ORIGINAL ARTICLE

Preparation of carbon fibers coated with epoxy sizing agents containing degradable acetal linkages and synthesis of carbon fiber-reinforced plastics (CFRPs) for chemical recycling

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Abstract
New epoxy resins containing degradable acetal linkages were synthesized by the addition reaction of bisphenol-A (BA) and epoxy-functionalized vinyl ethers containing hydrophilic oxyethylene chains, 2-(vinyloxy)ethyl glycidyl ether (VEGE) and 2-[2-(vinyloxy)ethoxy]ethyl glycidyl ether (VEEGE). Carbon fibers were applied with the obtained degradable epoxy resin-based sizing agents (designated as BA-VEGE and BA-VEEGE) in ordinary (1.4 ~ 2.2 wt%) or excess (6.4 ~ 13.4 wt%) amounts. Interfacial adhesion between the carbon fibers applied with the degradable epoxy resin-based sizing agents and matrix resins (bisphenol-A-type epoxy resin) was evaluated by the microdroplet method. Carbon fibers with both degradable epoxy resins as a sizing agent showed improved adhesive properties compared with the desized carbon fibers. Using the degradable sizing agent-applied carbon fibers, carbon fiber-reinforced plastics (CFRPs) were prepared by laminating prepreg sheets and heating them under pressure. The tensile properties of the CFRPs with $[0]_{50}$ lay-up did not depend on the structure of the sizing agents, but the tensile strength decreased as the amount of sizing agent used increased. On the other hand, the tensile properties of the CFRPs with $[0/90]_{12S}$ lay-up were not dependent on the structure or volume of sizing agents used. The impact toughness of the CFRPs was evaluated by the charpy impact test. When an ordinary volume of sizing agent was applied, the CFRPs with degradable epoxy resin-based sizing agents exhibited higher levels of impact strength than the commercial sizing agent-based CFRPs. However, applying an excessive volume of sizing agent to carbon fibers led to a decline in impact strength. The degradation reaction was conducted under acidic conditions by the treatment of HCl at room temperature or 70 °C. CFRPs with degradable epoxy resins as sizing agents in ordinary volumes were barely decomposed due to insufficient degradable regions in the CFRP components. However, the CFRPs applied with excess degradable sizing agents decomposed and carbon fibers were recovered.

Introduction

It is well known that one of the factors affecting the mechanical properties of composite materials such as carbon fiber-reinforced plastics (CFRPs) is the interfacial adhesion between fibers and matrix resins. Carbon fibers are applied with sizing agents primarily to improve their handling tractability and wettability. However, several studies have reported that the presence of sizing agents on carbon fiber surface improves the interfacial properties and hence the mechanical properties of the resulting CFRPs [1–3]. Although the detailed molecular structure of commercial sizing agents has not been clarified to users, it is suggested that epoxy compounds containing hydrophilic groups are generally used since the sizing process is performed in water during manufacturing [3–6]. There have been some reports on the effects of interfacial properties resulting from emulsifier volumes and the molecular weights of sizing agents [4, 5], but little has been reported on sizing agents with new functionality.
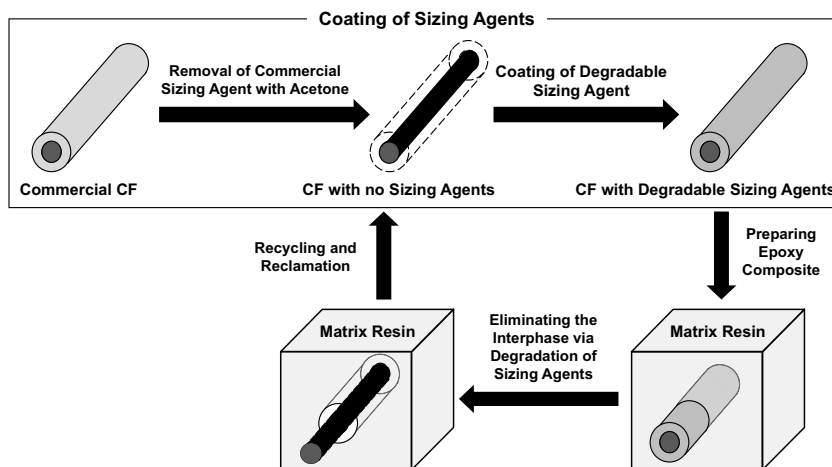
On the other hand, epoxy resins generally used for matrix resins of CFRPs form a three-dimensional crosslinked

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**Scheme 1** Schematic images of the carbon fiber recovery process

Scheme 2 Structures of conventional epoxy resin (jER828) and acetal linkage-containing epoxy resins (BA-VEGE and BA-VEEGE) used for sizing agents

structure when they are cured. This crosslinked structure offers chemical and heat resistance and excellent mechanical properties. However, as the cured epoxy resins are insoluble and infusible, it is difficult to recover carbon fibers from the wasted CFRPs. In addition, carbon fibers are expensive, and thus, it is desirable to recover and reuse them. For this reason, numerous CFRP recycling technologies are being reported on [7–11]. Examples include the thermal decomposition method in air or nitrogen atmosphere [7, 8] and the supercritical/subcritical solvolysis method [9–11]. While these are recycling technologies for CFRPs that use conventional matrix resins, their methods are costly and involve the realization of severe decomposition conditions. Thus, several studies have used matrix resins with degradable functions themselves to achieve decomposition under milder conditions [12–16]. In a previous study, we synthesized epoxy resins containing acetal linkages, which can be hydrolyzed under acidic conditions, and we prepared CFRPs by using them as a matrix [17–21]. It has been found that CFRPs using epoxy resins with acetal linkages hydrolyze under particular acidic conditions and generate carbon fibers and resin residues separately. However, when using these method, conventional matrix resins should be replaced with our degradable resins [17, 18, 19] or contain our degradable resins at least in some proportion in the conventional epoxy matrix [20, 21]. Therefore, the selection of matrix resins available is limited.

For this reason, we herein developed a new methodology using epoxy resins containing acetal linkages as sizing agents for carbon fibers. The functionalization of degradability into sizing agents is a new concept. In this study, new recyclable CFRPs were developed by using commercially available epoxy resin as a matrix, and carbon fibers were applied with degradable acetal linkage-containing epoxy resins as sizing agents in ordinary or excess amounts (Scheme 1). We synthesized the new epoxy resins containing degradable acetal linkages and oxyethylene chains to improve the
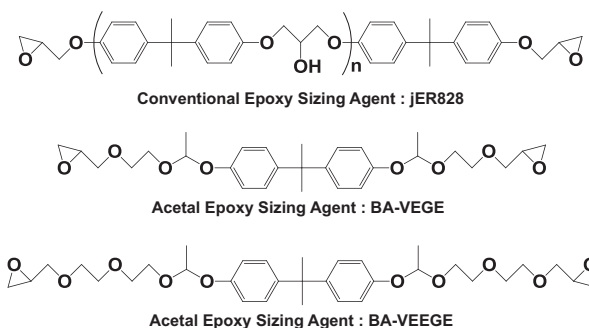
hydrophilicity (BA-VEGE and BA-VEEGE; Scheme 2). The performance of BA-VEGE and BA-VEEGE as sizing agents was evaluated from the adhesive properties by the microdroplet method and the mechanical properties measured by tensile and charpy impact tests of the prepared CFRPs. The degradation behavior of the prepared CFRPs was investigated based on whether or not carbon fibers can be separated and recovered from CFRPs even when degradation regions in the composites are present only at the interface between the carbon fibers and matrix resins (Scheme 3).

Experimental procedures

Materials

2-Hydroxyethyl vinyl ether (HEVE) and diethylene glycol monovinyl ether (DEGV) were supplied by Nippon Carbide Industries (Tokyo, Japan). Bisphenol-A-type epoxy resins (jER828 and jER1001) and dicyandiamide (DICY; curing agent; DICY15) produced by Mitsubishi Chemical (Tokyo, Japan) and 3-(3,4-dichlorophenyl)-1,1-dimethylurea
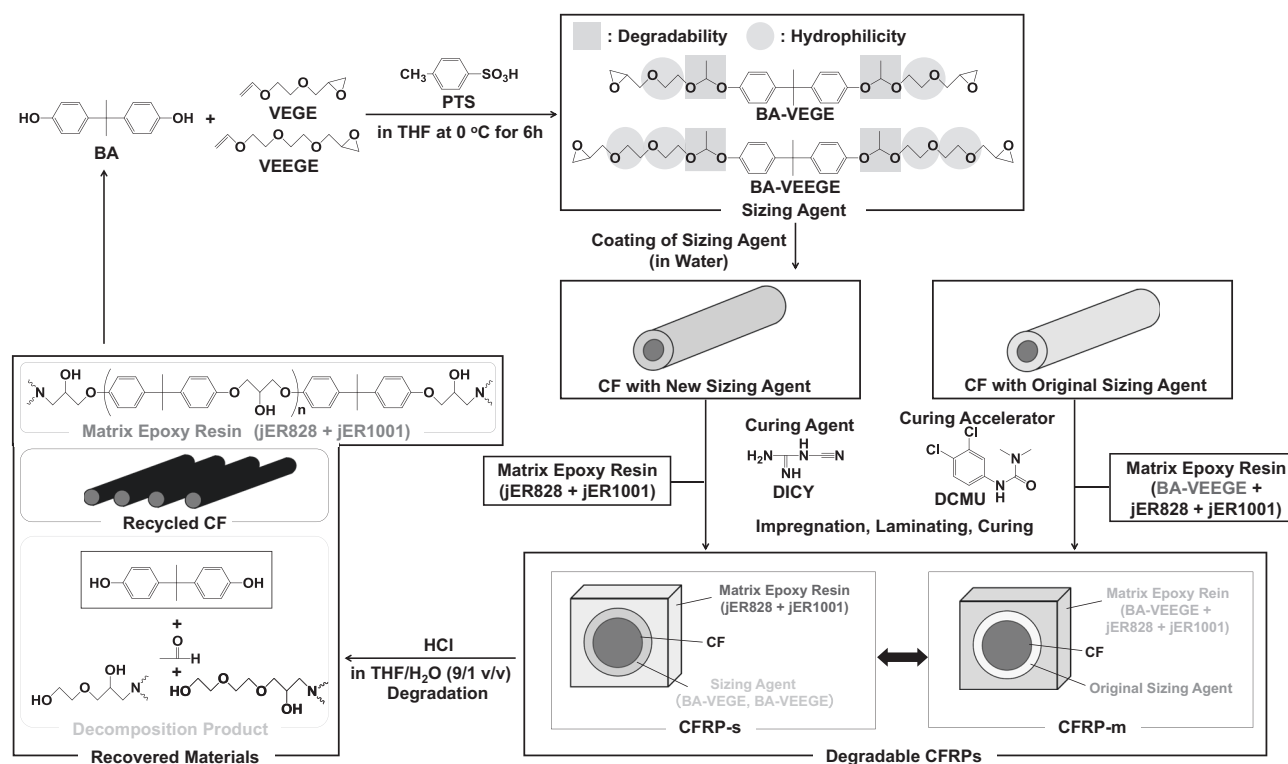
Scheme 3 Schematic images of the synthesis of acetal linkage-containing epoxy resins and of the preparation and degradation of acetal linkage-containing CFRPs

(DCMU; curing accelerator; DCMU99) produced by Hodogaya Chemical (Tokyo, Japan) were used as received: epoxy equivalent of jER828, 190 g/eq; epoxy equivalent of jER1001, 474 g/eq. Tetrahydrofuran (THF; solvent) was dried with molecular sieves (5 A 1/8; Wako, Osaka, Japan) overnight and distilled over lithium aluminum hydride. Carbon fibers (TR50S-15L) were supplied by Mitsubishi Chemical (Tokyo, Japan). The emulsifiers Softanol 30, 70, 90 and 120 and Adeka Pluronic L-34, L-44, L-62 and L-121 were supplied by Nippon Shokubai (Osaka, Japan) and Adeka (Tokyo, Japan), respectively.
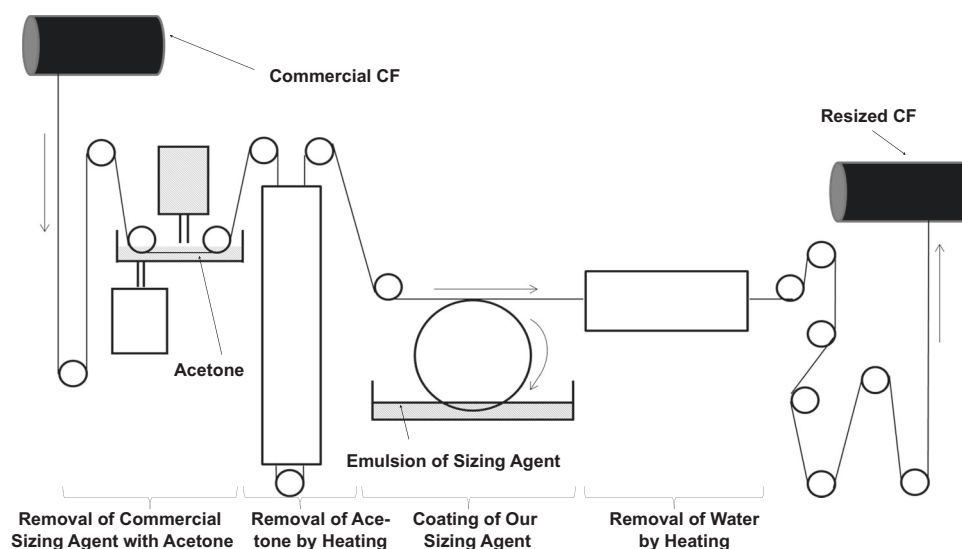
Synthesis of BA-VEGE and BA-VEEGE

2-(Vinyloxy)ethyl glycidyl ether (VEGE) was synthesized by the reaction of HEVE with epichlorohydrin (Wako, Tokyo, Japan) in the presence of NaOH [21]. HEVE (107.7 mL, 1.2 mol), NaOH (72.0 g, 1.8 mol), dimethyl sulfoxide (450 mL) and tetra-n-butylammonium bromide (2.5 g) were placed in a flask and stirred. Epichlorohydrin (140.9 mL, 1.8 mol) was added slowly, and the mixture was then stirred for an additional 24 h at room temperature. The resulting reaction mixture was poured into water and extracted with diethyl ether. The solution was then washed with sodium chloride aqueous solution and concentrated by evaporation. The obtained crude product was distilled under reduced

pressure to form VEGE: bp 68 °C/3 mmHg; isolated yield, 14%. To synthesize BA-VEGE, an additional reaction of bisphenol-A (BA) with VEGE was carried out with p-toluenesulfonic acid monohydrate (PTS) as a catalyst in THF at 0 °C for 6 h under a nitrogen atmosphere: $[BA]_0 = 0.50$ M; $[VEGE]_0 = 1.50$ M; $[PTS]_0 = 50$ mM [17, 18, 19]. The reaction was terminated by adding methanol containing a small amount of ammonia. Afterward, the reaction mixture was diluted in methylene chloride, washed with water and concentrated by evaporation. The obtained product was washed with n-hexane to form BA-VEGE; isolated yield, 67%. 2-[2-(Vinyloxy)ethoxy] ethyl glycidyl ether (VEEGE) was synthesized in a similar way for VEGE: bp 105 °C/2 mmHg; isolated yield, 33%. BA-VEEGE was synthesized by the reaction of BA with VEEGE as mentioned above to synthesize BA-VEGE, except the crude product was purified by silica gel column chromatography (eluent: hexane/THF (2/1 v/v)); isolated yield, 64%.

Applying sizing agents to carbon fibers

The carbon fiber sizing process using synthesized epoxy resins containing acetal linkages (BA-VEGE and BA-VEEGE) and a comparative bisphenol-A-type epoxy resin (jER828) was conducted by using a sizing agent-applying apparatus (Nicca Chemical Co., Ltd., Fukui, Japan) (Fig. 1).

Fig. 1 The application of sizing agents to carbon fibers

Commercial CF

Resized CF

Acetone

Emulsion of Sizing Agent

Removal of Commercial Sizing Agent with Acetone   **Removal of Acetone by Heating**   **Coating of Our Sizing Agent**   **Removal of Water by Heating**

Suitable emulsifiers for preparing sizing agent-based emulsion were selected from the emulsified state by the phase inversion emulsification method. The concentration of each epoxy resin in the emulsion was set to 6 wt% to apply ordinary amounts of the sizing agents onto carbon fibers (content ≈ 1 wt%). In addition, 18 wt%, 24 wt% and 30 wt% of BA-VEEGE in the emulsion were used to prepare sizing agent-coated carbon fibers in excess amounts. The sizing process was conducted in four steps as follows (Fig. 1). First, the original sizing agent was removed by immersing commercial carbon fibers in acetone. Second, acetone on the carbon fiber surface was removed by heating to 120 °C. Third, the sizing agent emulsion was applied to the carbon fiber at a roller rotation speed of 9.0 m/min. Finally, the carbon fibers were heated to 120 ~ 145 °C to remove water on the fiber surface. The winding speed of the carbon fibers was set to 3.0 m/min.

Preparation of CFRPs

The CFRPs were prepared based on previous studies [18, 19]. A mixture of different molecular weights of bisphenol-A-type epoxy resins (jER828: jER1001 = 40: 60 (wt%)) as a matrix resin, DICY as a curing agent and DCMU as a curing accelerator were used. These materials were kneaded by using a planetary mixer (PLM-2-1, Inoue Mfg., Inc., Kanagawa, Japan), and the mixture was coated onto release papers with a multicoater (M-500, Hirano Tecseed, Nara, Japan) to form thin resin sheets. The prepreg sheets were prepared by impregnating the thin resin sheets into the resized strands of carbon fibers with the thin prepreg sheet manufacturing machine developed by the Industrial Technology Center of Fukui Prefecture [22]. The resulting prepreg sheets were laminated according to the $[0]_{50}$ and $[0/90]_{12S}$ lay-up, as shown in Fig. 2. We use "0" and "90" to denote layers
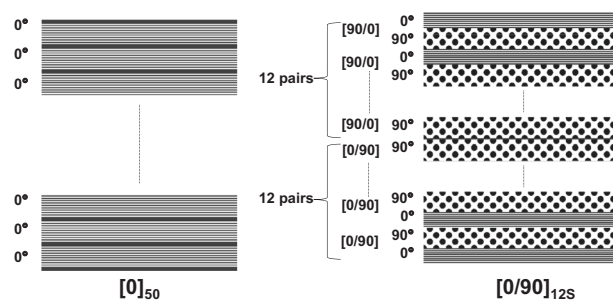
Fig. 2 Schematic image of $[0]_{50}$ and $[0/90]_{12s}$ configurations of the laminated prepreg sheets used for CFRP preparation

oriented in the direction of the carbon fibers of 0° and 90°, respectively, and "50" and "12" denote the number of repeated [0] and [0/90] layers, respectively. "S" denotes symmetry, where the grouped $[0/90]_{12}$ layers were laminated symmetrically. The laminated prepreg sheets were cured in an autoclave at 130 °C for 2 h at 0.5 MPa. The CFRPs using resized carbon fibers (Fig. 1) are referred to as CFRP-s. For comparison, the CFRPs were also prepared with commercial as-received carbon fibers, and the mixture of BA-VEEGE and bisphenol-A-type epoxy resin (jER828 + jER1001) as matrix resin is referred to as CFRP-m. Compositions used to prepare CFRPs are shown in Table 1.

Measurements

^{1}H NMR spectra were recorded on a Jeol JNM AL-300 instrument at room temperature with tetramethylsilane as an internal standard and chloroform-d as a solvent. The epoxy contents of BA-VEGE and BA-VEEGE were determined by chemical titration. BA-VEGE or BA-VEEGE (0.08 g) was dissolved in 25 mL of pyridine containing 0.2 mol/L

Table 1 Weight percentage ratio of each compound in the CFRP laminate

Samples	Sizing agent				Matrix epoxy resin		
	BA-VEGE (wt %)	BA-VEEGE (wt %)	jER828-containing emulsions (wt%)	Pluronic L-121 (wt%)	BA-VEEGE (wt %)	jER828 (wt %)	jER1001 (wt %)
CFRP-s jER828:2.5 wt%	0	0	2.5	0	0	39.0	58.5
CFRP-s BA-VEGE:2.5 wt%	2.5	0	0	0.3	0	38.9	58.3
CFRP-s BA-VEEGE:3.3 wt%	0	3.3	0	0.3	0	38.6	57.9
CFRP-s BA-VEEGE:10.6 wt%	0	10.6	0	1.1	0	28.3	60.0
CFRP-s BA-VEEGE:16.4 wt%	0	16.4	0	1.6	0	22.0	60.0
CFRP-s BA-VEEGE:24.4 wt%	0	24.4	0	2.4	0	23.2	50.0
CFRP-m BA-VEEGE:10.6 wt%	–	–	–	–	10.6	29.4	60.0
CFRP-m BA-VEEGE:16.4 wt%	–	–	–	–	16.4	23.6	60.0
CFRP blank	–	–	–	–	0	40.0	60.0

hydrochloric acid. The epoxy groups were reacted at 110 °C for 2 h, and the remaining acid was then back-titrated with 0.1 mol/L ethanolic potassium hydroxide using phenolphthalein as an indicator. The volume fraction of fiber (V_f) was measured on the basis of the JIS K7075. First, the density of CFRPs (10 mm × 10 mm × 2 mm) was measured via the hydrostatic weighting method with a density determination kit fitted to a Mettler Toledo balance using hexane as an auxiliary liquid. The CFRPs were immersed in nitric acid (50 mL) and then heated at 120 °C for 2 h. The carbon fiber strands were recovered by filtration and successively washed with water, methanol and acetone. The washed carbon fibers were then dried under reduced pressure at room temperature and V_f was calculated from the weight of the recovered carbon fibers and from the density of CFRPs and carbon fibers (1.82 g/cm³). The interfacial shear strength (τ) was measured by the microdroplet method with a MODEL HM410 apparatus (Tohei Sangyo Co., LTD, Tokyo, Japan) [4]. The epoxy resins were wetted onto a single carbon fiber to form microdroplets from their own surface tension. The formed microdroplets were cured at 130 °C for 2 h. The force required to debond a droplet from a carbon fiber (F_{max}) was recorded at a drawing speed of 0.12 mm/min using a 1 N load cell, and τ was calculated from $\tau = F_{max} / \pi dL$, where d is the diameter of the carbon fiber and L is the embedded length of the droplet. The measurement was conducted at least 30 times for each sample. Sizing agent content levels on the carbon fiber were measured using the solvent extraction method (JIS R7604). Carbon fibers with sizing agents (2 g or more) were immersed in acetone for 1 h and dried at 110 °C for 1 h. The recovered carbon fibers were then weighed. This approach was repeated until all sizing agents were completely removed. Finally, the sizing agent content was calculated from the weight of the carbon fibers before and after extraction of the sizing agents. The tensile testing of CFRPs was performed with a Shimadzu AUTOGRAPH AG IS (100 kN load cell). The $[0]_{50}$ and $[0/90]_{12S}$ laminates were applied at elongation speeds of 1.0 mm/min and 1.5 mm/min, respectively. A charpy impact test was conducted on the basis of the JIS K7111-1. The flatwise impact test was performed by using an impact testing apparatus (Yasuda Seiki Seisakusho, LTD.,

Hyogo, Japan) with 2 J capacity and 80 × 10 mm specimens. Scanning electron microscopy (SEM) was performed on a HITACHI S-3400N scanning electron microscope (Tokyo, Japan) at a 10.0 kV accelerating voltage. The degradation rate (%) was determined from the weight fraction of the residual resins after the decomposition test of the CFRPs:

$$\text{Degradation rate}(\%) = \frac{W_1 - W_2}{W_0} \times 100$$

where W_0, W_1, and W_2 represent the mass of resin in the composites before decomposition, the mass of the composites before decomposition and the mass of the mixture of residual resins and recovered carbon fibers after decomposition, respectively.

Results and discussion

Synthesis of epoxy resins containing acetal linkages, BA-VEGE and BA-VEEGE

Figure 3 shows ¹H NMR spectra of synthesized epoxy resins containing acetal linkages (BA-VEGE and BA-VEEGE). In both spectra, the signals due to the acetal methine and methyl are clearly observed as peak d (5.4 ~ 5.5 ppm) and peak e (1.5 ppm), respectively. Since other peaks can also be attributed to the structure shown in the figure, the desired products were obtained. The ratio of introduction of acetal linkages was determined from the area ratio of the peak c derived from the benzene ring to the peak d derived from the acetal methine. Epoxy content levels of BA-VEGE and BA-VEEGE measured by chemical titration were 304 g/eq (calc. 253 g/eq) and 321 g/eq (calc. 302 g/eq), respectively.

Applying sizing agents to carbon fibers: Screening of emulsifiers for sizing agents

The most suitable emulsifiers for emulsifying the synthesized degradable epoxy resin containing acetal linkages (BA-VEGE and BA-VEEGE) and conventional bisphenol-
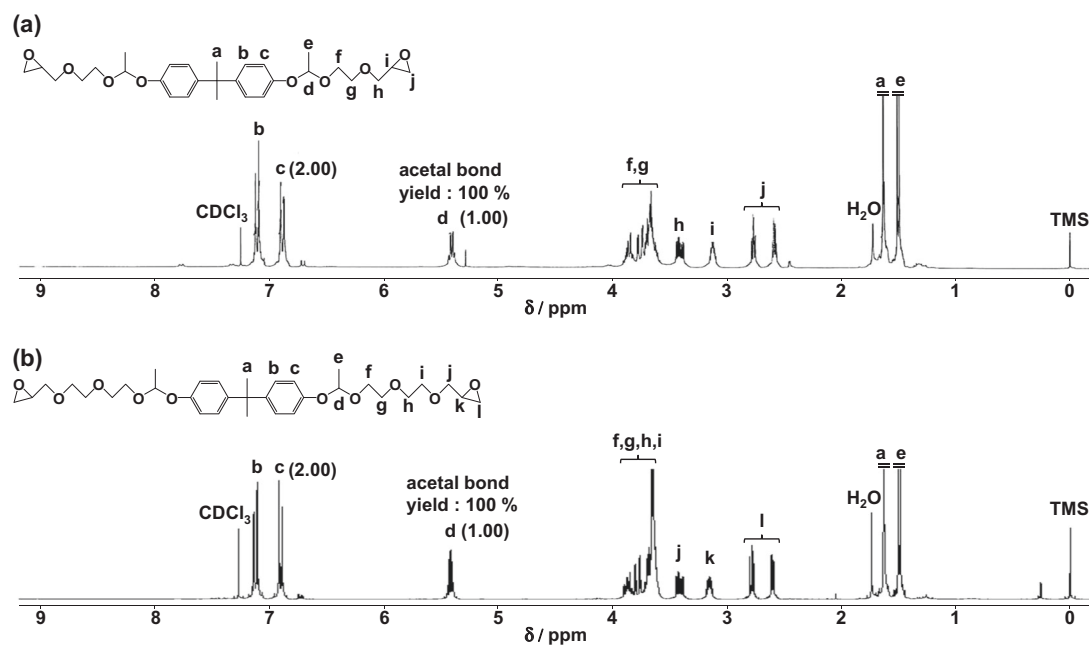
Fig. 3 ^{1}H NMR spectra of the epoxy resins: **a** BA-VEGE and (**b**) BA-VEEGE

Table 2 Emulsion state of each epoxy resin after 24 h[a)]

| Epoxy resins	Emulsifier							
	$C_{13}H_{28}-O\left(C_2H_4O\right)_n H$				$HO\left(C_2H_4O\right)_a\left(C_3H_6O\right)_b\left(C_2H_4O\right)_c H$			
	Polyoxyethylene alkyl ether				Polyoxyethylene - Polyoxypropylene			
	Softanol 30	Softanol 70	Softanol 90	Softanol 120	Pluronic L-34	Pluronic L-44	Pluronic L-62	Pluronic L-121
jER828	×	×	×	×	×	×	×	×
BA-VEGE	△	×	×	×	×	△	○	○
BA-VEEGE	△	×	×	×	×	×	△	○

a) ○···Complete emulsification. △…Partial emulsification. ×…No emulsification (Sizing agent : Emulsifier : Water = 5.5 : 0.5 : 94 (wt%)).

A-type epoxy resin (jER828) for comparisons were selected from the eight types of emulsifiers. Table 2 shows the resulting emulsified state of each epoxy resin after 24 h. Both degradable epoxy resins were most heavily dispersed in water when Adeka Pluronic L-121 was used as an emulsifier, and thus, we used it to apply sizing agents to carbon fibers. However, since the conventional epoxy resin jER828 did not uniformly disperse when an emulsifier was used, commercially available jER828-based emulsion (W2821R70, Mitsubishi Chemical, Tokyo, Japan) was applied directly to the carbon fibers. When the concentration of sizing agents in the emulsions reached 6 wt%, the contents reached 1.5 wt% for BA-VEGE (designated as CFRP-s BA-VEGE:2.5 wt%, Table 1), 2.2 wt% for BA-VEEGE (CFRP-s BA-VEEGE:3.3 wt%) and 1.4 wt% for jER828 (CFRP-s jER828:2.5 wt%). In addition, when applying BA-VEEGE at various concentrations in the emulsifier (18 wt, 24 wt and 30 wt%), contents reached 6.4 wt% (designated as CFRP-s BA-VEEGE:10.6 wt%, Table 1), 9.5 wt% (CFRP-s BA-VEEGE:16.4 wt%) and 13.4 wt% (CFRP-s BA-VEEGE:24.4 wt%), respectively.

Interfacial shear strength with degradable epoxy resin-based sizing agents

Figure 4 shows the average interfacial shear strength measured between the matrix resin and the carbon fibers applied with the degradable epoxy resin based-sizing agents. When each sizing
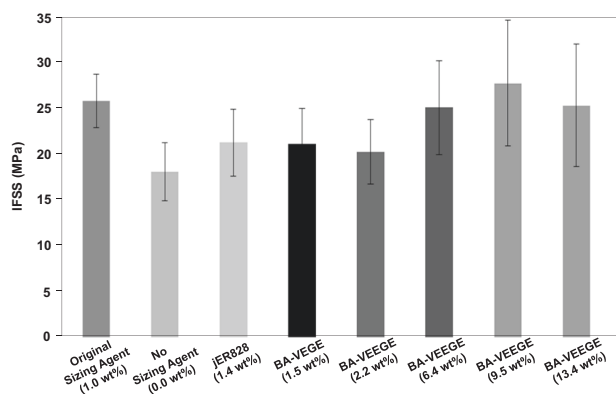
Fig. 4 Interfacial shear strength (IFSS) levels measured between carbon fibers and matrix epoxy resins: jER828 + jER1001

Fig. 5 Stress-strain behaviors of CFRPs $[0]_{50}$ lay-up: **a** CFRP-s jER828:2.5 wt%, **b** CFRP-s BA-VEGE:2.5 wt%, **c** CFRP-s BA-VEEGE:3.3 wt%, **d** CFRP-s BA-VEEGE:10.6 wt%, **e** CFRP-s BA-VEEGE:16.4 wt%, **f** CFRP-s BA-VEEGE:24.4 wt%, **g** CFRP-m BA-VEEGE:10.6 wt%, **h** CFRP-m BA-VEEGE:16.4 wt% and **i** CFRP blank

agent was applied onto carbon fibers in ordinary amounts (content: BA-VEGE, 1.5 wt%; BA-VEEGE, 2.2 wt%; jER828, 1.4 wt%), the interfacial shear strengths of BA-VEGE, BA-VEEGE and jER828 used for comparisons were 21.02 MPa, 20.22 MPa and 21.19 MPa, respectively. The carbon fibers with degradable epoxy resin-based sizing agents show almost the same strengths as those of the conventional epoxy resin jER828 used as a sizing agent. Carbon fibers with these sizing agents (BA-VEGE, BA-VEEGE and jER828) exhibited less interfacial shear strength than those using the commercial carbon fiber with an original sizing agent (25.69 MPa) but more strength than the desized carbon fiber (18.02 MPa). Therefore, the sizing agents indeed functioned to enhance the interfacial adhesion with matrix resins. We also found that as BA-VEEGE levels increased, the interfacial shear strength increased as follows: 6.4 wt%, 25.00 MPa; 9.5 wt%, 27.65 MPa; 13.4 wt%, 25.25 MPa. This occurred because the formation of a greater coated surface area on the carbon fibers by the sizing agent improved the shear strength.

Mechanical properties of the prepared CFRPs

The mechanical properties of the obtained CFRPs were evaluated by tensile and charpy impact tests. Figure 5 shows the stress-strain curves of CFRPs with $[0]_{50}$ lay-up. This tensile test was performed with the fiber direction set perpendicular to the tensile direction to detect the difference in interfacial adhesion between carbon fibers and matrix resins in the CFRP products. The maximum stress, strain at break and Young's modulus were as follows: (a) CFRP-s jER828:2.5 wt% ($V_f = 52.1\%$), 80.8 MPa, 1.32%, 7.78 GPa; (b) CFRP-s BA-VEGE:2.5 wt% ($V_f = 53.9\%$), 85.6 MPa, 1.66%, 7.23 GPa; (c) CFRP-s BA-VEEGE:3.3 wt% $V_f = 51.9\%$), 79.2 MPa, 1.49%, 7.21 GPa; (d) CFRP-s BA-VEEGE:10.6 wt% ($V_f = 47.6\%$), 78.6 MPa, 2.35%, 7.98 GPa; (e) CFRP-s BA-VEEGE:16.4 wt% ($V_f = 57.5\%$), 59.1 MPa,
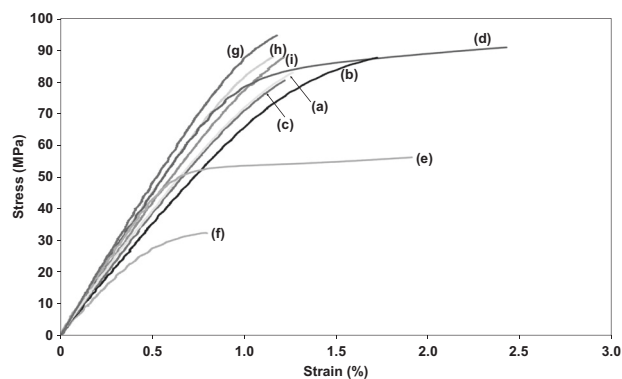
1.84%, 8.77 GPa; (f) CFRP-s BA-VEEGE:24.4 wt% ($V_f = 54.7\%$), 31.3 MPa, 0.74%, 5.50 GPa; (g) CFRP-m BA-VEEGE:10.6 wt% ($V_f = 51.7\%$), 89.0 MPa, 1.22%, 9.03 GPa; (h) CFRP-m BA-VEEGE:16.4 wt% ($V_f = 52.4\%$), 84.0 MPa, 1.12%, 8.77 GPa; (i) CFRP blank ($V_f = 49.7\%$), 83.3 MPa, 1.18%, 8.20 GPa. The CFRPs with an ordinary amount of sizing agent (a ∼ c) exhibited almost the same mechanical properties. Mechanical properties were not affected by the kind of sizing agent used. When BA-VEEGE was used as a matrix resin (Fig. 5g, h), the tensile properties of the CFRPs did not change considerably with BA-VEEGE content levels, but when BA-VEEGE was used as a sizing agent, CFRP-s BA-VEEGE:16.4 wt% and CFRP-s BA-VEEGE:24.4 wt% exhibited less tensile stress and elongation at break. However, CFRP-s BA-VEEGE:10.6 wt% exhibited the highest levels of elongation at break of all of the samples while maintaining tensile stress levels comparable to those of the conventional CFRP (CFRP blank). This result indicates that CFRP-s BA-VEEGE:10.6 wt% offers the best interfacial adhesion properties over the examined CFRP products. SEM images of tensile fracture surfaces of the BA-VEEGE sizing agent-based CFRPs are shown in Fig. 6. The various pores were observed on fracture surfaces of the CFRPs treated with excess amounts of the sizing agents (CFRP-s BA-VEEGE:16.4 wt% and CFRP-s BA-VEEGE:24.4 wt%). We postulate that excessive contents in carbon fibers tend to increase the porosity of CFRPs, and this may have led to a decline in tensile strength. This means that using an excessive amount of sizing agent results in the unfavorable matching of sizing agents and matrix resins at their interface. For example, the thickening of sizing agents may have resulted in insufficient curing at the interface and may have promoted formation of cracks.
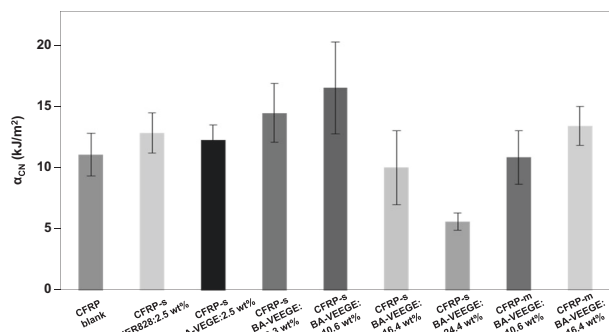
Figure 7 shows the stress-strain curves of CFRPs with $[0/90]_{12S}$ lay-up. The maximum stress, strain at break and

Fig. 6 SEM images of tensile fracture surfaces of CFRP-s BA-VEEGE:3.3 wt%, CFRP-s BA-VEEGE:10.6 wt%, CFRP-s BA-VEEGE:16.4 wt% and CFRP-s BA-VEEGE:24.4 wt%
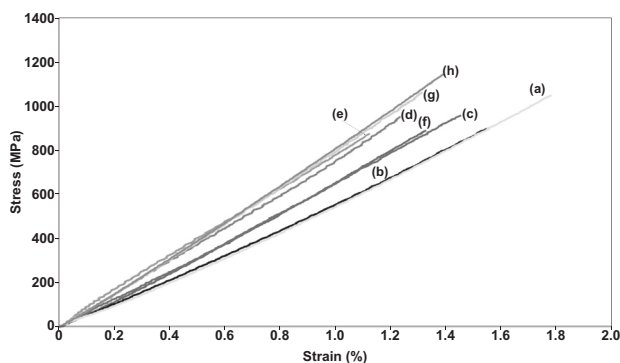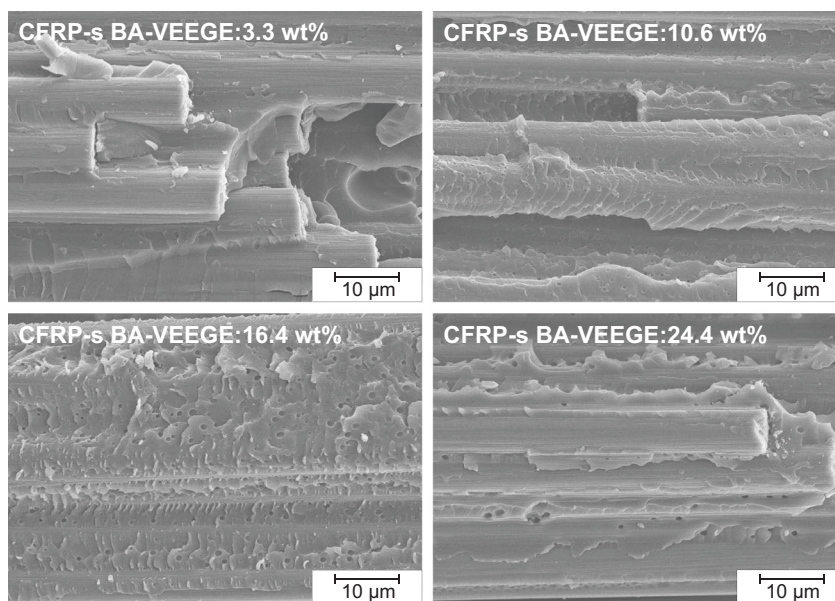
Fig. 7 Stress-strain behaviors of CFRPs with $[0/90]_{12s}$ lay-up: **a** CFRP-s jER828:2.5 wt%, **b** CFRP-s BA-VEGE:2.5 wt%, **c** CFRP-s BA-VEEGE:3.3 wt%, **d** CFRP-s BA-VEEGE:10.6 wt%, **e** CFRP-s BA-VEEGE:16.4 wt%, **f** CFRP-s BA-VEEGE:24.4 wt%, **g** CFRP-m BA-VEEGE:10.6 wt%, **h** CFRP-m BA-VEEGE:16.4 wt% and **i** CFRP blank

Fig. 8 Charpy impact strength of CFRPs with $[0]_{50}$ lay-up

Young's modulus are as follows: (a) CFRP-s jER828:2.5 wt% ($V_f = 55.6\%$), 1074 MPa, 1.76%, 52.4 GPa; (b) CFRP-s BA-VEGE:2.5 wt% ($V_f = 57.6\%$), 953 MPa, 1.57%, 50.1 GPa; (c) CFRP-s BA-VEEGE:3.3 wt% ($V_f = 52.3\%$), 944 MPa, 1.59%, 53.6 GPa; (d) CFRP-s BA-VEEGE:10.6 wt% ($V_f = 50.3\%$), 844 MPa, 1.23%, 62.7 GPa; (e) CFRP-s BA-VEEGE:16.4 wt% ($V_f = 54.8\%$), 866 MPa, 1.14%, 74.1 GPa; (f) CFRP-m BA-VEEGE:10.6 wt% ($V_f = 55.9\%$), 927 MPa, 1.23%, 70.4 GPa; (g) CFRP-m BA-VEEGE:16.4 wt% ($V_f = 48.9\%$), 984 MPa, 1.30%, 72.1 GPa; (i) CFRP blank ($V_f = 53.3\%$), 1112 MPa, 1.39%, 77.2 GPa. In this lamination configuration, all the CFRPs show almost the same levels of tensile strength, regardless of the structure and content. In general, the tensile strength of CFRPs with $[0/90]_{12S}$ lay-up

depends heavily on the strength of carbon fibers, and therefore, differences in types and content levels used did not significantly affected their tensile strength.

Figure 8 shows the results of the charpy impact test. Compared with the CFRP blank (11.1 kJ/m^2), CFRP-s jER828:2.5 wt%, CFRP-s BA-VEGE:2.5 wt% and CFRP-s BA-VEEGE:3.3 wt% containing ordinary amounts of sizing agent show slightly higher levels of impact strength (12.8 kJ/m^2, 12.3 kJ/m^2 and 14.5 kJ/m^2, respectively). Furthermore, CFRP-s BA-VEEGE:10.6 wt% showed the highest impact strength levels (16.5 kJ/m^2) of all the samples. As BA-VEEGE includes flexible oxyethylene chains, the impact could be absorbed. However, those using more excessive amounts of BA-VEEGE as a sizing agent (CFRP-s BA-VEEGE:16.4 wt%, CFRP-s BA-VEEGE:24.4 wt%) showed lower levels of impact strength (10.0 kJ/m^2, 5.6 kJ/m^2). The increase in porosity that occurred due to the excessive involvement of sizing agents likely lessened the impact strength levels, echoing the tensile test results obtained for
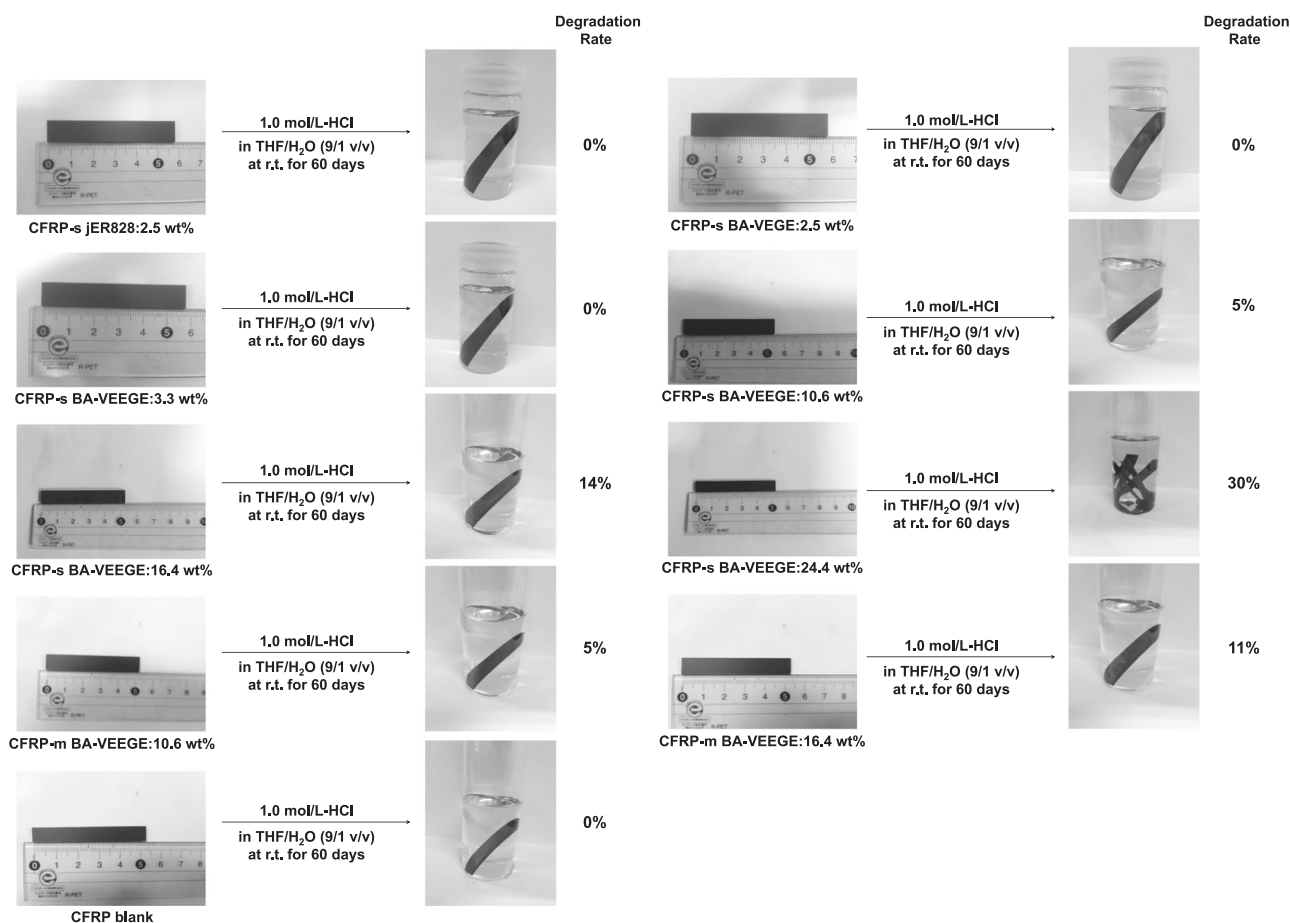
Fig. 9 Appearance of CFRPs before and after degradation with hydrochloric acid in THF/water (9/1 v/v) mixed solvent at room temperature for 60 days: CFRP-s jER828:2.5 wt%, CFRP-s BA-VEGE:2.5 wt%, CFRP-s BA-VEEGE:3.3 wt%, CFRP-s BA-VEEGE:10.6 wt%, CFRP-s BA-VEEGE:16.4 wt%, CFRP-s BA-VEEGE:24.4 wt%, CFRP-m BA-VEEGE:10.6 wt%, CFRP-m BA-VEEGE:16.4 wt% and CFRP blank

CFRPs with $[0]_{50}$ lay-up. For the CFRPs with BA-VEEGE used as a matrix resin, the impact strength levels improved as the BA-VEEGE content levels increased (CFRP-m BA-VEEGE:10.6 wt% and CFRP-m BA-VEEGE:16.4 wt%). This improvement also suggested that flexible oxyethylene chains of BA-VEEGE incorporated into the matrix resins effectively absorbed the impact. However, compared with the impact strength of CFRP-s BA-VEEGE:10.6 wt%, the impact strength of the CFRP-m BA-VEEGE series was still lower. Therefore, the BA-VEEGE at the interface is more effective at absorbing impact.

Degradability of CFRPs

The degradation of CFRPs with $[0/90]_{12S}$ lay-up was carried out by treating them with hydrochloric acid in THF/water (9/1 v/v) to recover the carbon fibers. Figure 9 shows images of the CFRPs before and after the reaction when the reaction was conducted with 1.0 mol/L-hydrochloric acid at room temperature for 60 days. As shown in Fig. 9, some of the carbon fibers could be recovered from only CFRP-s BA-VEEGE:24.4 wt% when treated with excess amounts of sizing agent. As the acetal linkage-containing epoxy resin levels in the CFRPs increased, the degradation rate also increased. The degradation rate was not affected by whether acetal linkage-containing epoxy resins were present on the fiber surface or in the matrix. Figure 10 shows the SEM images of a cross-section of the CFRPs before and after degradation. CFRPs with ordinary amounts of sizing agent did not show any changes throughout the degradation reaction; however, the degree of delamination increased as the degradable epoxy resin contents increased. In particular, the carbon fibers recovered from CFRP-s BA-VEEGE:24.4 wt% showed no residue on the carbon fiber surface.

To enhance the recovery efficiency of carbon fibers, the degradation of CFRPs at 70 °C for 10 days under otherwise identical conditions was also studied. As shown in Fig. 11, some carbon fibers could be recovered from CFRPs applied
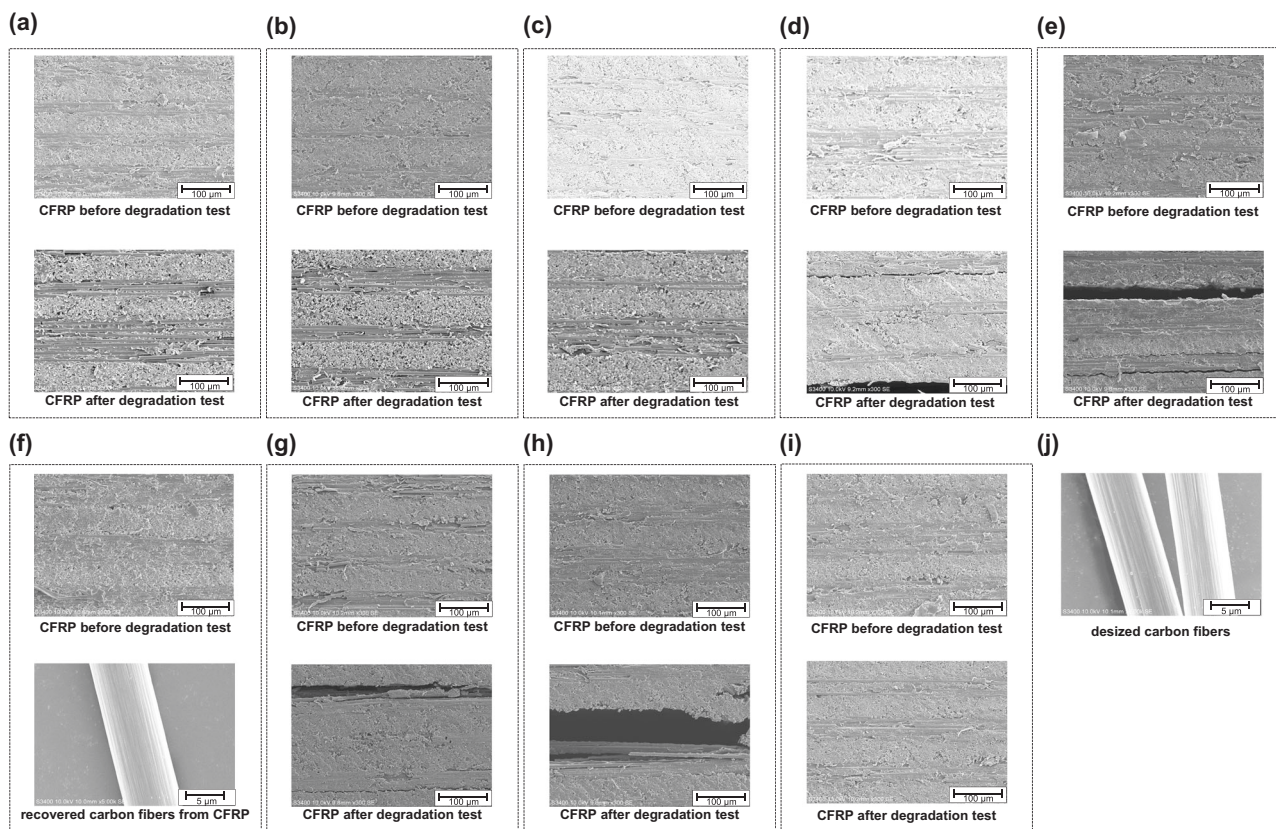
Fig. 10 SEM images of recovered carbon fibers or of cross-sections of CFRPs before and after degradation with hydrochloric acid in a THF/water (9/1 v/v) mixed solvent at room temperature for 60 days: **a** CFRP-s jER828:2.5 wt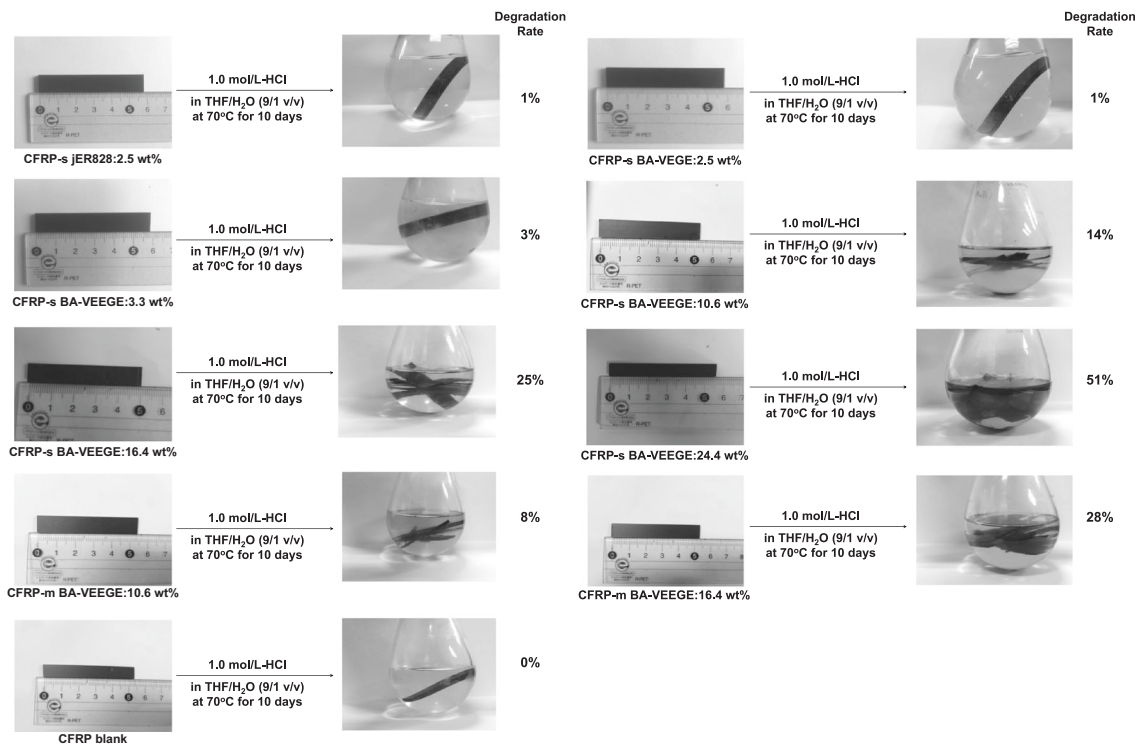%, **b** CFRP-s BA-VEGE:2.5 wt%, **c** CFRP-s BA-VEEGE:3.3 wt%, **d** CFRP-s BA-VEEGE:10.6 wt%, **e** CFRP-s BA-VEEGE:16.4 wt%, **f** CFRP-s BA-VEEGE:24.4 wt%, **g** CFRP-m BA-VEEGE:10.6 wt%, **h** CFRP-m BA-VEEGE:16.4 wt%, **i** CFRP blank and **j** desized virgin carbon fibers

with excess amounts of BA-VEEGE used as a sizing agent (CFRP-s BA-VEEGE:10.6 wt%, CFRP-s BA-VEEGE:16.4 wt% and CFRP-s BA-VEEGE:24.4 wt%) and from CFRPs with BA-VEEGE used as a matrix resin (CFRP-m BA-VEEGE:10.6 wt% and CFRP-m BA-VEEGE:16.4 wt%) by increasing the temperature. Furthermore, the degradation rate measured at 70 °C was higher than that measured at room temperature. The degradation rate was not affected by whether acetal linkage-containing epoxy resins were present at the interface or in the matrix. Figure 12 shows SEM images of cross-sections of the CFRPs before and after degradation. Among the CFRPs with ordinary amounts of sizing agent, CFRP-s BA-VEEGE:3.3 wt% showed the highest levels of delamination. This is likely attributable to the presence of higher levels of degradable sizing agent BA-VEEGE (content: 2.2 wt% against carbon fibers) than BA-VEGE (content: 1.4 wt% against carbon fibers). Thus, delamination was indeed accelerated with the use of degradable epoxy resins and even when using the ordinary quantity of sizing agent. Carbon fibers could be recovered except when using an ordinary amount of the sizing agent-based CFRPs. In particular, CFRP-s BA-VEEGE:24.4 wt% underwent effective degradation, and clean carbon fibers could be recovered with no damage to their surfaces.

Conclusions

Two kinds of acid-degradable acetal-linkage containing epoxy resins (BA-VEGE and BA-VEEGE) were synthesized for use as sizing agents for carbon fibers. The degradable epoxy resins performed well enough to be used as sizing agents in terms of interfacial shear strength levels between carbon fibers and matrix resins. When an ordinary volume of sizing agent was applied, the degradable sizing agent-based CFRPs exhibited almost the same tensile and impact strength levels as a conventional epoxy resin when using jER 828 as a sizing agent. Furthermore, for CFRP-s BA-VEEGE:10.6 wt%, the impact strength was improved while maintaining tensile strength, and some of the carbon fibers could be recovered when the degradation reaction was carried out with 1.0 mol/L-HCl in THF/water (9/1 v/v) at 70 °C for 10 days. Although the degradation conditions should be studied further to recover clean carbon fibers,

Fig. 11 Appearance of CFRPs before and after degradation with hydrochloric acid in a THF/water (9/1 v/v) mixed solvent at 70 °C for 10 days: CFRP-s jER828:2.5 wt%, CFRP-s BA-VEGE:2.5 wt%, CFRP-s BA-VEEGE:3.3 wt%, CFRP-s BA-VEEGE:10.6 wt%, CFRP-s BA-VEEGE:16.4 wt%, CFRP-s BA-VEEGE:24.4 wt%, CFRP-m BA-VEEGE:10.6 wt%, CFRP-m BA-VEEGE:16.4 wt% and CFRP blank
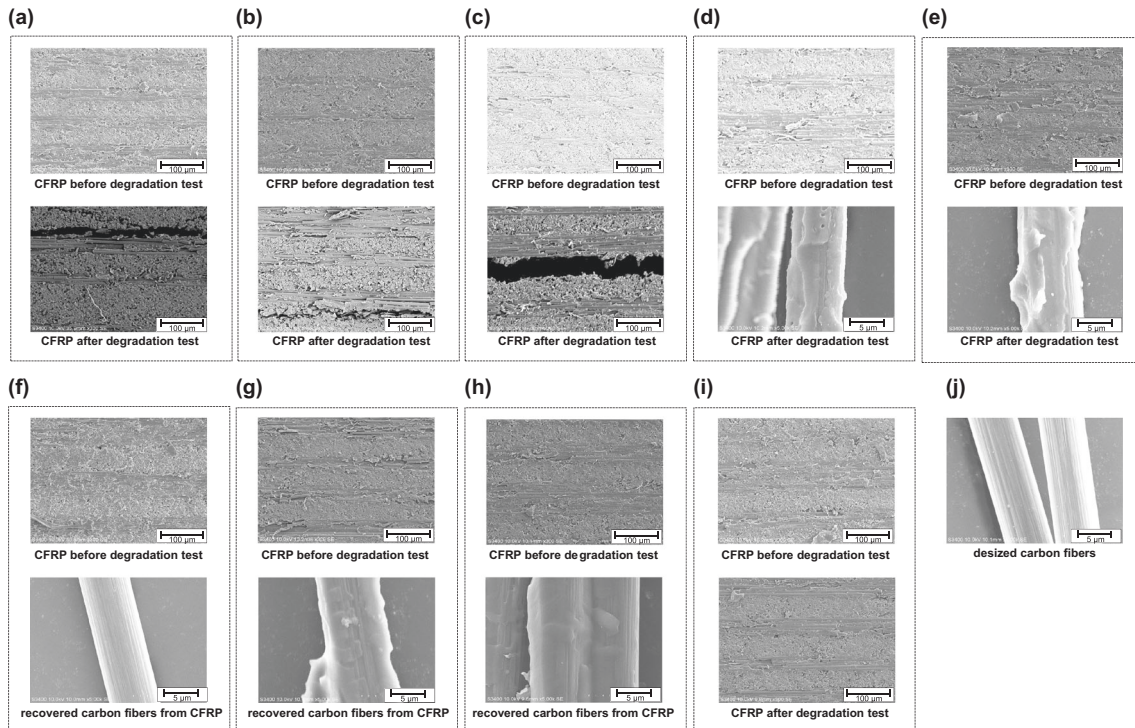
Fig. 12 SEM images of recovered carbon fibers or of cross-sections of CFRPs before and after degradation with hydrochloric acid in a THF/water (9/1 v/v) mixed solvent at 70 °C for 10 days: **a** CFRP-s jER828:2.5 wt%, **b** CFRP-s BA-VEGE:2.5 wt%, **c** CFRP-s BA-VEEGE:3.3 wt%, **d** CFRP-s BA-VEEGE:10.6 wt%, **e** CFRP-s BA-VEEGE:16.4 wt%, **f** CFRP-s BA-VEEGE:24.4 wt%, **g** CFRP-m BA-VEEGE:10.6 wt%, **h** CFRP-m BA-VEEGE:16.4 wt%, **i** CFRP blank and **j** desized virgin carbon fibers

acetal linkage-containing epoxy resins used as a sizing agent can be employed for new types of recyclable CFRPs.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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