaviors of the glass fiber were investigated.

2. Experimental

2.1. Materials

In the experiment, the matrix of the specimen of GFRP was BPF epoxy resin cured with DDM, which were provided by Dow Chemical Company and Mitsui Chemicals Incorporation, respectively. BPF epoxy resin was cured with DDM in weight ratio of 100:27 at 80 °C for 2 h, and the post curing was conducted at 150 °C for 4 h. In addition, PA, which was available from Ciba Specialty Chemicals Company, was used as curing agent when the decomposed products were repolymerized to prepare recycled resin. Fig. 1 shows the chemical structures of BPF epoxy resin, DDM, PA and the matrix of GFRP.

The reinforcement was E-glass fiber, being used in forms of glass cloth. T-glass fiber was employed for comparison with E-glass fiber. They were available from Nitto Boseki Company Incorporation. Table 1 gives the weight fraction of matrix and reinforcement in the GFRP specimens.

2.2. Decomposition experiments of GFRP

Two millimeter thick GFRP plate was cut into 25 mm wide, 60 mm long specimens. Each specimen fixed by a Teflon support bar was put into a 30 mm diameter glass tube, and then immersed in 70 ml of 4 M (mol/l) nitric acid solution. The test tubes were put into water bath at 80 °C.

Table 1
Weight fraction of glass fiber and matrix resin

	Matrix resin	Reinforcement
E-glass fiber FRP	BPF/DDM 64.5 wt%	E-glass fiber cloth 35.5 wt%
T-glass fiber FRP	BPF/DDM 68.0 wt%	T-glass fiber cloth 32.0 wt%

In a specific time, the specimen generally dissolved into nitric acid solution, and the solution became yellow. When the immersion time was long enough, the matrix entirely disappeared and only glass fiber remained in solution.

For the case, the GFRP specimen was decomposed incompletely, the weight change of matrix and fiber was examined by incinerating it. Matrix was gasified while inorganic compound, i.e., glass fiber remained during incineration. It was clear that the lost weight was for matrix and the remained for fiber.

2.3. Decomposition experiments of matrix

In order to investigate degradation behaviors of the matrix of GFRP, unreinforced BPF/DDM epoxy resin specimens were also immersed in nitric acid solution under the same decomposition conditions as the above-mentioned method.

As the resin was gradually decomposed, the insoluble yellowish brown solid products, namely residue, appeared and the acid solution became yellow. The remained specimens and residue were collected, and then dried at 50 °C for 2 weeks. The weight of dried specimens and residue were measured. After the yellow solution was cooled in ice water, no crystal was found. If nitric acid solution with higher concentration such as 6 M was used for immersion, crystal separated out because of breakage of the main chain of BPF epoxy resin and subsequent nitration under the attack of nitric acid [9,10]. Upon completion of three extractions of the yellow solution with ethyl acetate, the brown high-viscosity extract (referred to as extract) was obtained. Dried in vacuum under room temperature, it was also measured.

2.4. Degradation experiments of reinforcement

After the GFRP specimen was completely decomposed, glass fiber still remained in the solution. The glass fiber was collected, washed with a large excess of ion-exchange water and dried at 50 °C. It was found that the recovered E-glass fiber became very soft while the appearance of T-glass fiber hardly changed. In order to study corrosion behaviors of glass fiber in detail, neat glass fiber was also immersed under the same immersion conditions for comparison.

2.5. Preparation of recycled resin

By applying the proposed approach [1], the recycled resin was prepared by repolymerizing the decomposed products. As presented in Section 2.3, when BPF/DDM epoxy resin was dissolved in nitric acid solution, solution became yellow. The yellow solution underwent neutralization with sodium carbonate, extraction, refinement and dryness, and the neutralized extract (referred to as NE) was obtained. The process of neutralization and refinement of extract was presented in Fig. 2.

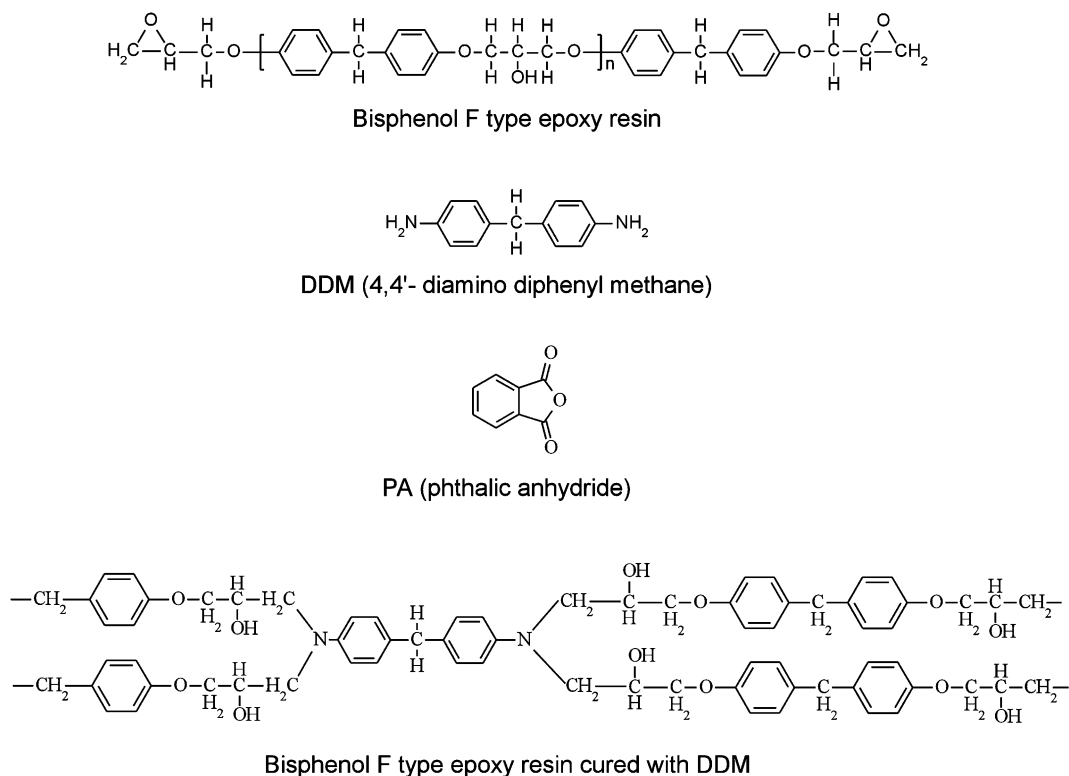


Fig. 1. Chemical structures of epoxy resin, curing agents and cured resin.

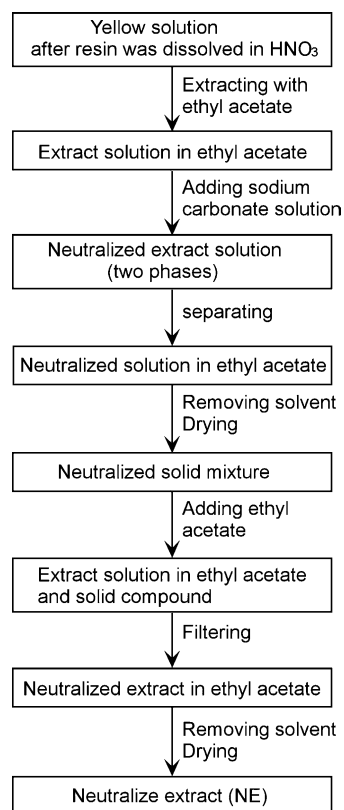


Fig. 2. Process of neutralization of extract.

NE was then repolymerized to prepare the recycled resin. Since NE could contribute hydroxyl group to bond with PA, it was employed to substitute a part of epoxy resin [11]. The proportions of addition of NE ranged from 5 to 30 wt% (the ratio of the weight of NE to the total weight of NE and BPF epoxy resin). The weighed BPF epoxy resin and NE were mixed at 115 °C after solvent removal and preheating of NE at 80 °C for about 1 h. Cured with PA, the mixture was cast to 2 mm thick plate of recycled resin at 115 °C for 8 h, followed at 130 °C for 10 h for post-curing. For comparison of properties with the recycled resin, virgin resin (BPF/PA epoxy resin) was produced under the same curing conditions.

2.6. 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 at 0.1 ml/min of flow rate. FT-IR was also applied to analyze their chemical structures.

Mechanical strength of the recycled resins and the virgin resin was measured by the three-point bending 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 discussions

3.1. Decomposition of matrix

3.1.1. Change of weight of matrix

Weight change of the unreinforced resin was compared with that of the matrix of GFRP, as shown in Fig. 3. The trend of their weight change was very close, as suggested that glass fiber did not evidently affect degradation of matrix of GFRP. For this reason, the conclusion obtained from the experiment using unreinforced resin was also applicable to matrix of GFRP.

3.1.2. Yields of decomposed products of matrix

The yields of the decomposed products of BPF/DDM epoxy resin are shown in Fig. 4 with the change of immersion time in 4 M nitric acid solution. Here yield referred to the weight ratio of the decomposed products to the initial resin. It could be seen that the resin was gradually decomposed, and completely disappeared at about 400 h, much longer than in the case of BPF/MDA resin, which completely disappeared at 100 h under the same conditions [1]. Since the resonance effect of the phenyl group on the unshared pair of electrons decreased the electron density at nitrogen atom [12], the nitrogen atom attaching to benzene ring in DDM was more stable than that bonding to quaternary carbon atom in MDA, as led to its slow degradation. Residue and extract increased with increase of immersion time. The yields of extract started to reduce when it reached its highest levels at 450 h, while increase of the yields of residue became slow from about 200 h. The extract yielded considerably high level of more than 60 wt% of initial resin at 450 h.

3.1.3. Analysis of decomposed products

From the SEC results of the residue, it was found that molecular weight peaks widely distribute in relatively high

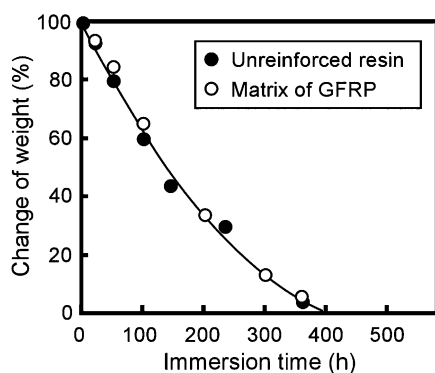


Fig. 3. Change of yields of unreinforced BPF/DDM epoxy resin and matrix of GFRP with immersion time (4 M nitric acid solution, 80 °C).

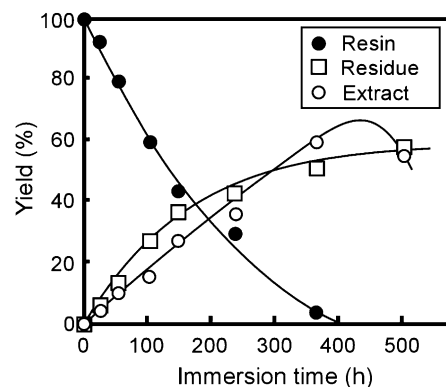


Fig. 4. Change of yields of decomposed products with immersion time (4 M nitric acid solution, 80 °C).

region. When the residue was immersed again in nitric acid solution with initial or higher concentration, it could continue to be decomposed. These results suggested that the residue was mixture of intermediate products with high molecular weight during decomposition process of the cured resin. Consequently, the residue cannot be easily repolymerized due to its high molecular weight. The following analysis will be dedicated to the extract by employing FT-IR and SEC.

FT-IR spectra of original resin and the extract obtained from the different immersion time are compared in Fig. 5. Nitro group and aromatic nitro groups absorbing strongly at 1350 and 1540 cm^{-1} , respectively, were found in the IR spectrum of the extract, as demonstrated that the original resin was nitrated during decomposition process. Furthermore, the absorption peaks of C–N bonds at 1110 cm^{-1}

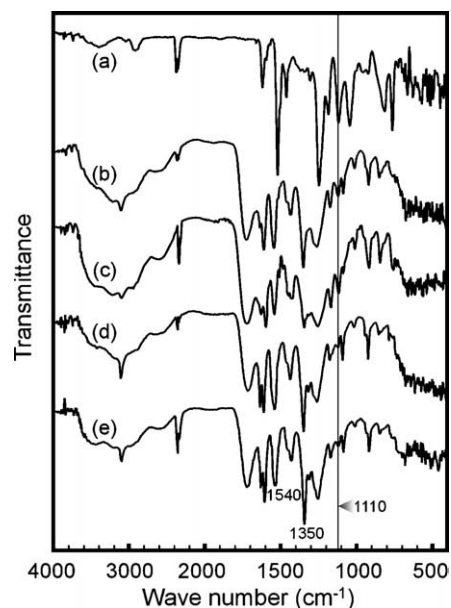


Fig. 5. FT-IR spectra of (a) BPF/DDM resin before immersion; (b) extract from BPF/DDM resin (immersion for 150 h); (c) extract from BPF/MDA resin (immersion for 150 h); (d) extract from BPF/DDM resin (immersion for 500 h); (e) extract from BPF/MDA resin (immersion for 500 h).

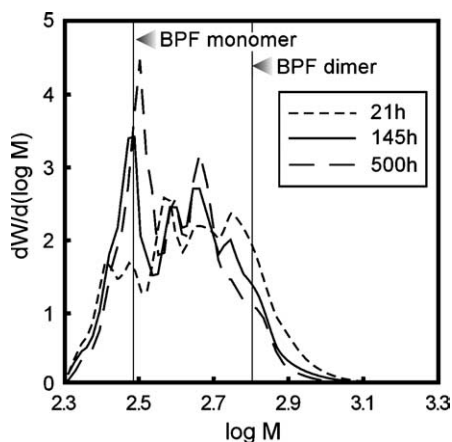
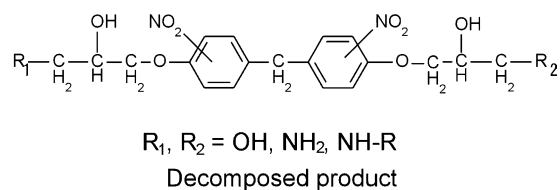


Fig. 6. Change of molecular weight distribution of extract with immersion time (4 M nitric acid solution, 80 °C).

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. In addition, the spectra of the extract of BPF/MDA epoxy resin were also plotted in Fig. 5 for comparison [1]. The spectra for both resins were found almost similar, as suggested that the crosslink in amine cured epoxy resin was broken to produce the extract with the backbone of BPF epoxy resin, regardless of type of amine.

The molecular weight distributions of the extract of BPF/DDM epoxy resin were obtained by analyzing the SEC results (Fig. 6). It was found that the peaks appearing in high molecular region shifted to low molecular region with increase of immersion time, the molecular weight of the extract nearly distributed in region between monomer and dimer of uncured BPF epoxy resin. It was supposed that the extract was mixture with low molecular weight compounds and its molecular weight became lower and lower with immersion time.

Based on the above FT-IR and SEC analyses, it was concluded that main products in the extract possessed the similar structures to monomer and dimer of uncured BPF resin. This conclusion is the same as the case of BPF/MDA epoxy resin [1]. The mechanism was depicted in Scheme 1. C–N bond was easily broken and benzene ring was nitrated under the attack of nitric acid, resulting in depolymerization of the network and formation of the decomposed products.



Scheme 2.

The molecular formula of the main decomposed product was supposed in Scheme 2. The nitro groups attaching to benzene ring, whose position and number were changeable, were illustratively described in the scheme. The end groups R_1 and R_2 might be OH, NH_2 or $NH-R$. As linkages of R_1 and R_2 continuously cleaved with immersion time, their molecular chain became short. When the end groups were very small molecule, the decomposed product was similar as structures of bisphenol F monomer, and therefore, it may be regarded as quasi-monomer. Note that most products of the extract retained the main chain, as made it possible that they could be repolymerized to prepare recycled resin for chemically recycling the epoxy resin. Furthermore, since the crosslink of all of amine cured epoxy resins was C–N bond, the recycling approach might be applicable to all other amine cured epoxy resins.

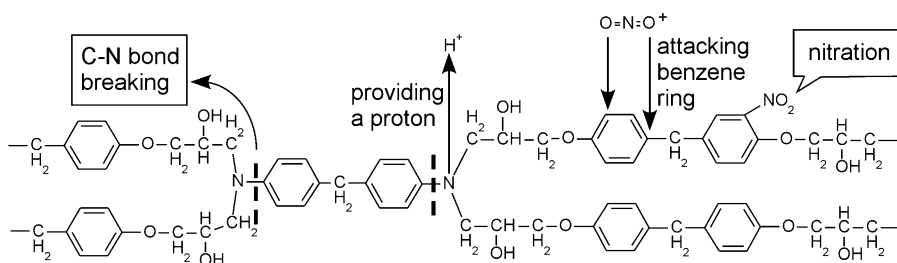
Meanwhile, as discussed in Section 3.1.2, C–N bond in aromatic amine was difficult to cleave and consequently long immersion time was needed to achieve high yield of the extract. If the immersion time was considerably long, the main chain could be broken, so that small molecule compounds were produced. The existence of small molecule compounds went against repolymerization for preparation of recycled resin, as will be further addressed in Section 3.2.1.

3.2. Analysis of recycled resin

3.2.1. Mechanical properties of recycled resin

Since the extract obtained from decomposition of BPF/DDM epoxy resin possessed the similar structure to monomer and dimer of BPF, it is possible to apply the recycling approach presented by the authors [1] to repolymerize neutralized extract (NE) with BPF epoxy resin using PA as curing agent.

To successfully reconstitute recycled resin, the selection of immersion time was key factor. Long immersion time



Scheme 1.

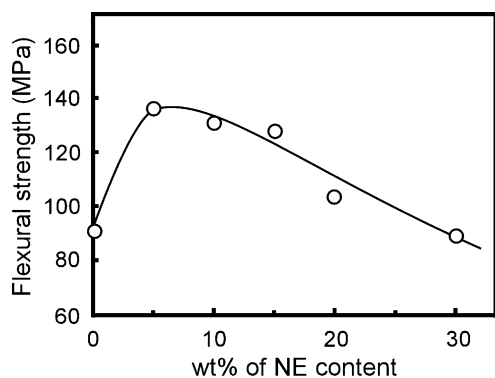


Fig. 7. Flexural strength of virgin resin and recycled resins with the content of NE.

contributed to high yield of the extract, but was not helpful to retain the main chain. To achieve relatively high yield while limit the content of small molecule compounds, the extract available from 250 h of immersion time was employed as raw material to replace a part of epoxy resin.

The flexural strength of recycled resins was evaluated from the three-point bending test, as shown in Fig. 7. When the content of NE was relatively small, say 5 wt%, the flexural strength was much higher than that of virgin resin; while, when the content exceeded a certain percentage, the strength gradually decreased. It was shown that the flexural strength of the recycled resin was higher than that of virgin resin until the content of NE was not more than 30 wt%. It could be stated that NE available from degradation of BPF/DDM epoxy resin could be applied to take place of a part of epoxy resin to react with curing agent for preparing recycled resin having good mechanical properties.

The curing reaction of acid anhydride can be accelerated in presence of the Lewis base, which played a role of catalyst in the reaction [13]. Since the crosslink reaction of BPF/DDM epoxy resin formed tertiary amine, its decomposed products, NE, might contain tertiary amine, which acted as the Lewis base. Besides, NE could react with PA, since it contributed hydroxyl group (see Scheme 2). With assistance of the tertiary amine catalyst, epoxy resin, NE and PA were crosslinked to form the network structure of thermosetting [1]. Consequently, the presence of tertiary amine resulted in the recycled resin formed higher density network than the virgin one under the same reaction conditions, which led to its high strength.

However, with increase of NE content, the introduction of lots of small molecules and polar nitro groups made the backbone more stiff and rod-like [14]. Consequently, the strength of recycled resins containing higher content of NE decreased even though tertiary amine accelerated the curing reaction.

On the other hand, the flexural modulus of recycled resin tended to increase with increase of NE content (Fig. 8). At the level of 30 wt%, the flexural modulus of recycled resin reached to about 5.0 GPa. Since the small molecules and polar nitro groups in NE made the backbone more stiff and

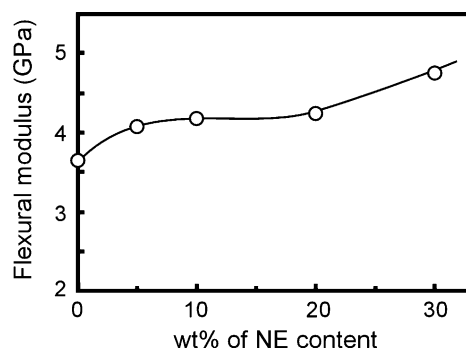


Fig. 8. Flexural modulus of virgin resin and recycled resins with the content of NE.

rod-like, the recycled resin became brittle and the flexural modulus increased. That is, the content of NE considerably influenced the flexural modulus of recycled resin.

3.2.2. Observation of fracture surfaces by SEM

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. 9(a), was flat and smooth, and the size of initial defect was large. In contrast, the surface of the recycled resin containing 15 wt% NE became rough and uniform, and had no significant defect (Fig. 9(b)), as accounted for its higher strength than that of the virgin resin. This observation also implied that epoxy resin, NE and PA sufficiently reacted to form better network.

When the content of NE increased to 20 and 30 wt%, shown respectively, in Fig. 9(c) and (d), the surface appeared uneven pattern, suggesting microphase separations occurred, which was caused by small molecule compounds contained in the extract. And the initial defect size became large with increase of the NE content. When the content was 30 wt%, the defect size was as large as in the virgin resin, agreeing with the fact that the two resins showed similar strength. This further confirmed that small molecules considerably influenced repolymerization of NE when the content of NE was high.

3.2.3. DSC analysis

The recycled resins were compared with the virgin resin by means of DSC analysis, whose results are presented in Fig. 10. For the case of NE content of 15 wt%, the recycled resin showed only single transition, which was almost not shifted compared with the virgin resin. This confirmed that epoxy resin, NE and PA sufficiently reacted to form uniform structure. When NE content increased to 20 wt%, except for a clear transition, a sign of a secondary transition appeared, indicating a small portion of a secondary phase introduced in the recycled resin, as was also observed in SEM photograph. When NE content increased to 30 wt%, two transitions appeared, showing there existed two phases, one of which corresponded to the recycled resin, and the other

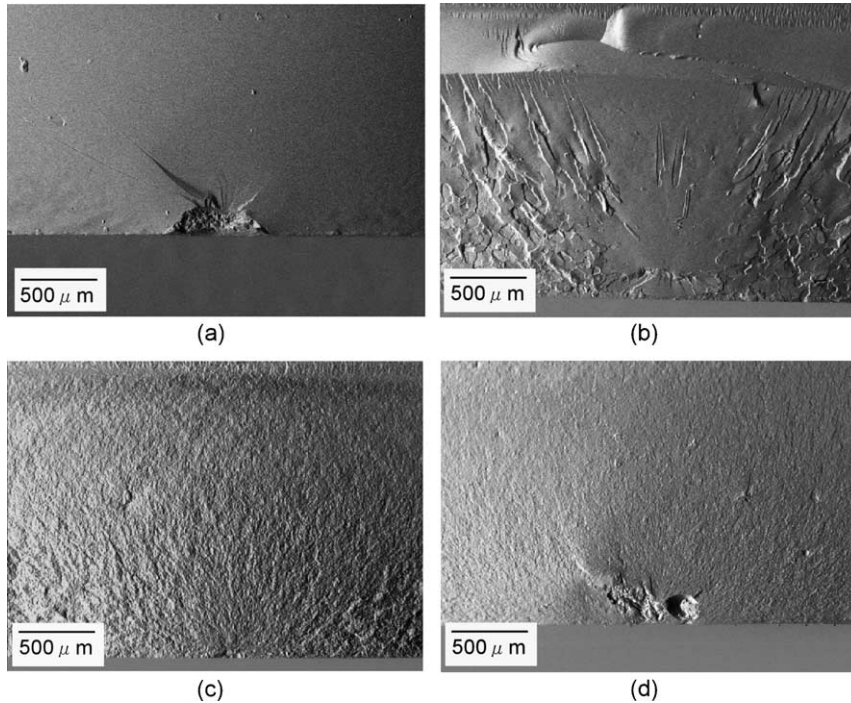


Fig. 9. SEM photographs of fracture surfaces: (a) virgin BPF/PA resin; (b) recycled resin containing 15 wt% of NE; (c) recycled resin containing 20 wt% of NE; (d) recycled resin containing 30 wt% of NE.

formed owing to small molecular compounds contained in NE. Obviously, when NE content increased, the content of small molecular compounds also increased, resulting in a secondary transition.

3.3. Degradation of glass fibers

Weight change of the reinforcement of E-glass fiber in GFRP was described in Fig. 11. For comparison, weight change of neat E-glass fiber under the same immersion conditions was also plotted in this figure. The weight of the E-glass fiber in GFRP significantly reduced from the beginning of immersion, and slowed down from 200 h when it lost 50 wt% of the original weight. In the case of neat E-glass fiber, after significant reduction at the beginning, the weight showed little change from about

100 h when it lost 60 wt% of the initial weight. The comparison showed that E-glass fiber in GFRP lost its weight slower than neat fiber, confirming that initial degradation occurred in the matrix on the surface of GFRP, and then the reinforcement was exposed to acid solution. This observation was consistent with analysis of weight change of the matrix discussed in Section 3.1.1.

Weight change of neat T-glass fiber was also compared in Fig. 11. It was seen that T-glass fiber lost only 1–2 wt% of original weight under the same immersion conditions. Its lost weight was far lower than that of E-glass fiber, which was related to solubility of their components including aluminum oxide (Al₂O₃), calcium oxide (CaO) and silicon oxide (SiO₂). Al₂O₃ and CaO were apt to dissolve in acid solution, while SiO₂ was difficult. It was known that the

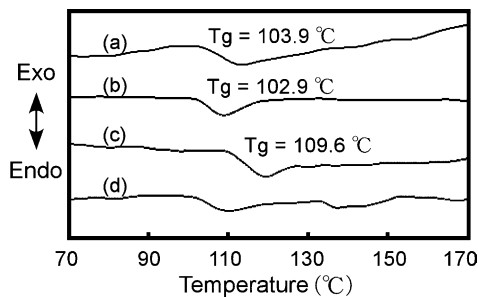


Fig. 10. DSC scans of recycled resins in comparison with virgin resin: (a) virgin BPF/PA resin; (b) recycled resin containing 15 wt% of NE; (c) recycled resin containing 20 wt% of NE; (d) recycled resin containing 30 wt% of NE.

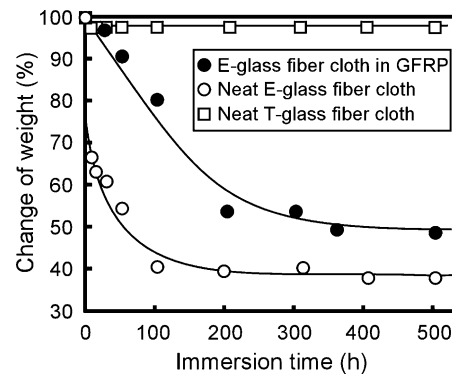


Fig. 11. Change of weight of E-glass fiber in GFRP and E- and T-glass fiber only with immersion time (4 M nitric acid solution, 80 °C).

content of Al_2O_3 and CaO in T-glass fiber was lower, but SiO_2 higher than in E-glass fiber, therefore, T-glass fiber possessed much more excellent corrosion resistance to nitric acid solution [15,16].

It can be said that, from recycling point of view, the proposed chemical recycling approach was more suitable to BPF/DDM resin reinforced with T-glass fiber than with E-glass fiber. And because T-glass fiber was more expensive, its reuse was more profitable. It is also noted that even in the case of using E-glass fiber as reinforcement, degradation of reinforcement did not affect decomposition and recycling of the matrix.

4. Conclusions

The proposed chemical approach to recycling BPF/MDA epoxy resin was successfully applied to recycle glass fiber reinforced BPF/DDM epoxy resin. The GFRP was firstly immersed in nitric acid solution, with the matrix decomposed and glass fiber separated and recovered. And then the decomposed product of extract was collected and neutralized. The neutralized extract was finally repolymerized to prepare recycled resin by substituting a part of BPF epoxy resin using PA as curing agent. The recycled resin exhibited good mechanical properties based on analyses of three-point blending test, SEM and DSC. The main conclusions are summarized as follows.

The applicability of the chemical recycling approach to BPF/DDM epoxy resin was acknowledged. This applicability attached great importance to the recycling approach, because DDM is the most widely applied amine curing agent in practice. Additionally, the applicability of the recycling approach might be extended to all of amine cured epoxy resin, whose crosslink was C–N bond.

The flexural strength of the recycled resin was much higher than that of virgin resin when the content of the neutralized extract was relatively small; while, the strength gradually decreased when the content exceeded a certain percentage. Until the content of the neutralized extract was

not more than 30 wt% of the virgin resin, the flexural strength was higher than that of virgin resin.

The reinforcement of glass fiber could be separated and recovered from GFRP after matrix of GFRP was decomposed in nitric acid solution. The existence of the reinforcement did not affect degradation of the matrix. The recycling approach was more suitable to BPF/DDM resin reinforced with T-glass fiber than with E-glass fiber since T-glass fiber possessed more excellent corrosion resistance to acid solution.

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