

Low viscosity and high toughness epoxy resin modified by *in situ* radical polymerization method for improving mechanical properties of carbon fiber reinforced plastics

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Abstract

In situ radical polymerization method, which is a method for toughening thermosetting resins by modifier polymers radically generated in the curing system of the resins, was applied to epoxy resin for the matrix of carbon fiber reinforced plastic (CFRP) to achieve both high fracture toughness of the cured resin and low viscosity of the resin composition. Benzyl methacrylate (BzMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) were selected as the modifier monomers, and the resulting cured epoxy resin having co-continuous phase separation with the polymerized modifier at a nanometer level showed 2.1 times higher fracture toughness (K_{IC}) than the unmodified cured resin. The modified epoxy resin system was then successfully applied to the fabrication of CFRP by resin transfer molding (RTM) due to its low viscosity in the uncured state. The resultant CFRP system showed 30% increase of the interlaminar fracture toughness (G_{IC}) from the unmodified system.

1. Introduction

Carbon fiber reinforced plastic (CFRP) is widely used in aerospace, sporting goods, marine and infrastructure applications in recent years because of its high strength, stiffness and light weight. In addition, application of CFRP for automotive parts is expected to expand in the near future because of environmental requirements especially for reducing fuel consumption. In high performance applications such as aerospace materials, CFRP is mainly fabricated from a prepreg, which is a sheet composed of carbon fibers and a thermoplastic or thermosetting resin pre-impregnated with the fibers. Prepregs are laminated to form components and cured in an autoclave with high pressure. In these applications, viscous resins are mainly used as the matrix of the prepreg to afford sufficient surface tackiness for laminating the prepreg sheets.

On the other hand, instead of autoclave curing, resin transfer molding (RTM), injection molding and infusion molding are selected as automotive parts manufacturing methods to reduce production cycle time. In these manufacturing methods, low viscosity of the resin is required because the resin needs to be impregnated into small gaps between the reinforcement fibers without applying high external pressure like autoclave curing [1]. Another property desired for CFRP in automotive applications is its high impact performance [2]. CFRP strength in the transverse direction, such as impact strength, is governed mainly by matrix resin properties. However, the matrix resins for CFRP, represented by thermosetting resins like epoxy resin, are relatively brittle materials with poor

resistance to crack initiation and growth.

Improvement of toughness of epoxy resin has been studied extensively in a number of previous researches. Addition of liquid elastomers such as carboxyl-terminated butadiene acrylonitrile rubber (CTBN) [3,4] and engineering thermoplastics like poly(ether sulfone) (PES) [5,6] and polyetherimide (PEI) [7,8] into epoxy resin is known to increase its toughness. However, the addition of the elastomers and thermoplastics can also increase viscosity of the epoxy resin mixture [9]. Fröhlich et al. have studied the effect of core/shell type hyperbranched block-copolyethers as toughening agents for anhydride-cured bisphenol-A type epoxy resin [10]. Their results indicated that the fracture toughness (K_{IC}) of the cured resin was increased from $0.67 \text{ MPa}\cdot\text{m}^{0.5}$ to $1.00 \text{ MPa}\cdot\text{m}^{0.5}$ (50% increase) as maximum with low viscosity of the resin composition ($81 \text{ mPa}\cdot\text{s}$ at $80 \text{ }^\circ\text{C}$). However, the tensile modulus of the cured resin was decreased from 3.35 GPa to 2.85 GPa .

In this research, we adopted “*in situ* radical polymerization method” as the toughening method of epoxy resin in order to achieve both good mechanical properties, including modulus, strength and fracture toughness, of the cured resin and low viscosity of the resin composition. Such the epoxy resin system can be expected to be utilized for the fabrication of CFRP by RTM. In the *in situ* radical polymerization method, vinyl monomers and radical polymerization initiators are added into the epoxy resin composition which includes a curing agent. Radical polymerization of the vinyl monomers and curing reaction of the epoxy can proceed together during the heating of the resin composition and the

corresponding thermoplastic modifier polymer can be generated from the vinyl monomers. In this method, the viscosity of the resin composition can be lowered because of the absence of high molecular weight components and the cured resin can be tough because of the presence of the thermoplastic polymer. Mimura et al. have studied toughening of epoxy resin by the *in situ* radical polymerization method [11]. They used styrene, *N*-phenylmaleimide (PMI) and benzyl methacrylate as the monomers of *in situ* generating toughening agents for phenol-cured bisphenol-A type epoxy resin. Their results indicated that K_{IC} was increased from $1.0 \text{ MPa}\cdot\text{m}^{0.5}$ to $2.5 \text{ MPa}\cdot\text{m}^{0.5}$ as maximum with low resin viscosity ($65 \text{ mPa}\cdot\text{s}$ at $100 \text{ }^\circ\text{C}$). We have also reported toughening of acid-anhydride-cured bisphenol-A type epoxy resin by vinyl polymers generated by *in situ* radical copolymerization of styrene, poly(oxyethylene)-grafted styrene and PMI [12]. In this case, K_{IC} was increased from $0.59 \text{ MPa}\cdot\text{m}^{0.5}$ to $1.60 \text{ MPa}\cdot\text{m}^{0.5}$ as maximum with keeping flexural properties and glass transition temperature. Therefore, an epoxy resin system most suitable for RTM is expected to be obtained if the *in situ* radical polymerization method using styrene/PMI systems can be applied to epoxy resin cured with aromatic diamines, which are widely used for curing agents of epoxy resin in CFRP applications due to their good reactivity and thermal properties. However, aromatic primary amines are known to react with maleimide double bond by Michael addition reaction [13,14]. This reaction can inhibit *in situ* radical copolymerization of PMI in aromatic-amine-cured epoxy resin, and therefore other vinyl compounds instead of PMI should be adopted as the monomers of *in situ* generating toughening agents.

In epoxy resins modified with linear thermoplastic polymers, control of phase separation structure between matrix resin and modifier polymer is an important factor to obtain a cured resin with good mechanical properties. Mimura et al. have examined the morphological effect of PES as the modifier on toughness of the cured epoxy resin, and a significant increase (up to 90%) in toughness was obtained only when PES formed a continuous phase morphology [6]. Iijima et al. have also revealed that toughening of epoxy resin was achieved by adding PMS-styrene-*p*-hydroxystyrene terpolymer as the modifier due to the expression of a co-continuous phase separation [15]. Furthermore, Kishi et al. have examined that the morphological effect on several properties of the cured epoxy resins by using the seven types of diglycidyl ether of bisphenol-A oligomers having different molecular weight distributions [16]. In their results, the cured resins with nanometer-level continuous phase morphology showed the highest K_{IC} with maintaining its high compression strength. On the basis of these studies, effective toughening of a thermosetting resin/modifier polymer system is expected to be achieved when a co-continuous phase separation structure between the resin matrix and modifier is realized at a nanometer level.

The objective of this study is to obtain an epoxy resin system with achieving both high mechanical properties, including toughness and strength, of the cured resin and low viscosity of the uncured resin, which can improve mechanical properties and processability of CFRP. To realize this goal, we constructed a system composed of diglycidyl ether of bisphenol-A (DGEBA), aromatic amine curing

agent and vinyl monomers not containing PMI. The *in situ* radical polymerization method was applied to this system and an optimal vinyl monomer composition was explored such that the corresponding *in situ* generated vinyl polymer had an appropriate miscibility with the cured resin matrix to express co-continuous phase separation at a nanometer level. Furthermore, the optimized epoxy resin system by the *in situ* radical polymerization method was applied to the fabrication of CFRP by using RTM.

2. Experimental

2.1. Materials

Figure 1 shows the compounds used for preparation of epoxy resin compositions in this study. DGEBA (jERTM 828, Mitsubishi Chemical Corporation (epoxy equivalent weight: 189 g/eq)) was used as the epoxy resin and 3,5-diethyl-2,4-toluenediamine (DETDA) (AradurTM 5200, Huntsman Advanced Materials) was used as the curing agent. All resin systems in this study were formulated with a 1:1 molar ratio of epoxide to active hydrogen of the curing agent. Regarding *in situ* radical polymerization of modifier polymers, benzyl methacrylate (BzMA) (Wako pure chemical Industries), isobornyl methacrylate (IMA) (Eternal Chemical Industry), *N*-phenylmethacrylamide (PMA) (Tokyo Chemical Industry) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) (Sigma Aldrich) were used as the monomers and dicumyl peroxide (DCP) (Sigma Aldrich, one-hour half-life temperature: 136 °C) was used as the radical polymerization initiator. BzMA, IMA and PEGMEMA

were distilled before use for removing polymerization inhibitor. Other chemicals were used as-received.

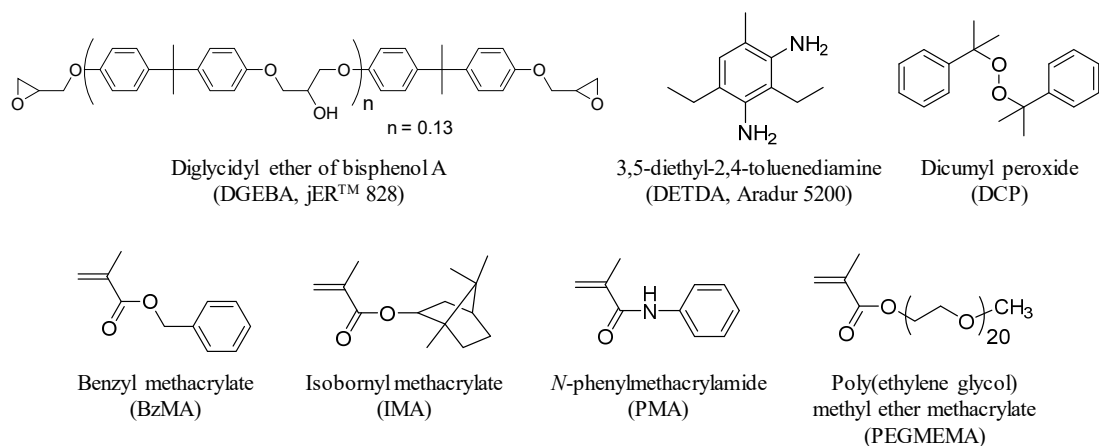


Figure 1. The compounds used in this study

2.2. Preparation method for cured epoxy resins

Epoxy resin compositions were prepared by the following process. BzMA, IMA, PMA, or a combination of BzMA and PEGMEMA as a modifier monomer was added to DGEBA and then stirred at 60–90 °C until homogeneous dissolution was confirmed. Then, the mixture was cooled down to 60 °C and DETDA and DCP were added. The resulting mixture was stirred at 60 °C until visually confirming complete dissolution. The mixture was then degassed in a vacuum oven at 60 °C for 30 minutes. After that, the mixture was poured into a mold having a plate-like cavity with a thickness of 2 mm and heat-cured in an oven at 120 °C for 5 hours and 180 °C for 2 hours.

2.3. Testing of the resin compositions

Differential scanning calorimetry (DSC) experiments were conducted with DSC Q2000 (manufactured by TA Instrument) using an aluminum pan. The tests were run from 0 °C to 300 °C at a rate of 5 °C/min. Viscosity of the resin compositions were measured in dynamic shearing mode with an ARES Rheometer (manufactured by TA Instruments) using parallel-plates (diameter of the plates: 40 mm, gap between the plates: 1 mm). The tests were run from 40 °C to 160 °C at a rate of 1.5 °C/min with a fixed frequency of 0.5 Hz.

2.4. Testing of the cured epoxy resins

All test specimens of the cured resins were prepared using a circular saw equipped with a diamond blade. The flexural strength, modulus and strain were determined by three-point bending test using a universal testing machine (Instron 5565 P8564, manufactured by Instron Japan Co., Ltd.) according to ISO178. The testing crosshead speed was 2.5 mm/min and the support span was 32 mm. The specimen dimension was 60 mm in length, 10 mm in width and 2 mm in thickness. A single-edge-notch 3-point bending (SENB) test was carried out to evaluate fracture toughness (K_{IC}) of the resins in accordance with ASTM standard D5045. The tests were performed on a universal testing machine (Instron 5565 P8564, manufactured by Instron Japan Co., Ltd.) at a testing crosshead speed of 10 mm/min. The specimen dimension was 60 mm in length, 12.7 mm in width and 6 mm in thickness.

For each specimen, the initial crack was generated by tapping with a fresh razor blade chilled with liquid nitrogen.

The glass transition temperature (T_g) of the cured epoxy resins was measured by a dynamic mechanical analyser (DMA Q800, manufactured by TA Instrument) in bending mode with a frequency of 1 Hz and increasing temperature from 40 °C to 250 °C at a rate of 2.5 °C/min. The T_g was determined from the onset point of storage modulus drop according to ISO 6721-4. The specimen dimension was 35 mm in length, 12.7 mm in width and 2 mm in thickness. The weight loss during heating of the cured resins was evaluated by thermo-gravimetric analysis (TGA) with a Bruker AXS TD-DTA 2000S instrument. About 10 mg of the cured resin was heated in an aluminum crucible from 40 °C to 500 °C at a heating rate of 10 °C /min in nitrogen atmosphere (50 mL/min flow).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to observe the morphology of the cured epoxy resins modified by *in situ* generated polymers. As for SEM observation, the fractured surface of the cured resins near the initial cracks after SENB test was sputter-coated with a thin platinum-palladium layer. The SEM observations were performed on a HITACHI S-4800 scanning electron microscope at an accelerating voltage of 5.0 kV. Regarding TEM observation, the cured epoxy resins were sliced by microtome and vapor-stained with RuO₄ aqueous solution. The TEM observations were performed on a JEM-2100F electron microscope (manufactured by JEOL Ltd.) at an accelerating voltage of 120 kV.

Average molecular weights of *in situ* polymerized BzMA were determined by gel permeation chromatography (GPC) (Prominence, manufactured by Shimadzu Corporation). To extract the polymerized BzMA from the cured epoxy resins, the resins were fractured and immersed into *N,N*-dimethylformamide (DMF) for 24 hours. The extracts were filtered and injected into a GPC analyzer (mobile phase: DMF). Low dispersed polystyrene (PS) samples were used as internal standards for calibration. ¹H-NMR analysis was conducted to investigate the residual BzMA monomer in the cured epoxy resin. The cured resins were fractured and immersed in deuterated dimethyl sulfoxide (DMSO-*d*₆) for 24 hours. The ¹H-NMR spectra of the extracts were recorded on a BRUKER DRX300 spectrometer (300 MHz).

2.5. Fabrication method for CFRP laminates

A non-crimp type unidirectional fabric of TORAYCA™ T800S-24K-10E carbon fiber (fiber areal weight: 190 g/m²) was used as a reinforcing fiber substrate. The CFRP laminates were prepared by vacuum-assisted resin transfer molding (VaRTM) method. Twenty plies of the fabric were aligned in the fiber direction and stacked on an aluminum tool plate preconditioned with a release agent. A polytetrafluoroethylene film having a width of 40 mm and a thickness of 13 μm was inserted between the center faces of the laminate (between the tenth and eleventh plies) to create the pre-induced crack for the interlaminar fracture toughness measurements. A peel ply and a resin distribution medium were

placed on the fabrics. The tool plate was covered with a nylon bagging film. After that the epoxy resin composition was injected at 60 °C for about 30 minutes under vacuum condition. After 5 hours of curing at 120 °C, the CFRP laminate was demolded and post-cured in an oven for 2 hours at 180 °C.

2.6. Mechanical testing of the CFRP laminates

All test specimens of the cured laminates were prepared using a circular saw equipped with a diamond blade. Interlaminar fracture toughness of Mode I (G_{IC}) was determined by double cantilever beam (DCB) test in accordance to JIS K7086. The test crosshead speed was set to 0.5 mm/min until the crack length reached 20 mm and was changed to 1 mm/min after the length reached 20 mm. The specimen dimension was 140 mm in length, 20 mm in width and 3.8 mm in thickness. Interlaminar fracture toughness Mode II (G_{IIC}) was determined by end notched fracture (ENF) test in accordance to JIS K7086. The test crosshead speed was 0.5 mm/min. The specimen dimension was the same as the DCB specimen. The DCB and ENF tests were performed on a universal mechanical test frame (Instron 5565 P8564, manufactured by Instron Japan Co., Ltd.).

3. Results and discussion

3.1. Determination of curing temperatures for the *in situ* radical polymerization method

We selected BzMA as a monomer for the *in situ* radical polymerization method by considering

both the difference in solubility parameter (SP) values between the monomer and epoxy resin composition (DGEBA/DETDA) and the difference in SP values between polyBzMA and the polymerized DGEBA/DETDA. The SP values of DGEBA and DETDA calculated by Fedors' method [17] are 10.6 and 10.8, respectively, and therefore the SP value of DGEBA/DETDA with epoxide/N-H = 1/1 (molar ratio) becomes 10.7. The SP value of the polymerized DGEBA/DETDA calculated by the same method is 12.5. On the other hand, the SP values of BzMA and polyBzMA are calculated to be 10.0 and 10.8, respectively. These SP values indicate that BzMA is highly miscible with the uncured DGEBA/DETDA and *in situ* polymerization of BzMA reduces the miscibility between polyBzMA and the epoxy resin matrix to some extent.

In order to determine curing temperatures for the epoxy resin systems modified by the *in situ* radical polymerization method, reaction behaviors of the unmodified epoxy resin composition (DGEBA/DETDA) and the modifier monomer system (BzMA/DCP) were examined by measuring DSC. The obtained DSC thermograms are shown in Figure 2 and the results are summarized in Table 1. From the DSC results, the exothermic onset temperatures of the control (DGEBA/DETDA) and BzMA/DCP were found to be 136 °C and 122 °C, respectively. Therefore, to advance sufficient amount of polymerization reaction of the modifier monomer before the epoxy resin reached glassy state, the first curing temperature was set at 120 °C. The second (and final) curing temperature was set at 180 °C to fully cure the epoxy resin matrix. The unmodified resin and the resin modified by the *in*

in situ radical polymerization method were actually cured by the condition of 120 °C/5 h + 180 °C/2 h, and they are indicated in Table 1 as the Control and B20, respectively. In order to confirm polymerization of BzMA during the curing process, the cured resins were fractured and immersed into DMF for 24 hours, and average molecular weights of the extracts were measured by GPC. The GPC charts shown in Figure 3 indicates that the extract of B20, which included 20wt% of the modifier, had the number-average molecular weight (M_n) of 5.0×10^4 and the weight-average molecular weight (M_w) of 9.6×10^4 , while the extract of the unmodified control showed no distinct peak. Therefore, the peak in the GPC chart of the B20 extract can be attributed to the *in situ* generated polyBzMA, and the curing condition is considered to be suitable for obtaining high molecular-weight modifier polymers by the *in situ* radical polymerization method.

Table 1. Results of DSC and GPC measurements

Entry	Epoxy resin ^{*1}	Curing agent ^{*1}	Modifier content		DSC ^{*3}	GPC ^{*4}	
			BzMA (wt%)	DCP (wt%)	Exothermic onset temperature (°C)	Mn	Mw
Control	DGEBA	DETDA	-	-	136	No peak	
BzMA/DCP	-	-	98.5	1.5 ^{*2}	122	Not measured	
B20	DGEBA	DETDA	20.0	0.3 ^{*2}	Not measured	5.0×10^4	9.6×10^4

*1 Epoxide/N-H = 1/1 (molar ratio)

*2 BzMA/DCP = 99/1 (molar ratio)

*3 Uncured resin

*4 Extract from the cured resin with DMF

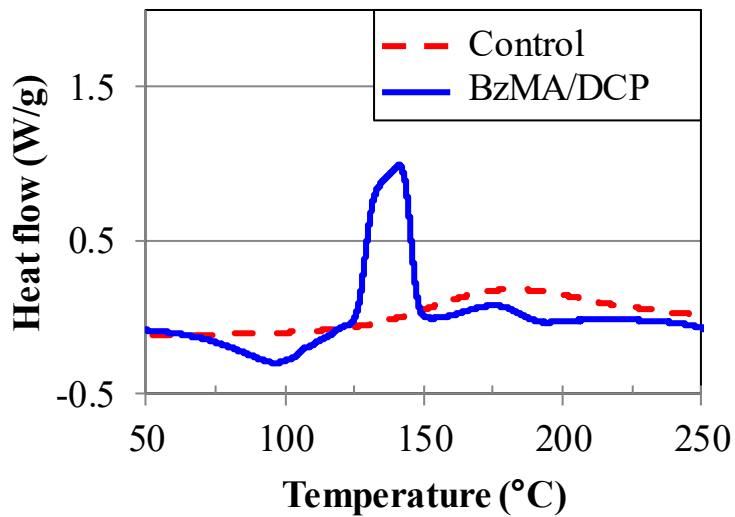


Figure 2. DSC thermograms of the unmodified epoxy resin (Control) and modifier monomer system (BzMA/DCP)

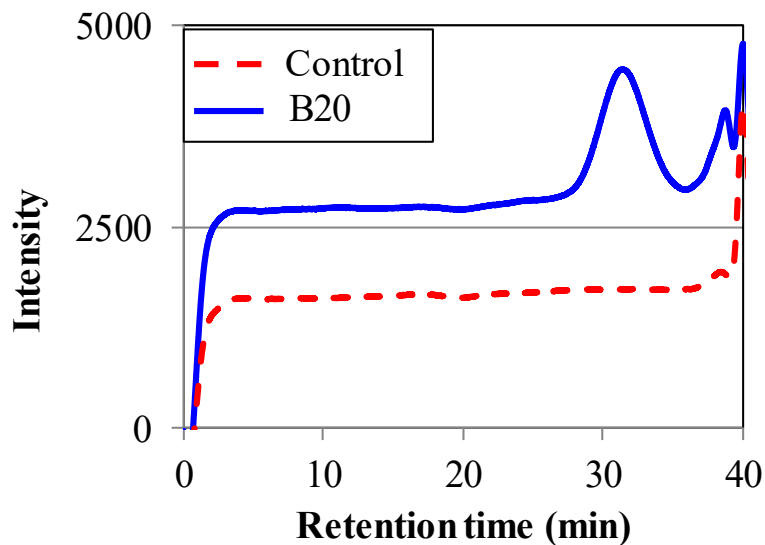


Figure 3. GPC charts of the extracts from the cured resins.

3.2. Toughening of the epoxy resin by *in situ* generated vinyl polymers

We firstly examined the effect of SP value of vinyl monomers on toughening of the epoxy resin by *in situ* radical polymerization method. In addition to BzMA, IMA and PMA were selected as the monomers (Figure 1). The SP values of polyIMA and polyPMA are 9.5 and 12.8, respectively. Since the SP values of polyBzMA and the cured DGEBA/DETDA are 10.8 and 12.5, respectively, as described in the section 3.1, the order of miscibility of the modifier polymers with the cured resin is expected to be polyPMA > polyBzMA > polyIMA. The results of flexural test and SENB test for the cured epoxy resin systems modified with 10wt% of *in situ* generated polyIMA, polyBzMA and polyPMA are shown in Table 2, and SEM micrographs of the fractured surfaces near the initial cracks after SENB test of I10, B10 and P10 are shown in Figure 4. As expected from close SP values of

polyPMA and the cured matrix resin, no phase separation was observed on the fractured surface of P10 (Figure 4d). The fractured surfaces of B10 and I10 showed sea-island type phase separations, but the size of island domain of B10 was smaller than that of I10 (Figures 4b and 4c). This difference in the domain size is consistent with the trend expected from the SP values of the modifier vinyl polymers. Significant increase in the fracture toughness (K_{IC}) was achieved only at B10, which shows the spherical island domain less than 1 μm in diameter, and B10 showed no decrease in flexural modulus and strength from the unmodified resin. These results indicate that BzMA is more appropriate modifier monomer than IMA and PMA for toughening of the epoxy resin composed of DGEBA/DETDA by the *in situ* radical polymerization method due to its high miscibility with the uncured resin composition and moderate miscibility with the cured matrix resin.

Table 2. Effect of the type of modifier monomer on the properties of the cured resin system

Entry ^{*1, *2}	Modifier content ^{*3}			SENB test		3-point bending test					T _g ^{*4} (°C)	
	BzMA	IMA	PMA	K _{IC} (MPa·m ^{0.5})		Strength (MPa)		Modulus (GPa)		Failure strain (%)		
	(wt%)			Ave.	σ	Ave.	σ	Ave.	σ	Ave.		σ
Control	-	-	-	0.61	0.05	125	1	2.9	0.0	11.7	1.5	172
B10	10	0	0	0.76	0.09	125	7	3.1	0.0	10.7	4.1	149
I10	0	10	0	0.67	0.08	132	1	3.1	0.0	14.3	0.1	147
P10	0	0	10	0.61	0.03	136	1	3.4	0.0	14.8	1.6	142

*1 Epoxy resin: DGEBA, Curing agent: DETDA (Epoxide/N-H = 1/1 (molar ratio))

*2 Curing condition: 120 °C/5hour+180 °C/2hour

*3 DCP content was 1 mol% in total modifier monomers

*4 Determined by onset temperature of storage modulus curve from DMA measurement

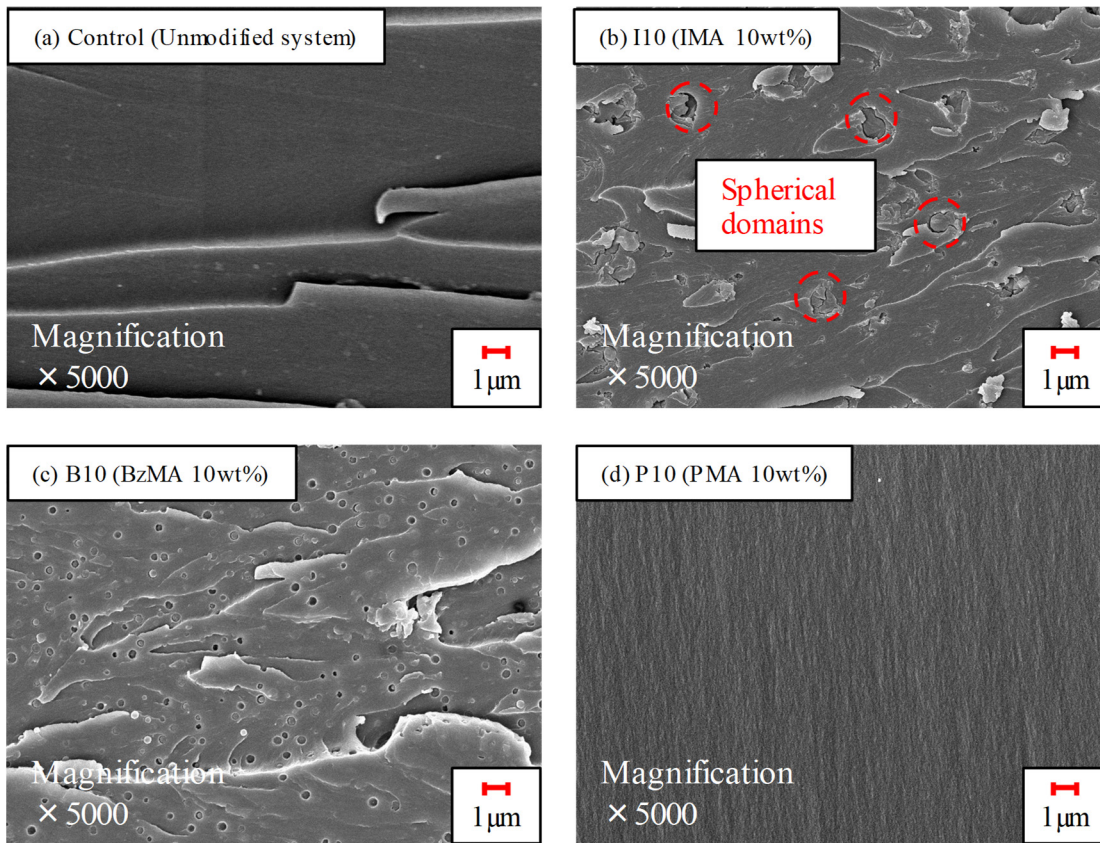


Figure 4. SEM micrographs of fractured surfaces of the cured epoxy resin systems after SENB test; (a) unmodified system (Control), (b) 10wt% IMA system (I10), (c) 10wt% BzMA system (B10), (d) 10wt% PMA system (P10)

The effect of the *in situ* generated polyBzMA as a modifier on mechanical properties of the cured epoxy resin was then investigated by varying the content of BzMA added to the uncured resin system. Table 3 shows flexural test and SENB test results for the cured epoxy resin systems. There is a tendency that the toughness (K_{IC}) is increased drastically with increasing BzMA content and B20 showed 101% increase from the unmodified control. However, the flexural strength of B20 decreased by 29% from the unmodified control. Figure 5 shows SEM observation results of the fractured surfaces near the initial cracks after SENB test of the cured epoxy resins. B10 showed a sea-island type phase

separation and the spherical island domain size was in the range of 200–500 nm in diameter. We considered that the spherical polyBzMA rich domains could cause crack branching, reduce the stress at the crack front and increase the toughness of B10 to some extent. This morphological effect on K_{IC} is in good agreement with the results for PES/epoxy polymer blends examined by Mimura et al [6], including no observation of obvious shear deformation near the crack tip. B20 also showed a sea-island type phase separation in the SEM observation and the spherical island domain size was in the range of 1–2 μm in diameter, while several spherical domains were aggregated and thus formed continuous phase. K_{IC} of B20 is considered to have been further improved from B10 since the crack propagated through this modifier continuous phase. On the other hand, flexural strength of B20 was decreased probably because of the aggregation of the polyBzMA-rich island domains and insufficient interfacial adhesion between the low miscible polyBzMA-rich and epoxy-rich domains. These aggregation and interface would work as the defects. Iijima et al. studied toughening of amine-cured DGEBA epoxy resin by *N*-phenylmaleimide-styrene copolymers [15], and they have also reported that the flexural strength was decreased when the interfacial adhesion of micrometer-level co-continuous phases composed of the epoxy matrix and the modifier was not high.

Table 3. K_{IC} and flexural properties of the cured epoxy resin systems

Entry ^{*1, *2}	Modifier content ^{*3}			SENB test		3-point bending test						T_g ^{*4} (°C)
	BzMA	PEGMEMA	Total	K_{IC} (MPa·m ^{0.5})		Strength (MPa)		Modulus (GPa)		Failure strain (%)		
				Ave.	σ	Ave.	σ	Ave.	σ	Ave.	σ	
Control	-	-	-	0.61	0.05	125	1	2.9	0.0	11.7	1.5	172
B10	10	0	10	0.76	0.09	125	7	3.1	0.0	10.7	4.1	149
B20	20	0	20	1.23	0.04	89	2	3.0	0.1	3.5	0.0	163
B8P2	7.5	2.5	10	0.66	0.11	128	3	3.2	0.0	10.3	3.6	140
B11P4	11.3	3.7	15	0.94	0.04	126	1	3.1	0.0	9.8	0.9	147
B17P3	16.7	3.3	20	1.26	0.09	111	2	2.8	0.1	9.3	3.4	156
B15P5	15	5	20	1.01	0.03	123	6	3.1	0.1	12.8	3.4	150
B13P7	13.3	6.7	20	0.89	0.04	117	2	2.9	0.0	9.6	3.9	147

*1 Epoxy resin: DGEBA, Curing agent: DETDA (Epoxide/N-H = 1/1 (molar ratio))

*2 Curing condition: 120 °C/5hour+180 °C/2hour

*3 DCP content was 1 mol% in total modifier monomers

*4 Determined by onset temperature of storage modulus curve from DMA measurement

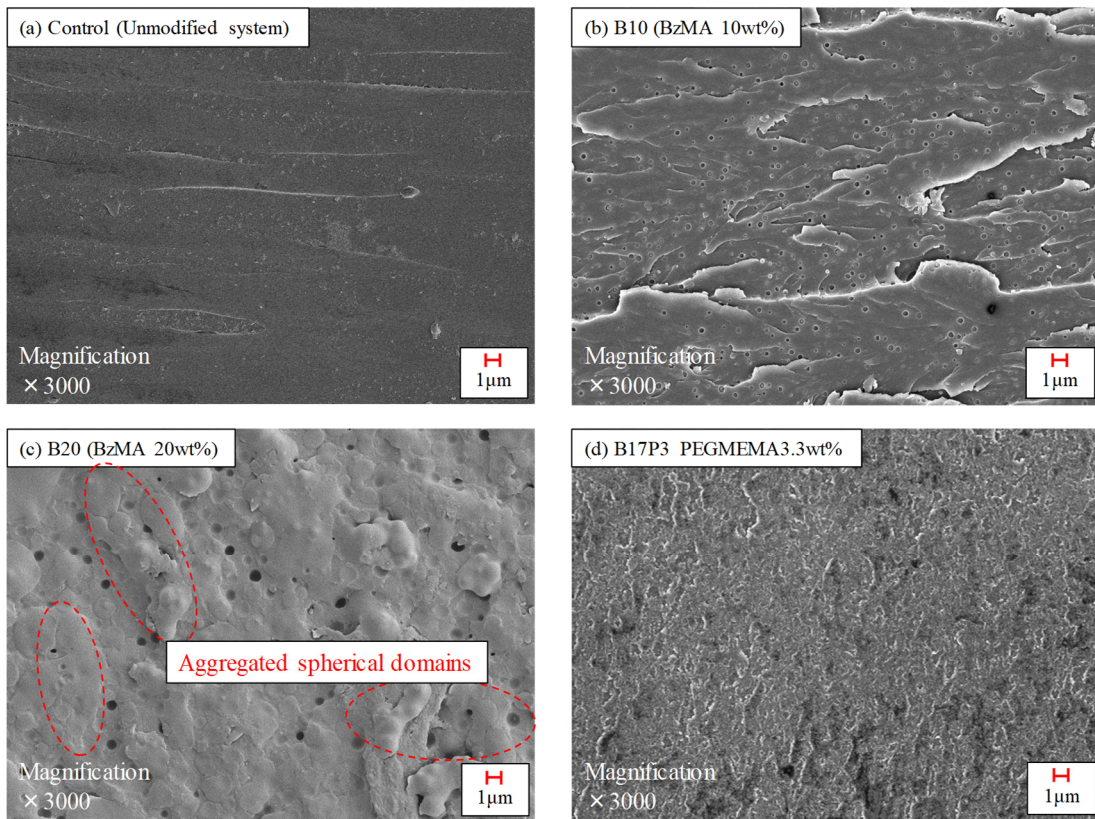


Figure 5. SEM micrographs of fracture surfaces of the cured epoxy resin systems after SENB test; (a) unmodified system (Control), (b) 10wt% BzMA system (B10), (c) 20wt% BzMA system (B20) and (d) 20wt% BzMA-PEGMEMA copolymer system (B17P3)

3.3. Investigation of residual vinyl monomers in the cured resin

In the *in situ* radical polymerization method, it may be possible that not all of the modifier monomers are polymerized during curing process, and therefore some residual monomers may remain in the cured resin. To investigate the existence of the residual monomers, extraction of the non-crosslinked components from the cured resin toughened by the *in situ* generated polyBzMA (B20 in Table 3) and ¹H-NMR measurement of the extract were conducted. The cured B20 was fractured and immersed in DMSO-*d*₆ for 24 hours. The unmodified control was also evaluated in the same method as a comparison. The ¹H-NMR spectra of the extracts are shown in Figure 6, and that from B20 showed two peaks derived from the vinyl group of the BzMA monomer at 6.1 and 5.7 ppm and a broad peak derived from the methyl group of polyBzMA at 0.5–1.2 ppm. On the other hand, the extract from the unmodified control did not show a distinct peak around 6 ppm.

These results indicate that not only polyBzMA but also its monomer was present in the cured resin. However, it is considered that the extraction of BzMA monomer is much easier than that of polyBzMA, and therefore actual existing ratio of BzMA monomer in the cured resin is expected to be much lower than the result of the ¹H-NMR measurement. Thus, in order to investigate the amount of the residual BzMA monomer in the cured resin toughened by the *in situ* radical polymerization method, TGA of B20 and the uncured control was carried out. Boiling temperature of BzMA is 233 °C at atmospheric pressure, and a few percent of water and impurities are generally included in a cured epoxy resin. Thus,

we considered that the residual amount of BzMA monomer can be estimated from the difference in weight loss between the unmodified control and B20 around 233 °C. As shown in the TGA results in Figure 7 and Table 4, weight loss of the unmodified control and B20 were similar value until 200 °C, and therefore about 1.5wt% weight loss can be regarded as originating from water and impurities included in the cured epoxy resin. Furthermore, the differences in weight loss between the unmodified control and B20 were 0.4% at 233 °C and 0.6% at 250 °C. From these results, it is estimated that about 0.4–0.6wt% of the modifier monomer remained in B20, and the value is less than the amount of the water and other impurities contained in the resin.

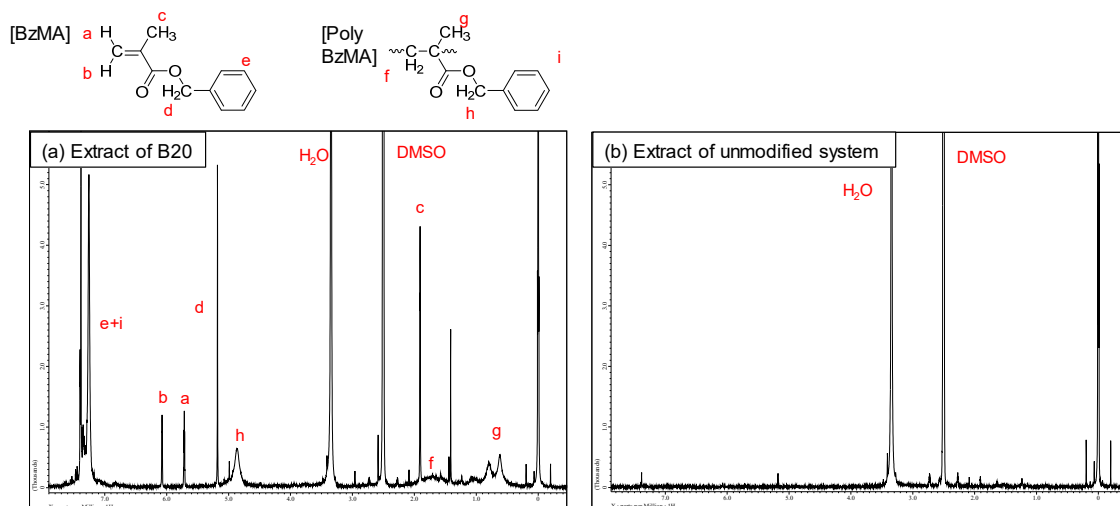


Figure 6. ¹H-NMR spectra of the extracts of the cured epoxy resins obtained by immersing in DMSO-*d*₆.

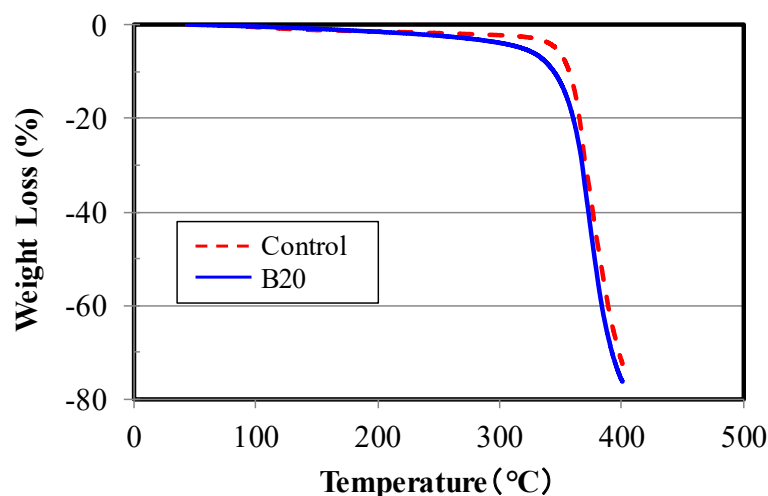


Figure 7. TGA charts of the cured epoxy resins

Table 4. Weight loss at several temperatures in TGA of the cured epoxy resins

Entry	Weight loss (%)					
	at 100 °C	at 200 °C	at 233 °C	at 250 °C	at 300 °C	at 350 °C
Control	0.6	1.5	1.7	1.8	2.3	6.4
B20	0.4	1.6	2.1	2.4	3.9	12.7
Δ weight loss	0.2	0.1	0.4	0.6	1.6	6.3

3.4. Toughening of the epoxy resin by *in situ* generated BzMA-PEGMEMA copolymers

From the results of the section 3.2, formation of non-aggregated continuous modifier phase with finer dispersion is expected to be important to achieve an increase in toughness without decreasing flexural strength. In order to realize such the phase structure, we selected PEGMEMA (Figure 1) as a comonomer of BzMA. PEGMEMA has a poly(ethylene glycol) structure, which can interact with -OH, -NH and other polar groups by hydrogen bonding and dipolar interaction, in its side chain. We have proved that introduction of poly(ethylene glycol) side chain on the *in situ* generated styrene-PMI

copolymer increased interaction between the modifier polymer and acid-anhydride-cured bisphenol-A type epoxy resin, leading to decrease in the domain size of the phase separation and increase in the interfacial adhesion between the separated phases [12]. Therefore, the same effect on the phase separation can be expected by introducing poly(ethylene glycol) side chain into the *in situ* generated polyBzMA.

The effect of the addition of PEGMEMA on mechanical properties and morphology of the cured resins was investigated by varying the BzMA/PEGMEMA ratio and the total monomer loading. The mechanical properties are shown in Table 3 and the effect of PEGMEMA content on K_{IC} and flexural strength with maintaining 20wt% total monomer loading is depicted in Figure 8. These results revealed that the flexural strength was increased with increasing PEGMEMA content and K_{IC} was slightly decreased when the PEGMEMA content was above 5wt%. As shown in Table 3, B17P3 modified by 16.7wt% of BzMA and 3.3wt% of PEGMEMA showed the highest toughness and similar flexural strength to the unmodified control. SEM micrograph of the fractured surfaces near the initial cracks after SENB test of B17P3 is shown in Figure 5d and no distinct phase separation was observed on the surface of B17P3, while B20 had micro-scaled modifier rich domains (Figure 5c). To clarify the modifier-rich domain, the specimens after SENB test were immersed in tetrahydrofuran (THF) for 24 hours and the fractured surfaces were observed by SEM. As a result, holes less than 100 nm in diameter, which derived from the extracted modifier domains, were observed on the fractured surface of B17P3

(Figure 9a). On the other hand, no such holes were observed on the fractured surfaces of B15P5 and B13P7 modified by the same weight of copolymers containing higher ratios of PEGMEMA than B17P3 (Figures 9b and 9c), and this implies nearly homogeneous morphology of B15P5 and B13P7. The detailed morphology of B17P3, B15P5 and B13P7 were investigated by TEM observation. As shown in Figure 10a, it was found that B17P3 had nanometer-sized co-continuous phase separation structure, and B17P3 is considered to have exhibited the best mechanical properties, including toughness, by virtue of this morphology. Under this type of phase separation structure, the crack inevitably propagates the modifier phase as well as the epoxy resin phase, and thus toughness is significantly improved. In addition, better flexural strength of B17P3 than B20 implies that the continuous modifier phase of B17P3 did not have the defects like the aggregated continuous phase observed in B20 and that interfacial adhesion between the epoxy and modifier phases was increased by the addition of PEGMEMA. On the other hand, TEM photographs of B15P5 and B13P7 indicate that domain size of the phase separation became smaller as the ratio of PEGMEMA in the modifiers was increased (Figures 10b and 10c). In these systems, clear co-continuous phase structures were no longer observed, and the interfaces between the epoxy resin matrix and the modifier were also ambiguous. It is considered that these morphological changes induced by the higher ratios of PEGMEMA in the modifiers decreased the K_{IC} s of B15P5 and B13P7 than that of B17P3. Regarding the glass transition temperatures, the T_g of B17P3 was decreased from the unmodified control (172 °C)

due to the addition of the modifier polymer, but still maintained a high value of 156 °C. The Tgs of B15P5 and B13P7 were lower than that of B17P3 because of the increase in the amount of poly(ethylene glycol) side chain.

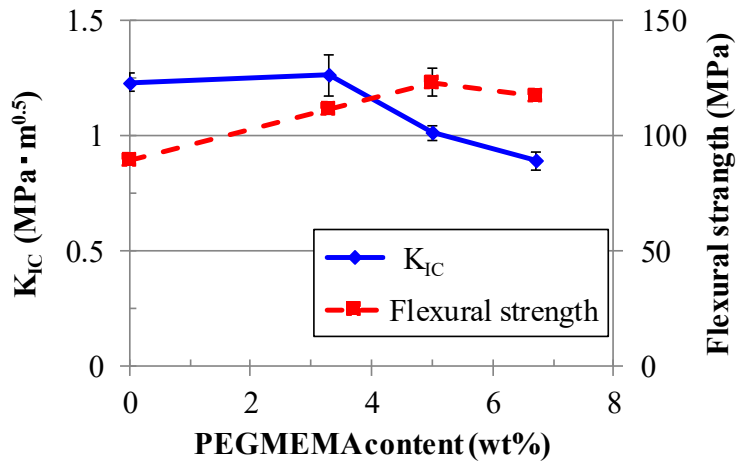


Figure 8. Influence of PEGMEMA content on K_{IC} and flexural strength of the cured epoxy resin systems (modifier content was fixed as 20wt%)

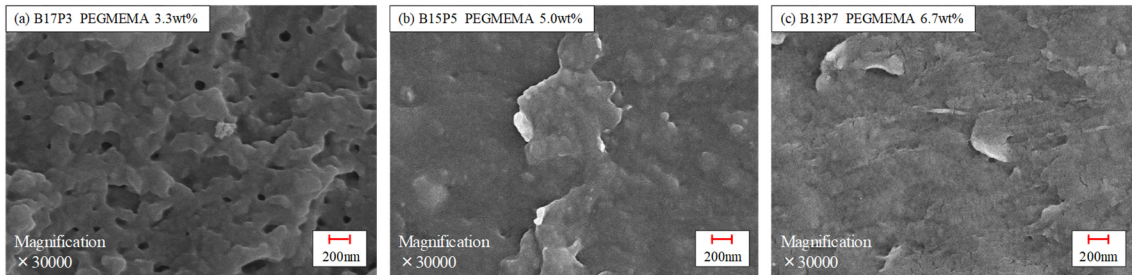


Figure 9. SEM micrographs of fractured surfaces of the cured epoxy resin systems with different PEGMEMA contents after SENB test (The specimens were immersed in THF for 24 hours before the SEM observations.)

(a) B17P3 (BzMA/PEGMEMA = 16.7/3.3 (w/w)), (b) B15P5 (BzMA/PEGMEMA = 15.0/5.0 (w/w)), (c) B13P7 (BzMA/PEGMEMA = 13.3/6.7 (w/w))

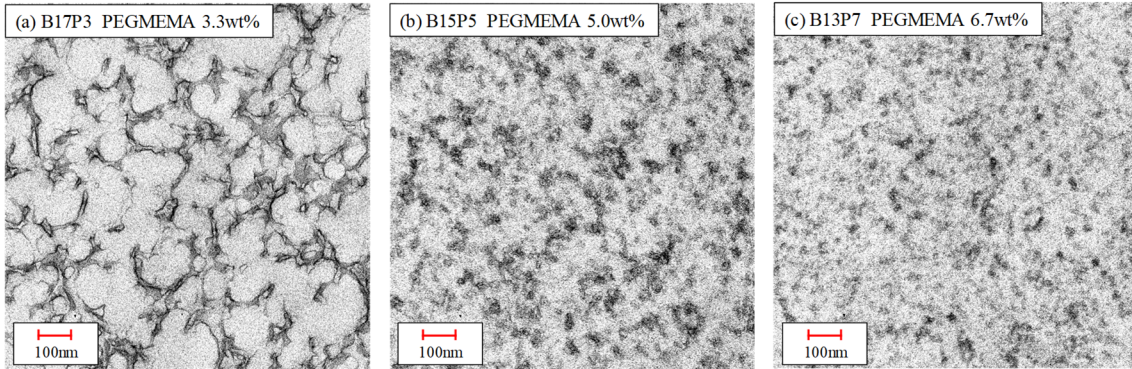


Figure 10. TEM micrographs of the cured epoxy resin systems with different PEGMEMA contents (The sample was stained with RuO_4 , White area: epoxy-rich domain, Dark area: BzMA-PEGMEMA-copolymer-rich domain)

(a) B17P3 (BzMA/PEGMEMA = 16.7/3.3 (w/w)), (b) B15P5 (BzMA/PEGMEMA = 15.0/5.0 (w/w)), (c) B13P7 (BzMA/PEGMEMA = 13.3/6.7 (w/w))

3.5. Fabrication and mechanical properties of the CFRP laminate

From the results of the previous sections, it is expected that the *in situ* radical polymerization method can be applied as a modification method of CFRP. Thus, we examined the application of the B17P3 resin system in Table 3, which was modified by BzMA/PEGMEMA and showed the best mechanical properties, to fabrication of CFRP by VaRTM method. Figure 11 shows the viscosities of the uncured B17P3 and unmodified control systems. B17P3 showed lower viscosity than the unmodified control because the viscosities of BzMA and PEGMEMA are lower than those of DGEBA and DETDA. Owing to the low viscosity of the uncured B17P3, cured CFRP panels for mechanical testing were successfully fabricated by VaRTM method.

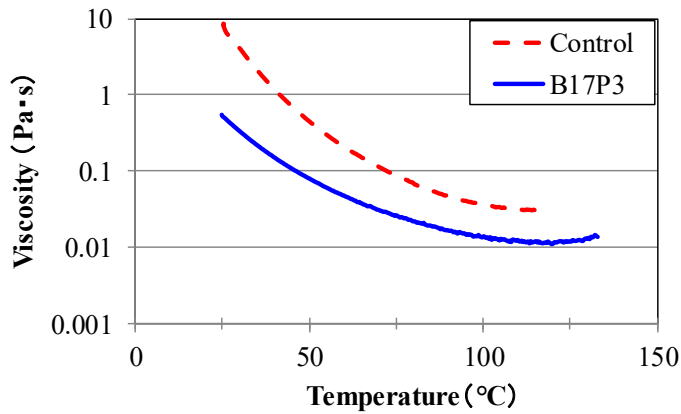


Figure 11. Viscosities of the uncured epoxy resin compositions

Figure 12 shows interlaminar fracture toughness of the CFRP laminates measured according to the testing method specified in JIS K7086. As a result, although the G_{IIC} of the B17P3 system decreased by 12% than the unmodified control, its G_{IC} was improved by 30% over the unmodified control. The improvement G_{IC} can be attributed to the increase in toughness of the resin in the CFRP laminate. These results indicate that the *in situ* radical polymerization method can be effective for enhancing the mode I interlaminar fracture toughness while maintaining low viscosity of the uncured resin composition. It is still unclear that G_{IIC} of the CFRP laminate was not enhanced while toughness of the CFRP matrix was improved by the *in situ* radical polymerization method. However, the results of G_{IC} and G_{IIC} in this study are consistent with several previous reports about the relationship between resin toughness and interlaminar fracture toughness of CFRP laminates [1,18]. Other factors such as strength of interfacial interaction between carbon fiber and matrix resin can also affect G_{IC} and G_{IIC} properties of CFRP laminates. We believe that it is possible to increase G_{IIC} of CFRP toughened by

the *in situ* radical polymerization method by applying other types of sizing agent to the carbon fibers.

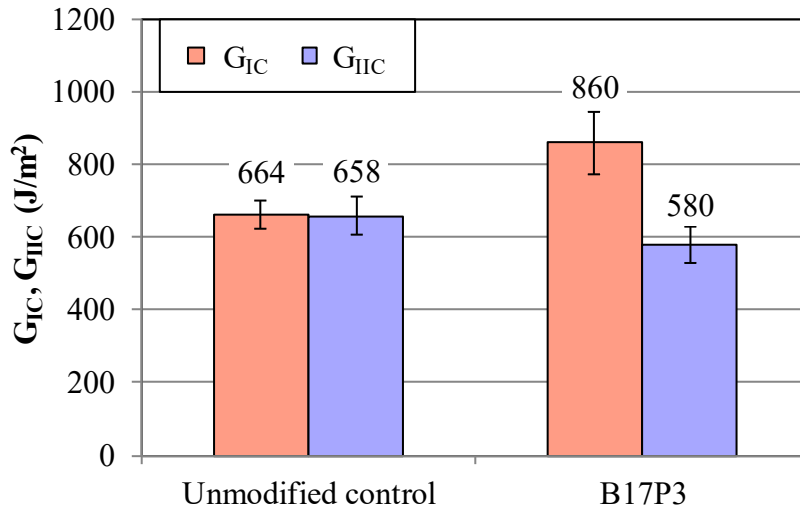


Figure 12. Interlaminar fracture toughness of the CFRP laminates.

4. Conclusion

In order to achieve both good mechanical properties, including toughness and strength, of the cured resin and low viscosity of the uncured resin composition, “*in situ* radical polymerization method” was applied to epoxy resin for the matrix of CFRP. BzMA was selected as a modifier monomer to enhance the K_{IC} of the cured epoxy resin. The resulting modified resin system containing 20wt% of *in situ* generated polyBzMA showed 2.0 times higher K_{IC} than the unmodified system. However, its flexural strength decreased by 29% from the unmodified system due to the aggregation of the polyBzMA-rich island domains and insufficient interfacial adhesion between the low miscible polyBzMA-rich and epoxy-rich domains. To enhance the miscibility between the epoxy resin and *in situ* generated

polyBzMA and improve interaction at the interphase between epoxy-rich and modifier-rich domains, PEGMEMA was selected as a comonomer of BzMA. As a result of addition of PEGMEMA, the optimized resin system had co-continuous phase separation at a nanometer level, and its K_{IC} was improved by 2.1 times from the unmodified system (from $0.61 \text{ MPa}\cdot\text{m}^{0.5}$ to $1.26 \text{ MPa}\cdot\text{m}^{0.5}$) with suppressing the decrease in flexural strength. This modified resin system showed lower viscosity than the unmodified resin system, and thanks to this low viscosity, VaRTM method was successfully applied to the fabrication of cured CFRP panels for mechanical testing. The CFRP system composed of the epoxy resin system modified by *in situ* generated BzMA/PEGMEMA showed 30% increase of G_{IC} from unmodified system. These results demonstrated that the “*in situ* radical polymerization method” can be effective for enhancing fracture toughness of CFRP laminates while maintaining low viscosity of the uncured resin composition.

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