# CFRP Recycling Technology Using Depolymerization under Ordinary Pressure

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We have developed carbon fiber reinforced plastic (CFRP) recycling technology using depolymerization of cured epoxy resin (EP) under ordinary pressure. Carbon fiber (CF) was recovered from used tennis rackets by dissolving EP with tripotassium phosphate as a catalyst and benzyl alcohol as a solvent at 200 °C for 10 hours. We were able to produce non-woven fabrics with the recovered CF using a carding machine. With these fabrics we then produced recycled CFRPs, and measured their mechanical properties. Their properties were nearly equal to the CFRP using commercial fresh CF non-woven fabric. At the same time, the depolymerized EP cured with acid anhydride was analyzed with HPLC and NMR. Our results showed that the depolymerization was proceeded by a transesterification to produce diesters and bis-diols, which can be used for recycled EP.

## 1 Introduction

CFRP has been rapidly and extensively used in transportation equipment such as aircraft and automobiles due to their light weight that improves fuel efficiency. Manufacturing CF, however, involves prolonged and high-temperature heating process, and considerable energy. The results of a life cycle assessment (LCA) indicate that CFRP is not an environmentally friendly material. Fuel can be saved when CFRP is used to reduce the weight of a transportation system, but Takahashi et al. of Tokyo University implied in their estimate that this is a minor effect seen only in commercial transportation systems1), 2). They also suggested that the best option would be to reuse CF, recovered from used transportation systems, in equivalent transportation systems.

None of the recycling technologies used to recover CF from CFRP and reused in CFRP has yet come into commercial use, but technologies are under discussion as shown in **Table 1**.

Toray Industries, Inc., Teijin Ltd. and Mitsubishi Rayon Co., Ltd. are studying recycling technologies using a thermal decomposition technique in which resins are decomposed and removed at 500 °C to 700 °C3), 4). In 2010, they commissioned the recycling work to the recycling plant of Japan Coke & Engineering Co., Ltd., located in Ohmuta, Fukuoka prefecture, where 1,000 tons of recycled CFRP are produced annually. Here, a thermal decomposition technique is used, but preprocessing such as pulverization is omitted. Takayasu Co., Ltd. developed a technology to recover longer CFs5). It also developed a technique to cut recovered CFs to any length, and produces high-quality non-woven fabric using both dry and wet methods. The facility has a capacity of 5 tons/month.

Okajima, et al. of Shizuoka University are carrying out a research project sponsored by NEDO to study CFRP recycling technologies using supercritical alcohol6), 7). EP, which is the CFRP matrix resin, is decomposed to recover CF using supercritical methanol. Remoldable thermosetting resin is produced by removing methanol from the decomposed resin and adding a curing agent.

Table 1　CFRP chemical recycling technologies in Japan

| Item | Thermal decomposition | | Supercritical fluid technique | Subcritical fluid technique | Depolymerization under ordinary pressure |
|---|---|---|---|---|---|
| Organization | Toray Industries,<br>Teijin,<br>Mitsubishi Rayon | Takayasu | Shizuoka University | Kumamoto University | Hitachi Chemical |
| Temperature | 500–700 ℃ | Not known | 250–350 ℃ | 300–400 ℃ | 200 ℃ |
| Pressure | Ordinary pressure | Ordinary pressure | 5–10 MPa | 1–4 MPa | Ordinary pressure |
| Solvent | None | None | Methanol | Benzyl alcohol | Benzyl alcohol |
| Catalyst | None | None | None | Alkali metal salt | Alkali metal salt |
| Preprocessing | Pulverization | None | Pulverization | None | None |
| Processing capacity | 1,000 tons/year | 60 tons/year | （5 L） | （0.5 L） | 12 tons/year（200 L x 2 baths） |

Goto, et al. of Kumamoto University are studying a method of recycling CFRP using subcritical alcohol[8), 9)]. When high-boiling alcohol such as benzyl alcohol is heated at 300 °C to 400 °C to turn it subcritical, and used for CFRP treatment, the whole resin decomposes within an hour. No catalyst is needed for decomposition, but CF is less damaged when alkali metal salt is used as the catalyst. This method, using high-boiling alcohol, is characterized by a relatively low pressure of around 4 MPa, which may eliminate the cost required for the dissolution bath with supercritical fluid.

Depolymerization under ordinary pressure was developed to establish a recycling business profitable for the economy by recovering and reusing CFs and resins from CFRP at low cost and energy. CFRP recycling technology using the depolymerization under ordinary pressure is discussed in subsequent sections.

## 2 Outline of Depolymerization under Ordinary Pressure

Depolymerization under ordinary pressure is a technique to depolymerize and dissolve cured resins using a treatment liquid consisting of alcohol solvent and alkali metal salt as a catalyst. When this technique is applied to composite materials containing thermosetting resins such as unsaturated polyester resin (UP), the resins in the composite depolymerize and dissolve, and inorganic substances such as metal, glass fiber (GF) and CF can be separated and recovered [10)-12)].

A treatment liquid consisting of tricalcium phosphate ($K_3PO_4$) as the catalyst and benzyl alcohol (BZA) as the solvent is used for CFRP treatment. Both $K_3PO_4$ and BZA are approved food ingredients, and their safety for the human body is unquestionably high. When CFRP is treated with this treatment liquid at around 200 °C under ordinary pressure, the cured EP immediately depolymerizes and dissolves, allowing the CF to be recovered intact. The treatment time depends on the CFRP thickness, but the whole EP dissolves in about 10 hours.

Compared with other chemical recycling techniques, this approach to depolymerization under ordinary pressure has three characteristics: Processing is under ordinary pressure, resins are recovered, and no preprocessing such as pulverization is necessary. All these features result from the discovery of an optimum combination of catalysts and solvents to selectively break the specific bond in resins. Treatment under ordinary pressure denotes low facility costs. Moreover, continuous processing facilitates more economical mass production. Recovered resins, when recomposed, can be reused as high value materials. Because this approach eliminates preprocessing, no fragmentation and pulverization costs are incurred, and applications of recovered materials may be increased. When resins are pulverized, the length of the recovered fiber tends to be short, less than 1 mm, hindering efforts to reuse them as reinforcing materials. In terms of safety, depolymerization under ordinary pressure eliminates the danger of dust explosions and pneumoconiosis caused by pulverization.

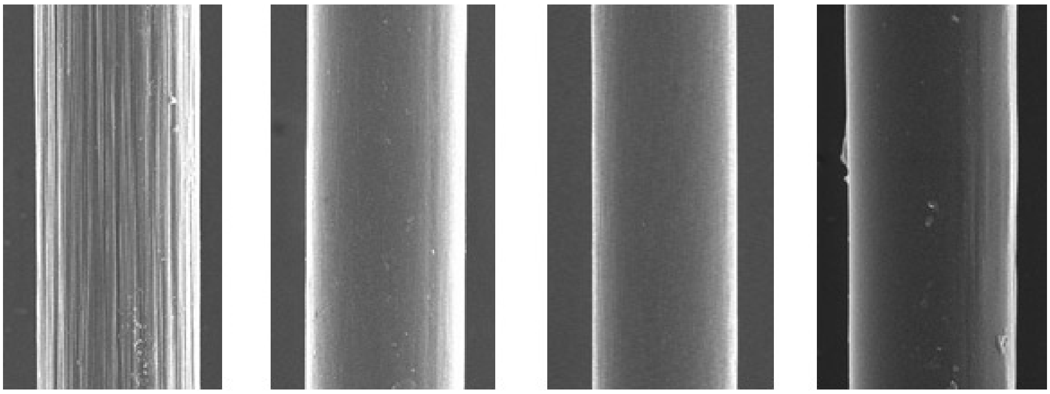
## 3 Dissolution of CFRP

**Figures 1** and **2** show the results of depolymerization under ordinary pressure for processing used tennis and badminton rackets, typical sports equipment, using CFRP[13)]. All tennis rackets were made of FRP, and the material recovered was CF containing a little GF. Aluminum frames, wooden grips, and CF used for shafts were recovered from the badminton rackets in this experiment. As the strings of both tennis and badminton rackets dissolved during treatment, we estimated they were made of polymer esters. Recovering aluminum and wood intact is one of the characteristics of this approach as shown in the experimental results.

**Figure 3** shows the SEM photographs of CFs recovered from a tennis racket and a molded part of transportation equipment using depolymerization under ordinary pressure, and **Table 2** the results of single fiber tensile tests[14)]. For comparison, CF recovered with pyrolysis and fresh CF are also presented. The surface profile of the CF recovered from the molded part using depolymerization under ordinary pressure is approximately equivalent to that of fresh CF. The regularity of vertical lines seen in CF recovered from the tennis racket indicate they are not caused by damage. The results of tensile tests on these CFs are equal or exceed those on the fresh CF, suggesting their high potential for use as reinforcing materials.

Figure 1 A treated CFRP tennis racket, before (left) and after (right)

Figure 2 A treated CFRP badminton racket, before (left) and after (right)



Tennis racket Molded part Pyrolysis Fresh CF mat

Figure 3 SEM photographs of Recovered CFs

Table 2 Results of single fiber tensile tests of recovered CFs

| Item | Tennis racket | Molded part | Pyrolysis | Fresh CF mat |
|---|---|---|---|---|
| Tensile strength (MPa) | 3,200 | 4,393 | 3,459 | 3,198 |
| Tensile modulus (GPa) | 188 | 303 | 301 | 152 |
| Elongation (mm) | 0.34 | 0.29 | 0.23 | 0.21 |

## 4 Development of Recovered CF Applications

CFs recovered from CFRP were flocculating, and we thought this would reduce the production efficiency of CFRP and inhibit the production of quality CFRP. To solve this problem, we examined how to produce non-woven fabric using recovered CF. Either a dry or wet method can be used to produce non-woven fabrics, and either was found to allow non-woven fabric to be produced from recovered CF [14]. A carding machine was used in the dry method, and a paper pressing machine in the wet process to produce wadding from cotton, etc. As CF is conductive, the processing machine must be sufficiently insulated.

A carding machine was introduced to produce non-woven fabric from recovered CF in the dry process. Using this machine, CF was opened and carded, and several thin CF sheets, shown in **Figure 4**, were layered to produce non-woven fabric. **Figure 5** shows the non-woven fabric produced from the recovered CF. From this non-woven fabric, CFRP was experimentally produced

Figure 4 Production of recovered CF non-woven fabric with a carding machine

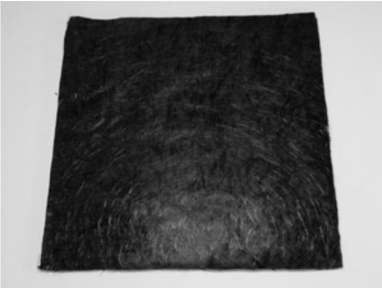


Figure 5 Recovered CF non-woven fabric

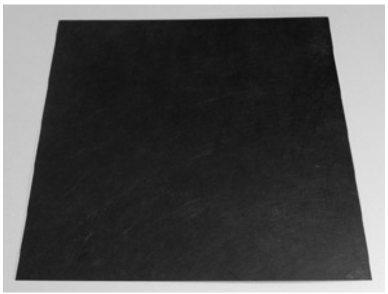


Figure 6 Recycled CFRP using recovered CF non-woven fabric

with the compression molding method. **Figure 6** shows the molded recycled CFRP. Similar to comparisons of single fibers, **Figures 7** and **8** show the results of tensile tests, and **9** and **10** the results of bending tests in comparison with non-woven fabric made of CF recovered with pyrolysis and CFRP using a fresh CF mat[15].

From these test results, no significant differences emerged between any of the recovered CFs and CFRP from a fresh CF mat, suggesting these CFs can be used for CFRP. All properties are reduced with CF content exceeding 25 %; probably due to imperfect carding, rather than defects in the machine or condition.

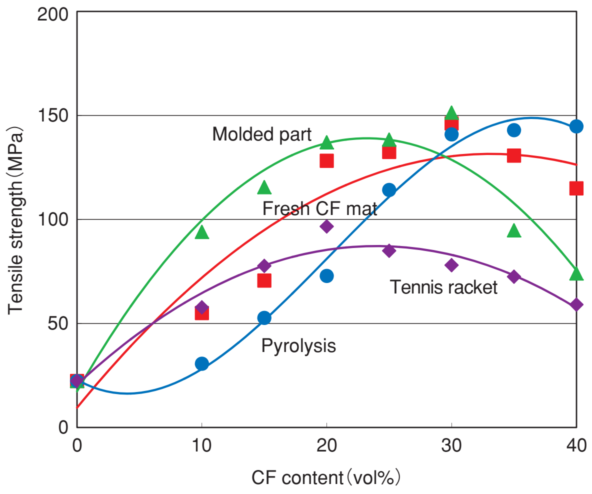


Figure 7  Tensile strength of recycled CFRPs

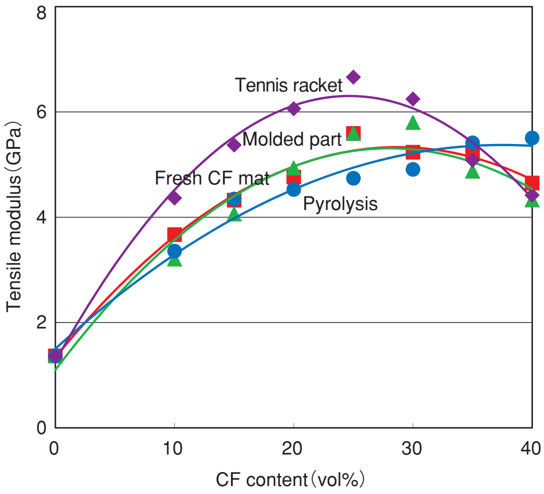


Figure 8  Tensile modulus of recycled CFRPs

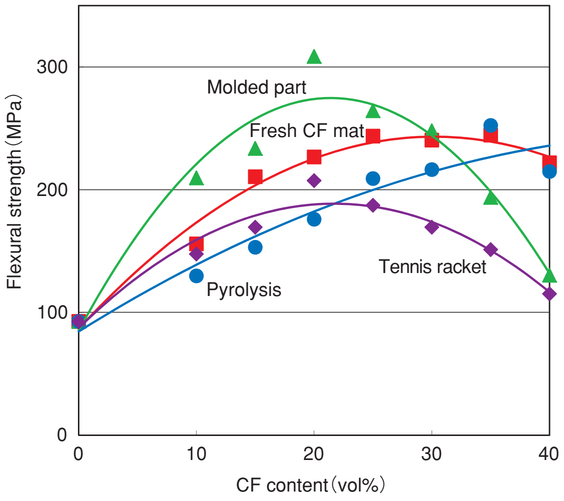


Figure 9  Flexural strength of recycled CFRPs

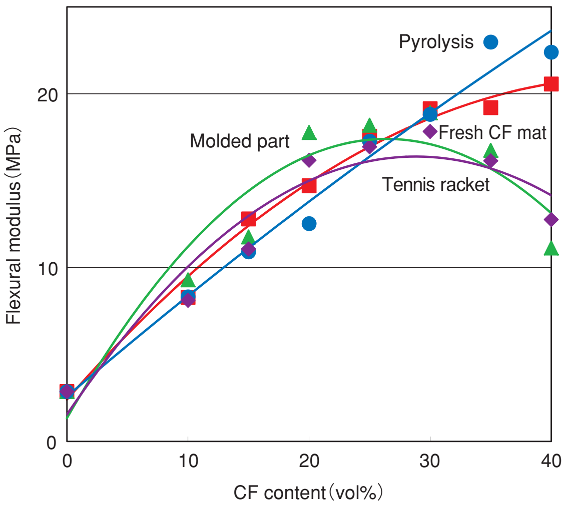


Figure 10  Flexural modulus of recycled CFRPs

## 5 Development of Recovered Resin Applications

EPs mainly used for CFRP include amine curing EP (EP/Am) and acid anhydride curing EP (EP/Ah) for which amine (Am) and acid anhydride (Ah) are used as hardener respectively. In depolymerization under normal pressure, a transesterification is used for depolymerization for exchanging ester bonds in the resin structure with solvent, i.e. mono alcohol. This technique was therefore applied only to CFRPs of EP/Ah, but we found that it could also be used for EP/Am through detailed settings on the depolymerization under ordinary pressure[16]. The mechanism of depolymerization of EP/Am is under analysis, but this approach has become available for recycling almost all CFRPs with detail settings.

The depolymerization mechanism of EP/Ah has already been found. Depolymerization is triggered by a transesterification, and depolymerized products with benzyl ester or diol at the end of their chemical chains are generated[17]. **Figure 11** shows the estimated depolymerization reaction formulas of EP/Ah.

EP prepolymer may be regenerated by degenerating these products.

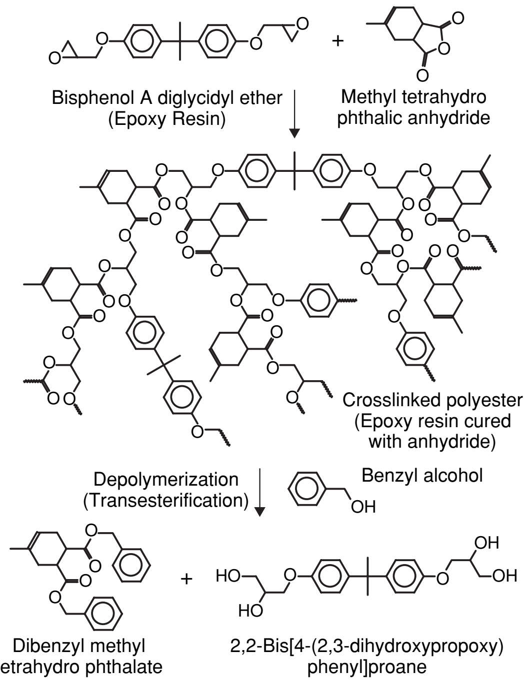


Figure 11 A estimated depolymerization reaction of EP/Ah

## 6 LCA of Recovered CFs

Tennis rackets made of CFRP having 50 wt% of CF content were used as samples subject to dissolution. After the samples had been treated with depolymerization under ordinary pressure, all the resins dissolved in 10 hours, whereupon EP-depolymerized products and CFs were recovered. Three categories of treatment, 1,000, 2,000 and 17,000 rackets/month were respectively defined. Facilities and processing conditions suitable for these categories were determined, and the required energy for dissolution, cleaning and drying processes was calculated and totaled to determine the overall energy required to recover CFs.

The energy required for 1,000, 2,000 and 17,000 rackets/month is 91, 78 and 63 MJ/kg, respectively (**Figure 12**). A breakdown of energy for 17,000 rackets/month revealed that the distillation energy was 38 MJ/kg, accounting for about 60 % of the total[18]. To save more energy required to recover CFs, we plan to examine a new method of regenerating cleaning liquids.

Compared with the energy required to manufacture fresh CFs, i.e. 286 MJ/kg[19), 20)], the energy is smaller in all other categories, and about 1/4 or less in the category of 17,000 rackets/month (**Figure 13**).

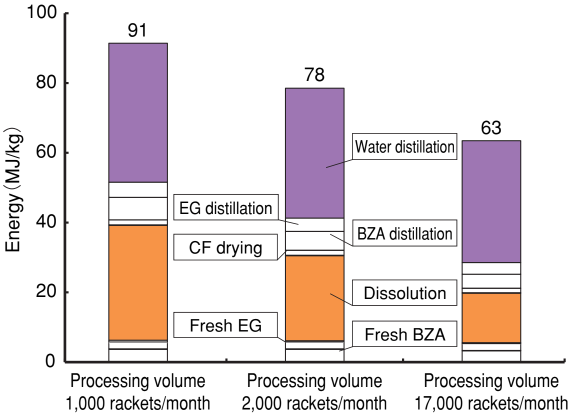


Figure 12 Energy of recovered CF by dissolving method under ordinary pressure

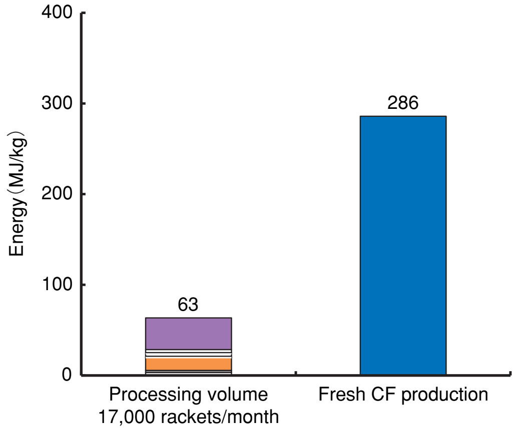


Figure 13 A comparison of energy of a recovered CF by dissolving method under ordinary pressure with a fresh CF on the market

## 7 Conclusion

Japanese companies have a substantial share of CF and CFRP markets, and related technologies are representative in Japan. Japan is also regarded as the most advanced nation for CFRP recycling technologies at present. Although papers on chemical recycling technologies for CFRP using, for example, supercritical propanol 21) have begun to appear overseas, almost all of them concern CF recovery technologies using pyrolysis. However, large projects targeting the development of recovered CF applications have been launched in Europe and the U.S., in which numerous researchers and engineers have participated.

Conversely, projects relating to the development of CFRP technologies do exist, but recycling technologies are merely one of objectives for these projects in Japan. There are no national projects solely targeting the development of CFRP recycling technologies. Hitachi Chemical started a business promotion project focusing on CFRP recycling in April 2012. Commercial operation is currently under discussion together with CF processing companies, CFRP manufacturers, CFRP users, and other stakeholders.

These technologies have been adopted and promoted in the 2005–2006 regional new industry creation technology development subsidy program sponsored by the Kanto Bureau of Economy, Trade and Industry.

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