Microwave degradation of carbon fiber reinforced plastics in choline chloride

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Abstract. In spite of resin recycling of carbon fiber reinforced plastics (CFRP) is very important as well-known on the viewpoint of environmental protection and resource conservation, the development of effective resin recycling had hardly been investigated. In this study, we investigated the operating conditions for microwave decomposition of CFRP using various alcohols as solvents. In order to avoid rapid absorption of microwaves into carbon fibers (CF), choline chloride was added to the solvent for microwave degradation. Ethylene glycol monoallyl ether (EGMA) was used as a solvent in order to reuse the resin part. Double bonds could be introduced into the resin degradation products. The preparation of cured products by condensation reaction by using the resin degradation products was also successful.

Introduction

It has been well known that the use of carbon fiber reinforced plastic (CFRP) is extremely effective in reducing the weight of sports tools, such as tennis rackets, fishing rods, and golf shafts. In recent years, lightweight airplanes and automobiles made of CFRP have become popular to save petroleum-based fuels for climate change strategy. General CFRP is a composite material manufactured from epoxy resin with a carbon fiber framework and is expected to be one of the next-generation materials with hard and tough properties. However, most waste CFRP products are disposed of in landfills without any treatment due to their hardness. Carbon fiber (CF), produced by carbonizing polyacrylonitrile or pitch at about 3000°C, is a valuable carbon resource that can be reused by recovering it from CFRP. Thus, the recycling of CFRP is an important issue that needs to be solved immediately in terms of environmental protection and resource conservation [1, 2].

Recycling methods of CFRP by distillation carbonization [3, 4], supercritical fluid [5 – 7], atmospheric pressure dissolution [8], and microwave thermolysis [9] have been reported. This distillation carbonization method uses that the gas produced in the dry distillation of CFRP as a heating source burns through the dry distilled CFRP to recover CF finally [3, 4]. Therefore, the resin portion cannot be recycled in this method. In the supercritical water treatment of acid anhydride-cured CFRP, the resin decomposed at a reaction pressure of 26 MPa and a reaction temperature of 380°C, producing phenolic resin monomer as a product. When supercritical methanol was used at a reaction pressure of 10 MPa and a reaction temperature of 270°C, the products mainly contained methyl ester structures. Furthermore, supercritical acetone was also reported to be effective for amine-cured CFRP [5, 6]. In the atmospheric pressure dissolution, Benzyl alcohol solvolysis at 200°C in the presence of a tripotassium phosphate catalyst under ambient pressure conditions requires a prolong reaction time of 10 hours [8]. However, these recycling methods of CFRP have only recovered carbon fiber, and a total recycling method that includes the reuse of epoxy resin has not been established [1, 2].

For glass fiber reinforced plastics (GFRP), we recently found that the non-catalytic pressurized microwave degradation method is effective for recycling resin parts and glass fibers [10]. However, when the pressurized microwave degradation method is applied to CFRP, CF strongly absorbs microwaves to cause discharge phenomena and often the generation of sparks. At this time, it is expected that low-boiling compounds will rapidly evaporate or flammable compounds will ignite around the CF, causing an uncontrollable and rapid increase in pressure due to the gases generated.

In this study, we investigated the operating conditions for microwave decomposition of CFRP using various alcohols as solvents. Furthermore, in order to avoid rapid absorption of microwaves by CF, choline chloride as an ionic compound was added to the solvent for microwave decomposition. Ethylene glycol monoallyl ether (EGMA) was used as a solvent in order to reuse the resin part. Double bonds were introduced into the resin degradation products [10], and polymerization by condensation reaction was attempted.

Experimental section

Materials

Small pieces (4 mm x 4 mm, thickness 3mm) of carbon fiber reinforced plastic (CFRP-A, Japan) were used for microwave degradation. FT-IR measurement of CFRP-A confirmed that the resin portion is acid anhydride cured, based on the existence of a C=O absorption band at 1731.9 cm^{-1}. Resin content in CFRP-A was found to be 43.7 % based on the mass of carbon fiber after the combustion experiment. Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), benzyl alcohol, glycerol, phenol, ethylene glycol monoallyl ether (EGMA), and deuterated chloroform were supplied by Kanto Chemical Co., Inc (Japan). Choline chloride, diethanolamine hydrochloride (DAH), and triethanolamine hydrochloride (TAH) as ionic compounds were supplied by Tokyo Chemical Industry Co., Ltd. (Japan). Tetramethylsilane (TMS, ACROS ORGNICS) and 1,4-bis(trimethylsilyl)benzene (BTMSB, Tokyo Chemical Industry Co., Ltd.) were used as internal standards for NMR. Unsaturated polyester (157BQTN) was supplied by Showa Denko (Japan), and curing agent (Kayamek M) supplied by Kayaku Akzo.

Microwave degradation of CFRP (Fig. 1)

Microwave Reactor (Biotage Initiator+8, Sweden) was used for microwave degradation of CFRP-A. A 5-mL glass vial was used for pressurized microwave degradation of CFRP-A. The vial containing solvent, stirrer, and CFRP-A chip was mounted on the Initiator+8. Microwave output was controlled manually on a continuous basis so that the prescribed temperature and pressure were maintained during microwave irradiation. The output operation was performed automatically by a 23-step execution program with reference to the appropriate manual output controls.

Extraction of the resin degradation products was performed using 20 mL of heated chloroform for 90 minutes. Suction filtration was used to separate the extract from the insoluble material. The extract was concentrated by evaporating the chloroform using an evaporator under reduced pressure. Kugelrohr distillation was performed to separate the degradation residues from the higher boiling compounds. The weight loss and the degradation ratio of the resin were determined from the weight of the resin degradation products after drying. In the degradation reaction with choline chloride, the extraction of choline chloride was repeated three times with 20 mL of water after extraction with heated chloroform.

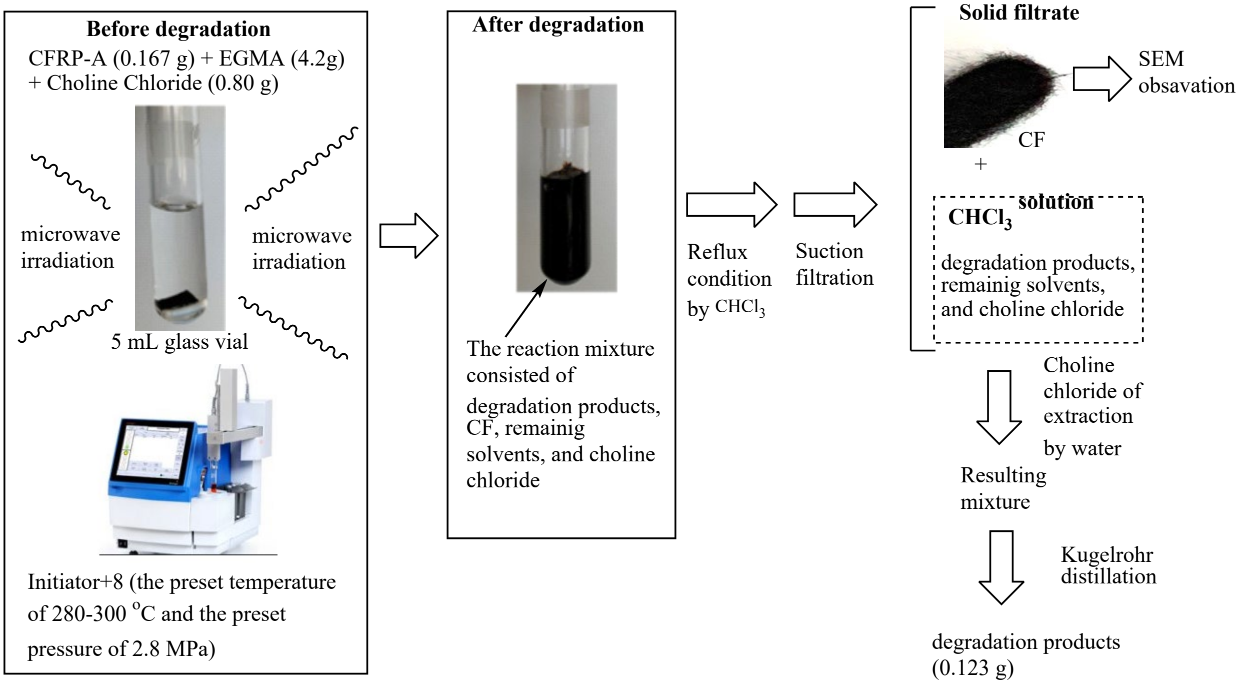


Figure 1. The schematic daiagrams of the experimental procedure

The weight reduction ratio of CFRP and the reaction ratio of the resin are defined by the following equations.

The weight reduction ratio of CFRP = 1 – (Weight of residue)/(Initial weight of CFRP) (1)
The degradation ratio of the resin =
(The weight reduction ratio of CFRP)/(Resin content of CFRP) (2)

Characterization

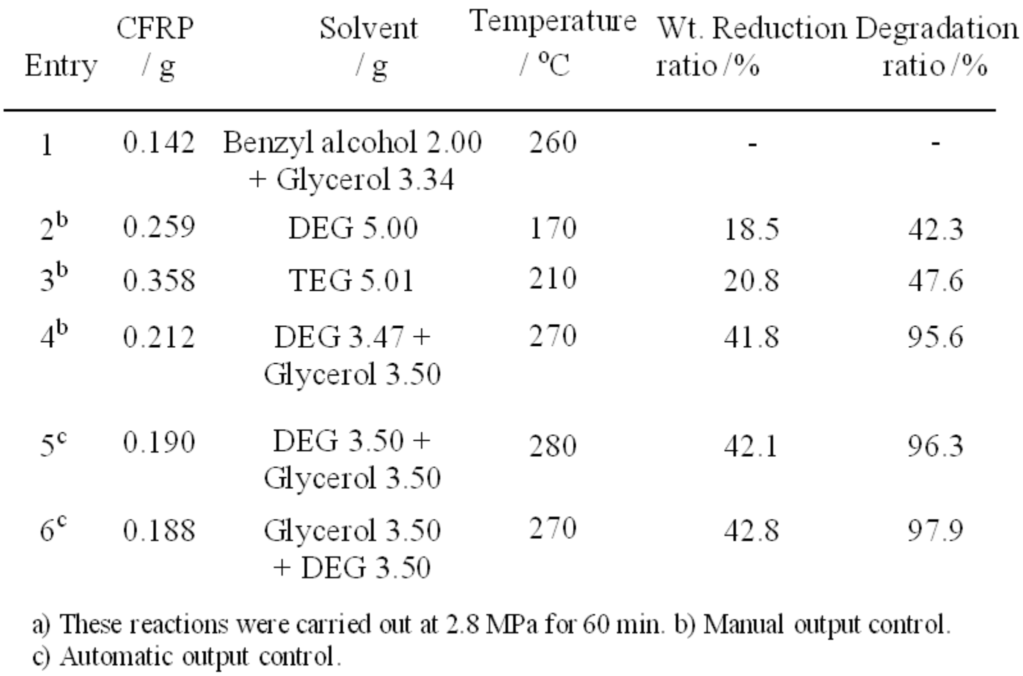
Fourier transform infrared (FT-IR) spectra were measured via an attenuated total reflection (ATR) method using a Perkin Elmer Spectrum 100 spectrometer (Perkin Elmer, USA). The nuclear magnetic resonance (NMR) spectra were recorded in deuterated chloroform using TMS or BTMSB by a superconducting Fourier transform NMR spectrometer ESC270 (JEOL, Japan). The scanning electron microscopy (SEM) image of CF after the degradation was observed by 3D real surface view microscope VE-8800 (Keyence Corp., Japan).

Results and discussion

Microwave Degradation of CFRP

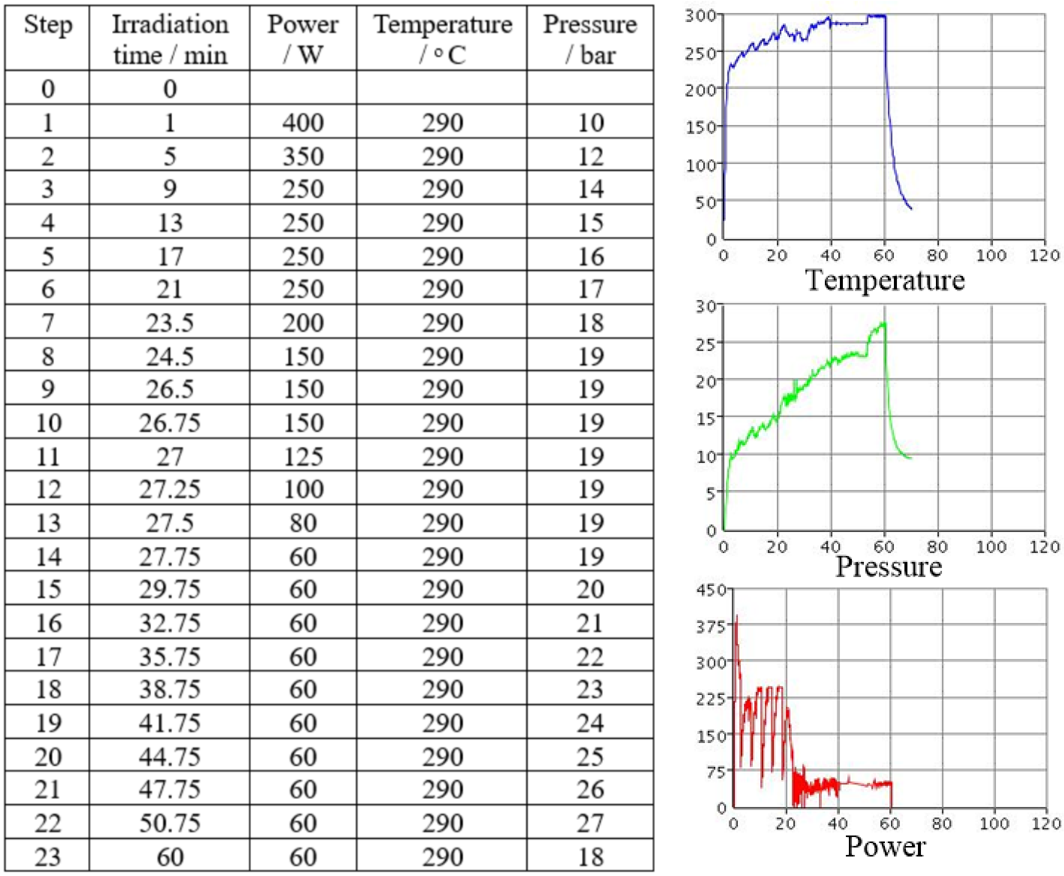
In microwave heating of CFRP, carbon fibers in CFRP selectively absorb microwaves and are rapidly heated from the inside. Table 1 shows the results of CFRP degradation by pressurized microwave heating when various alcohols are used as solvents. For the first CFRP degradation reaction using benzyl alcohol and glycerol (Entry 1), the Initiator+8 automatically stopped after 18 minutes from the start of the reaction due to the collapse of the vial by pressurization. The next microwave heating was performed with continuous manual adjustment of microwave output to prevent rapid pressure increase. As a result, after 3 hours of microwave irradiation, the resin degradation ratios with DEG and TEG were 42.3% (Entry 2) and 47.6% (Entry 3), respectively. When DEG and GC were mixed at a mass ratio of 1:1 (Entry 4), the temperature could be maintained at 270°C after 1 hour of microwave irradiation, resulting in a resin degradation ratio

Table 1. Pressurized microwave degradation of CFRP-A[a].



Entry	CFRP / g	Solvent / g	Temperature / °C	Wt. Reduction ratio /%	Degradation ratio /%
1	0.142	Benzyl alcohol 2.00 + Glycerol 3.34	260	-	-
2[b]	0.259	DEG 5.00	170	18.5	42.3
3[b]	0.358	TEG 5.01	210	20.8	47.6
4[b]	0.212	DEG 3.47 + Glycerol 3.50	270	41.8	95.6
5[c]	0.190	DEG 3.50 + Glycerol 3.50	280	42.1	96.3
6[c]	0.188	Glycerol 3.50 + DEG 3.50	270	42.8	97.9

a) These reactions were carried out at 2.8 MPa for 60 min. b) Manual output control.
c) Automatic output control.



Step	Irradiation time / min	Power / W	Temperature / °C	Pressure / bar
0	0			
1	1	400	290	10
2	5	350	290	12
3	9	250	290	14
4	13	250	290	15
5	17	250	290	16
6	21	250	290	17
7	23.5	200	290	18
8	24.5	150	290	19
9	26.5	150	290	19
10	26.75	150	290	19
11	27	125	290	19
12	27.25	100	290	19
13	27.5	80	290	19
14	27.75	60	290	19
15	29.75	60	290	20
16	32.75	60	290	21
17	35.75	60	290	22
18	38.75	60	290	23
19	41.75	60	290	24
20	44.75	60	290	25
21	47.75	60	290	26
22	50.75	60	290	27
23	60	60	290	18

Figure 2. Setting of power, temperature, and pressure in the automatic output control program

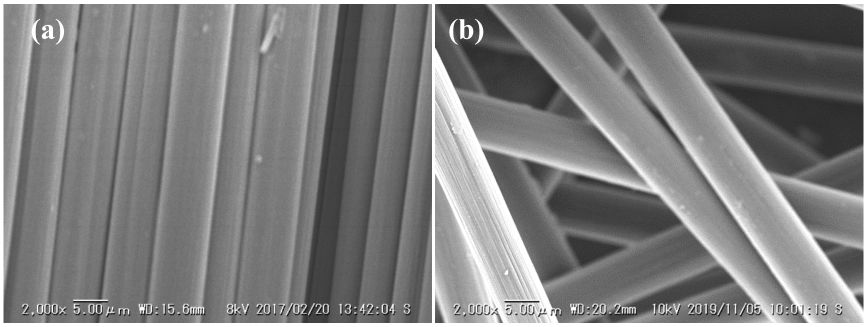


Figure 3. SEM observations of (a) virgin CF and (b) recovered CF of Entry7.

of 96.3 %. Approximately 100 experiments in which the pressure and temperature were gradually increased by manually controlling the output were examined, and it was confirmed that the temperature and pressure could be stably and simultaneously raised and boosted even after simplifying to automatic control of the 23-step output created as shown in Fig.2 (Entry 5). The results of the experiments repeated by automatic output control were almost identical, confirming reproducibility (Entry 6).

Fig. 3 shows SEM images of CF surface (photo (b) in Fig. 3) recovered after the Entry 7 experiment. Compared to virgin CF (photo (a) in Fig. 3), there was no significant damage or dimensional change due to microwave heating, but grooves were formed along the fiber axis on the surface.

Microwave Degradation of CFRP-A with Choline Chloride

In the experiments using alcohols as solvents, complex operating conditions were obtained to obtain high resin degradation rates, but excessive microwave absorption by the carbon fibers in the CFRP formed internal hot spots and sometimes caused the breakdown of the pressure-resistant vessel. Therefore, to suppress the selective absorption of microwaves by CF, we performed microwave degradation of CFRP-A by adding choline chloride as an ionic compound with high microwave absorption capacity into EGMA (Entry7 in Table 2). Surprisingly, in the degradation

Step	Irradiation time / min	Power / W	Temperature / °C	Pressure / bar
0	0			
1	1	400	300	20
2	5	350	300	27
3	54	250	300	30

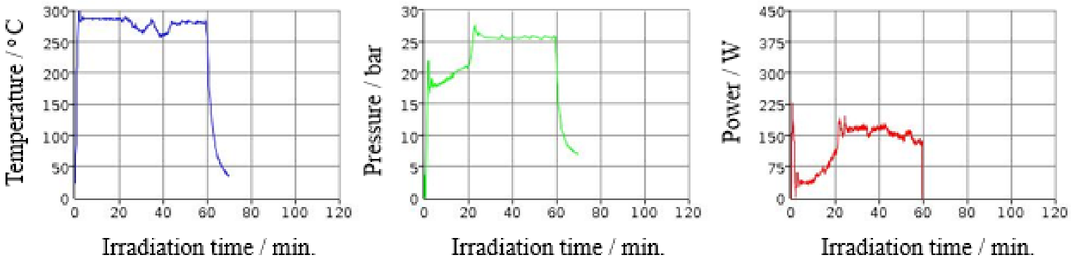
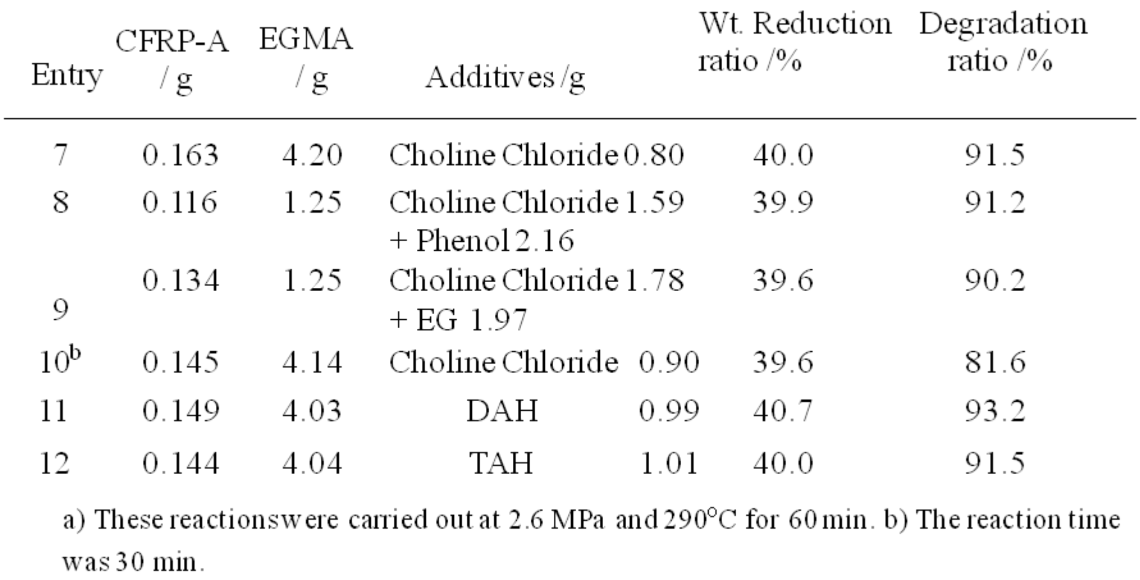


Figure 4. Setting of simple three-step program for pressure-controlled degradation reaction in Entry 7.

Table 2. Effect of choline chroride derivatives for pressurized microwave degaradation of CFRP-A^a.



Entry	CFRP-A / g	EGMA / g	Additives /g	Wt. Reduction ratio /%	Degradation ratio /%
7	0.163	4.20	Choline Chloride 0.80	40.0	91.5
8	0.116	1.25	Choline Chloride 1.59 + Phenol 2.16	39.9	91.2
9	0.134	1.25	Choline Chloride 1.78 + EG 1.97	39.6	90.2
10^b	0.145	4.14	Choline Chloride 0.90	39.6	81.6
11	0.149	4.03	DAH 0.99	40.7	93.2
12	0.144	4.04	TAH 1.01	40.0	91.5

a) These reactionswere carried out at 2.6 MPa and 290°C for 60 min. b) The reaction time was 30 min.

experiments shown in Table 2, a simple three-step program was used to perform a pressure-controlled degradation reaction (Fig. 4). The degradation of CFRP-A using the mixture of EGMA and choline chloride resulted in a resin degradation ratio of 91.5 %. Further addition of EG or phenol as an aid to miscibility in the mixture of choline chloride and EGMA was also investigated (Entry 8 and 9). However, the addition of EG and phenol did not change the resin degradation ratio. DAH and TAH were used in the microwave decomposition experiments of CFRP-A instead of choline chloride (Entry 11 and 12). When DHA was used under the same conditions as Entry 7, the resin degradation ratio was 93.2%. when TAH was used, Initiator+8 stopped after 7 minutes microwave irradiation due to a sudden increase in pressure. The next reaction, in which the ratio

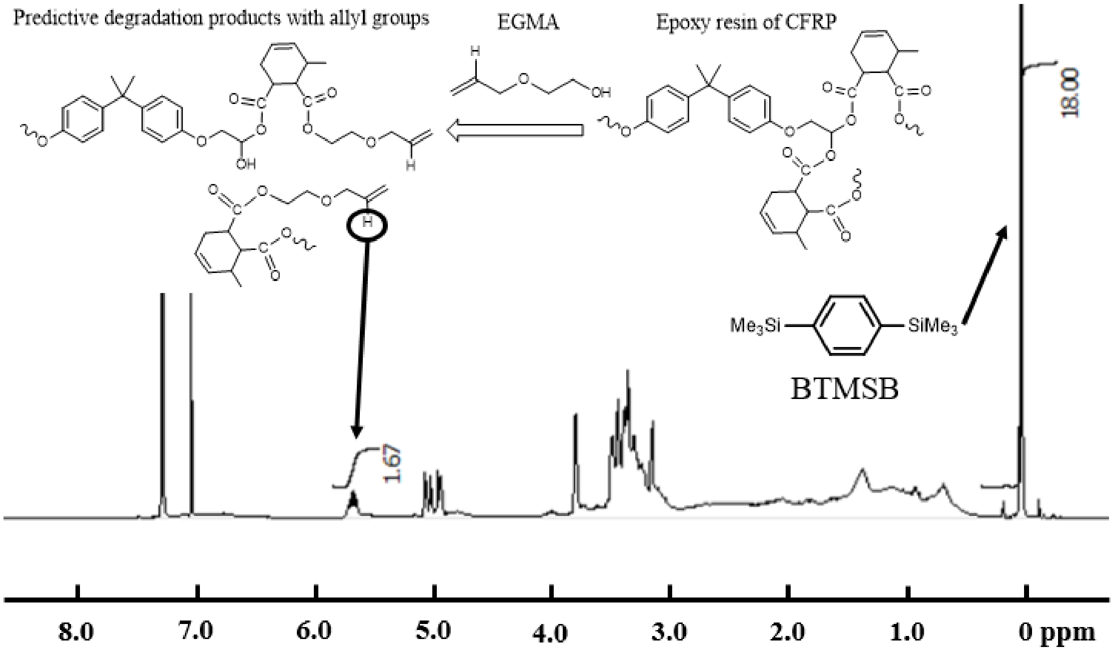


Figure 5. ^{1}H-NMR analysis for the calculation of allyl groups in the degradation products by using BTMSB.

of TAH was increased, yielded results comparable to those obtained with choline chloride. These results fully suggest that choline chloride derivatives with quaternary ammonium salt and ethanol structures and EGMA form an ionic mixture that can effectively suppress the microwave absorption of CF.

Structural Analysis of Resin Degradation Products

Fig.3 shows ^{1}H-NMR spectra of the resin degradation products. ^{1}H-NMR analysis of the resin degradation products (Entry 7) showed four chemical shifts of the crosslinking-reactive allyl groups introduced by EGMA at 3.8 (2 protons of methylene in allyl group), 4.9, 5.1, and 5.7 (three protons of vinyl moiety in allyl group) ppm. In addition, not so large chemical shifts of the methylene protons of the by-product EGMA oligomer [5] were observed around 0.5-1.5 ppm and 3.2-3.5 ppm. FT-IR analysis of the resin degradation product showed the main absorption bands of the OH group (3393.9 cm^{-1}) and the C=O group (1729.9 cm^{-1}). It is presumably suggested that a considerable amount of the EGMA oligomer was simultaneously removed by three times aqueous washing for choline chloride removal.

The use of 1,4-bis(trimethylsilyl)benzene (BTMSB, 0.0436 mmol) as an internal standard in the 1H-NMR analysis allowed the calculation of the mole concentration of allyl groups (0.0728 mmol) introduced into 0.0505g of the resin degradation product (Entry 7, Fig. 3). From the results of 1H-NMR analysis, the concentration of allyl groups in the resin degradation product was calculated to be 1.44 mmol/g.

Preparation of cured products using resin degradation products

The cured product was prepared using resin degradation products to confirm the cross-linking reactivity of the allyl group introduced by EGMA. The resin degradation product (Entry 7, 1.0 g), unsaturated polyester (157BQTN, 3.0 g), and a curing agent (Kayamek M, 0.06 g) were mixed. After 3 days of mixing and standing in the room temperature condition, the mixture was completely cured (Fig. 6). It is suggested that the allyl groups introduced into the resin degradation products are capable of cross-linking reaction with unsaturated polyesters. Furthermore, in the TG-DTA measurement of the cured product none rapid weight loss showed that the cured product had a structure with a sufficiently dense three-dimensional crosslinked structure. We will plan to carry out strength measurements in the future.

Figure 6. A cured product using resin degradation products of Entry 7 and unsaturated polyester.

Summary

(1) The degradation reaction of CFRP in various alcohols under the pressurized microwave irradiation proceeded well without the rupture of the vessel when the pressure increase was adjusted in detail by the output control.

(2) The addition of choline chloride derivatives was effective to suppress the rapid absorption of microwave on the CF, making the output control simple.
(3) When EGMA was used as a reactive solvent, the resin decomposition products with allyl groups, which have crosslinking reactivity by curing reaction, were formed.
(4) The microwave degradation reaction of CFRP is an effective recycling method for the CF and the resin by using EGMA and choline chloride derivatives.

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References

[1] S. Pimenta, S.T. Pinho, Recycling carbon fibre reinforced polymers for structural applications: technology review and market outlook, Waste Management, 31 (2011) 378-392. https://doi.org/10.1016/j.wasman.2010.09.019

[2] H. Sukanto, W. W. Raharjo, D. Ariawan, J. Triyono, Carbon fibers recovery from CFRP recycling process and their usage: A review, 2021 IOP Conference Series Materials Science and Engineering, 1034, 012087. https://doi.org/10.1088/1757-899X/1034/1/012087

[3] H. Itazu, H. Kamiyoshi, H. Moritomi, Recycling of Carbon Fiber using Two-stage Thermal Treatment System, Haikibutu shigenjunkan gakkaishi, 24 (2013) 371-378. https://doi.org/10.3985/mcwmr.24.371

[4] H. Itazu, M. Itazu, H. Moritomi, Apparatus for regenerative treatment of carbon fiber, JP4949123.

[5] I. Okajima, K. Watanabe, S. Haramiishi, M. Nakamura, Y. Shimamura, T. Sako, Recycling of carbon fiber reinforced plastic containing amine-cured epoxy resin using supercritical and subcritical fluids Author links open overlay panel, J. Supercrit. Fluids, 119 (2017) 44-51. https://doi.org/10.1016/j.supflu.2016.08.015

[6] I. Okajima, K. Yamada, T. Sugeta, T. Sako, Decomposition of epoxy resin and recycling of CFRP with sub- and supercritical water, Kagaku Kogaku Ronbunshu, 28 (2002) 553-558. https://doi.org/10.1252/kakoronbunshu.28.553

[7] L. Weihao, H. Haihong, L. Yun, L. Lei, C. Huanbo, L. Zhifeng, Life cycle assessment and energy intensity of CFRP recycling using supercritical N-butanol, Journal of Material Cycles and Waste Management, 23 (2021) 1303-1319. https://doi.org/10.1007/s10163-021-01206-7

[8] K. Shibata, CFRP Recycling Technology using Depolymerization of Epoxy Resin under Ordinary Pressure, Hitati-Kasei Tecnical Report, 24 (2013) 358-363. https://doi.org/10.3985/mcwmr.24.358

[9] D. Jianying, X. Lei, Z. Libo, P. Jinhui, G. Shenghui, L. Jianhua, K. Sivasankar, Recycling of carbon fibers from CFRP waste by microwave thermolysis, Processes (2019), 7(4), 207. https://doi.org/10.3390/pr7040207

[10] K. Ikenaga, H. Nagamitsu, T. Kikukawa, K. Kusakabe, A new recycling process for recycled plastic production from glass fiber reinforced plastics, 2018 OP Conference Series Materials Science and Engineering, 458, 012034. https://doi.org/10.1088/1757-899X/458/1/012034