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Abstract

The challenge of developing epoxy-foam adhesives for automotive applications lies in the difficulties associated with finding the optimal composition ensuring both high expansion ratio and mechanical strength. Herein, epoxy-foam adhesives based on epoxy composites were prepared and evaluated for automotive applications. The curing behavior was studied by differential scanning calorimetry, and the morphology was characterized non-destructively by micro X-ray computed tomography. Increasing the content of rubber-modified epoxy (RME) retarded the curing reaction by increasing the expansion ratio and affected the lap shear strength. A high expansion ratio and suitable mechanical strength was observed for epoxy-foam adhesives containing 10 or 15 wt% RME.

Keywords

Epoxides; Toughened adhesives; Non-destructive testing; Mechanical properties of adhesives

1. Introduction

Epoxy adhesives have found many applications in the automotive industry. For example, epoxy-foam adhesives are frequently placed between two automotive panels and, after foaming, fill the gap between them (Fig. 1). By this process, epoxy-foam adhesives provide both reinforcement of panels and the development of a watertight structure. Hence, epoxy-foam adhesives must have both mechanical strength for reinforcement and high expansion ratio for watertight structure. As these two properties are inversely correlated [1], it is important to find the optimal composition that would provide a suitable mechanical strength for automotive applications.

Epoxy-foam adhesives consist of an epoxy resin, a curing agent, a foaming agent, and other fillers. Upon heating, they undergo the curing and foaming reactions shown in Fig. 2. The chemical foaming agent (CFA) imparts a high expansion ratio but low mechanical strength to epoxy-foam adhesives [1-5]. Thus, specific strategies are needed to improve the mechanical strength of epoxy-foam adhesives.

The expansion ratio and morphology of polymeric foams are typically characterized by 2D cross-sectional scanning electron microscopy (SEM) measurements [1-3, 6-9]. However, SEM enables the

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Chemical foaming agent, CFA; scanning electron microscopy, SEM; micro X-ray computed tomography, micro X-ray CT; silane-modified epoxy, SME; rubber-modified epoxy, RME; differential scanning calorimetry, DSC.

observation of the sample surface, and evaluation of the internal structure requires the destruction of epoxy-foam adhesives [1]. On the other hand, micro X-ray computed tomography (CT) is a powerful technique for the non-destructive observation of the internal structure of polymeric foams by generating 3D images [10-13], and allows the determination of porosity, pore size distribution, and morphology of epoxy-foam adhesives. Thus, micro X-ray CT was used to non-destructively characterize the morphology of epoxy-foam adhesives.

In this work, we prepared epoxy-foam adhesives containing various amounts of bisphenol-A type epoxy, silane-modified epoxy (SME), rubber-modified epoxy (RME), and CFA, with the aim to identify epoxy-foam adhesives with a high expansion ratio and suitable mechanical strength. The mechanical properties were measured by single-lap shear test, and the effect of the amount of RME added was evaluated. By the process, we could obtain optimal composition ensuring both high expansion ratio and suitable mechanical strength.

2. Material and methods

2.1 Materials

Three epoxy resins were used for preparing epoxy composites, namely, bisphenol-A diglycidyl ether resin (YD-128, Kukdo Chemical Co., Ltd., Republic of Korea), SME resin (KSR-177, Kukdo Chemical Corp. Ltd., Republic of Korea), which can be used for improving adhesion to an automotive steel plate, and nitrile-butadiene RME resin (R-1309, Kukdo Chemical Co., Ltd., Republic of Korea), which has a toughening effect on thermosetting polymers [14-16]. For curing, a dicyandiamide curing agent (CG-1200, Air products and chemicals, Inc., USA) and a latent accelerator (UR-500, AlzChem, Germany) were blended with the epoxy resins. Modified sodium bicarbonate (Kycerol-92, Kumyang Co., Ltd., Republic of Korea) was used as a CFA, and calcium carbonate (5HB, OMYA, Switzerland) was added as a filler. Detailed information on the materials employed in this work are shown in Table 1.

2.2 Blending and curing

Epoxy composites with various compositions were prepared as shown in Table 2, keeping the weight ratio of the two curing agents constant and setting the ratio of total equivalent weight of epoxy to amine groups to 1.71. The calcium carbonate filler was added in order to control the total mass. The weight fraction of the CFA was 2.4 wt% in all samples except for non-foam samples. Samples without foaming agent were prepared to analyze the effect of RME in epoxy composites. All samples were cured at 453 K for 20 min.

2.3 DSC

The curing behavior of epoxy-foam adhesives was evaluated by DSC (DSC Q200, TA Instruments, USA). The exothermic curing reaction was performed by placing the same amount (8 mg) of each sample in the aluminum pan, and increasing the temperature from 303 K to 453 K at a constant rate of 5 K/min. During this process, the heat flow was measured by DSC.

2.4 Micro X-ray CT

The morphology was determined from the 3D images obtained using micro X-ray CT (Skyscan 1272, Bruker, Belgium). Specimens were prepared by placing uncured samples (2 g) in the oven (453 K, 20 min) for curing and foaming, and a 50 kV X-ray head was rotated around the specimens from 0° to 190°. During rotation, tomographic images were acquired every 0.6° and converted to 3D images. Software (CT Analyzer, Bruker, Belgium) was used for image reconstruction to evaluate porosity, pore size distribution, and the internal structure of the epoxy-foam adhesives.

2.5 Single-lap shear test

The mechanical properties of the epoxy-foam adhesives were measured by single-lap shear test. A steel plate (CR340, thickness = 1.6 mm) of the same grade used in automotive body construction was used as an adherent. The adhesives were applied on the steel plate (12.5 × 25 × 0.5 mm^3) followed by curing and foaming (453 K, 20 min). A universal testing machine (Allround Line Z010, Zwick, Germany) was used to measure the stress during fracture of adhesives with a strain rate of 10 mm/min. At the fracture point, lap shear strength was defined by maximum stress, and the fracture energy (J/m^2) was calculated by integrating the stress (MPa)-distance (mm) curve. Stress and strain were calculated by dividing the applied force by the area of contact and the distance by the adhesive thickness, respectively.

3. Results and discussion

3.1 Curing behavior of epoxy-foam adhesives

The curing behavior of epoxy-foam adhesives was studied by DSC with results obtained shown in Fig. 3. Because of the exothermic nature of the curing reaction between epoxy and amine groups, an exothermic peak was observed for all samples (Fig. 3 (a)). The reaction enthalpy per unit mass (J/g) was calculated by integrating the heat flow (W/g)-temperature (K) curve and dividing it by the temperature increase rate. The temperature at maximum heat flow ($T_{\mathrm{max(heat\ flow)}}$) and reaction enthalpy per unit mass were also examined, as shown in Fig. 3 (b). Notably, $T_{\mathrm{max(heat\ flow)}}$ increased with the addition of RME, indicating that RME retarded the overall curing reaction. This was attributed to the significantly higher epoxy equivalent weight and molecular weight of RME as compared to those of other epoxy resins. In addition, epoxy-foam adhesives with a high RME content showed a low reaction enthalpy per unit mass due to the high epoxy equivalent weight and low functionality per unit mass.

3.2 Morphology of epoxy-foam adhesives

The morphology of epoxy-foam adhesives was characterized non-destructively by micro X-ray CT providing the 3D images shown in Fig. 4, where the pore sizes are indicated by different colors. Interestingly, different color distributions were observed for each sample, suggesting that RME affected the pore growth.

In addition, the porosity and expansion ratio of epoxy-foam adhesives were calculated using Eq. (1) and (2):

$$\text{Porosity (\%)} = \frac{V_{\mathrm{pore}}}{V_{\mathrm{total}}} \times 100 \qquad (1)$$

$$\text{Expansion ratio (\%)} = \frac{V_{\mathrm{total}}}{V_{\mathrm{total}} - V_{\mathrm{pore}}} \times 100 \qquad (2)$$

where V_{pore} and V_{total} represent the sum of pore volumes and the total volume of the measured region, respectively.

As shown in Table 3, the porosity and the expansion ratio increased with the addition of RME, suggesting that a high RME content resulted in greater expansion of epoxy-foam adhesives. Based on the report of Takiguchi et al. that pore size and expansion ratio are related to curing behavior [6] with a slow curing rate resulting in greater expansion, our result was attributed to the retarding effect of RME on the curing reaction (Fig. 3).

As can be seen from Fig. 5, the pore size distribution shifted toward larger sizes when RME 10 wt% and 15 wt% were added, as also demonstrated by the color change in the 3D images.

Moreover, the average and standard deviation of pore size were calculated (Fig. 6). Because of reaction delays, these values increased with the addition of RME, with a maximum obtained for the sample containing 15 wt% RME. Interestingly, although the reaction was retarded also by 20 wt% RME, the pore size standard deviation substantially decreased. This suggests that pore agglomeration was restricted by the high RME loading resulting in the formation of relatively small pores.

Morphological studies by micro X-ray CT show that the porosity and expansion ratio increased with the addition of RME, but no significant difference was observed between RME 10 and 20 wt%. In other words, the expansion ratio increased with increasing RME content, reaching a plateau value of about 330% above a 10 wt% loading.

3.3 Mechanical properties of epoxy and epoxy-foam adhesives

During mechanical deformation, stress imposed on rubber particles dispersed within an epoxy can lead to toughness enhancement mechanisms due to stress concentrating effects resulting from modulus differences between rubber and epoxy. [14]. As shown in Fig. 7 (a) and (b), the lap shear strength and elongation of epoxy adhesives increased with the addition of RME. Moreover, the variation in fracture energy with RME content (Fig. 7 (c)) indicates that RME affected the degree of toughening of the epoxy adhesives.

In the epoxy-foam adhesives, the lap shear strength and fracture energy increased with the addition of 5 wt% RME, but decreased with further increases in RME content up to 20 wt% (Fig. 8). Such a decrease was attributed to the porous structure of the epoxy-foam adhesives due to the toughening effect of the RME. The increase in porosity and expansion ratio reduces the density of epoxy-foam adhesives, leading to a decrease in their mechanical strength [1]. Hence, epoxy-foam adhesives with RME contents of 10 and 15 wt% showed high porosity (~70%), whereas their lap shear strength was lower than that of adhesives with 5 wt% RME. When RME 20 wt% was added, the lap shear strength of the epoxy-foam adhesives decreased because of the critical RME concentration. In rubber-toughened polymers, the content and distribution of rubber particles plays an important role in the mechanical properties. Above the critical concentration, the added rubber particles are very close and can interact with each other, leading to reduced mechanical strength [17].

Unlike epoxy-foam adhesives, the decrease in lap shear strength from RME 0 to 20 wt% was not observed for epoxy adhesives (Fig. 7), suggesting that epoxy and epoxy-foam adhesives had different critical concentrations. In epoxy adhesives, the stress would be concentrated on the rubber particles only, whereas in epoxy-foam adhesives, the stress concentration occurred on both the pore surface and the rubber particles. Because pores are unable to dissipate energy, the interaction between pores and rubber particles could weaken the toughening effect of rubber particles. Thus, rubber particles must be distant from both pores and other rubber particles. This indicates that the critical concentration of rubber particles in epoxy-foam adhesives was lower than that in epoxy adhesives.

Notably, epoxy-foam adhesives containing RME 5 wt% showed the highest lap shear strength, whereas the addition of RME 10 and 15 wt% resulted in a lap shear strength similar to that of epoxy-foam adhesives with RME 0 wt%. Hence, an increase in expansion ratio (~330%) and simultaneous preservation of the mechanical strength could be achieved by the addition of RME 10 or 15 wt%.

4. Conclusions

Epoxy-foam adhesives were prepared by foaming epoxy composites containing different amounts of RME for automotive applications. The RME retarded the curing reaction, thus affecting the growth of pores and finally resulting in high porosity and expansion ratio (>300%), as demonstrated non-destructively by micro X-ray CT. The lap shear strength of epoxy-foam adhesives increased with the addition of RME 5 wt%, whereas adhesives containing RME 10 and 15 wt% showed a lap shear strength similar to those with RME 0 wt%. Notably, using a proper amount of RME (10 or 15 wt%), a high expansion ratio was achieved while preserving a suitable mechanical strength, which makes these materials promising for automotive applications. However, because we only focused in this study on a chemical foaming agent, it would be appropriate to compare the results obtained here with other potential foaming agents such as a capsulated blowing agent. Thus, future research will focus on new epoxy-foam adhesives prepared with capsulated blowing agents to determine the optimum foaming agents for superior properties in automotive applications.

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Figure Captions:

Fig. 1. Epoxy-foam adhesives between automotive panels (a) before and (b) after foaming

Fig. 2. (a) Foaming and (b) curing mechanism

Fig. 3. Curing behavior of epoxy-foam adhesives: (a) DSC curves, (b) $T_{\mathrm{max(heat\ flow)}}$ (Temperature at maximum heat flow) and enthalpy per unit mass

Fig. 4. 3D images of epoxy-foam adhesives: (a) RME 00/Foam, (b) RME 05/Foam, (c) RME 10/Foam, (d) RME 15/Foam, (e) RME 20/Foam, (f) color parameters for pore size

Fig. 5. Pore size distribution in epoxy-foam adhesives: (a) RME 00/Foam, (b) RME 05/Foam, (c) RME 10/Foam, (d) RME 15/Foam, (e) RME 20/Foam

Fig. 6. Average and standard deviation (SD) of pore size in epoxy-foam adhesives

Fig. 7. Lap shear test of epoxy adhesives: (a) S-S curve, (b) lap shear strength and elongation, (c) fracture energy

Fig. 8. Lap shear test of epoxy-foam adhesives: (a) S-S curve, (b) lap shear strength and elongation, (c) fracture energy

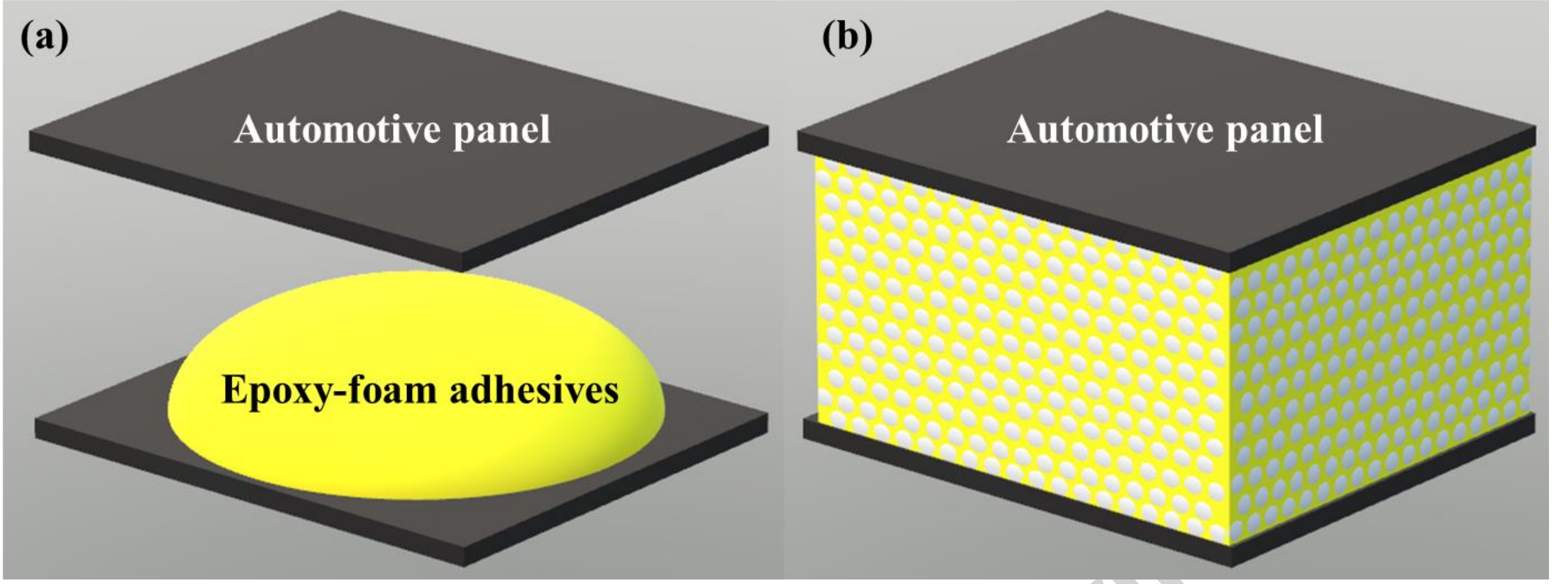
(a)
Automotive panel
Epoxy-foam adhesives
(b)
Automotive panel

Fig. 1

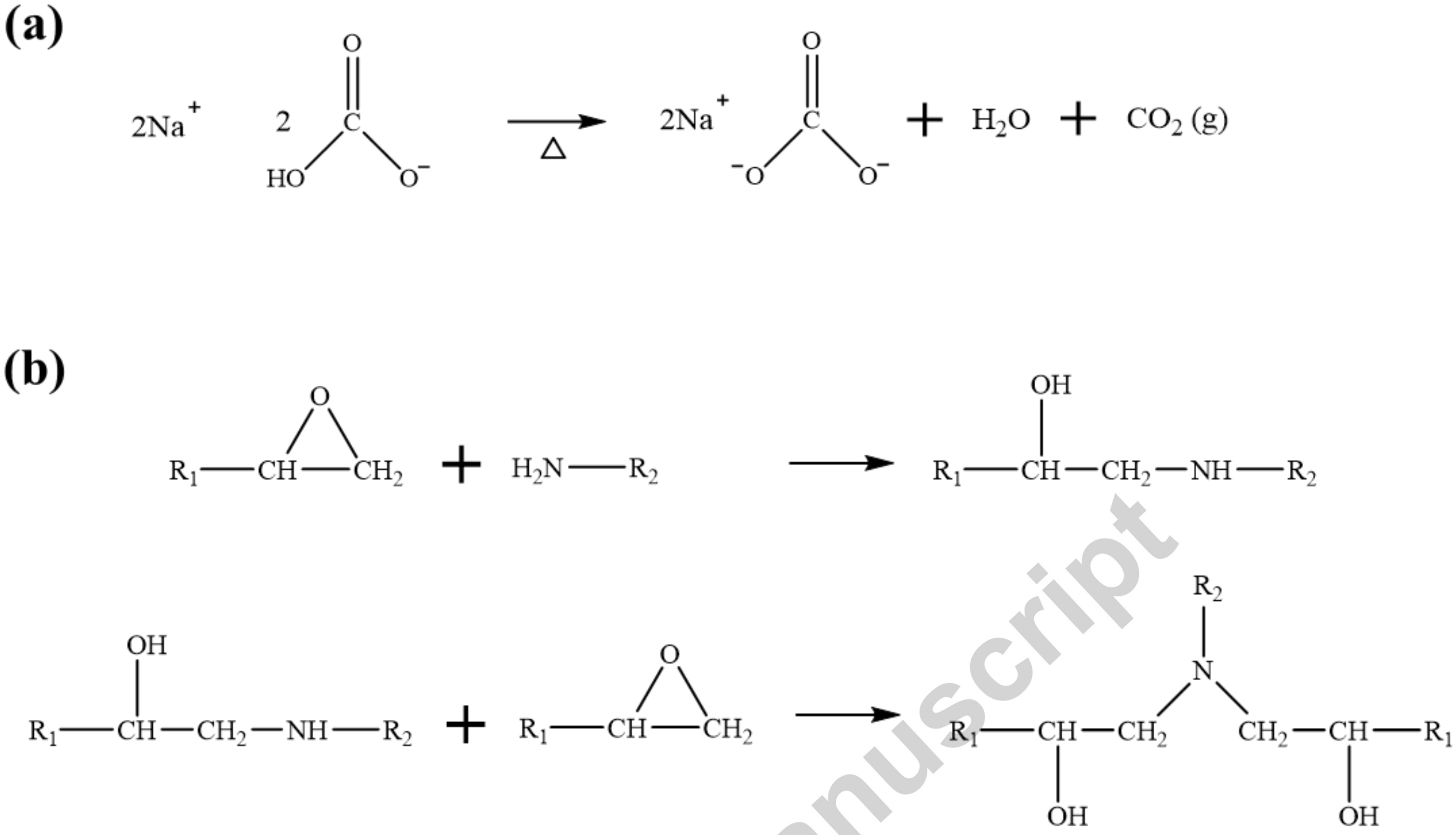

Fig. 2

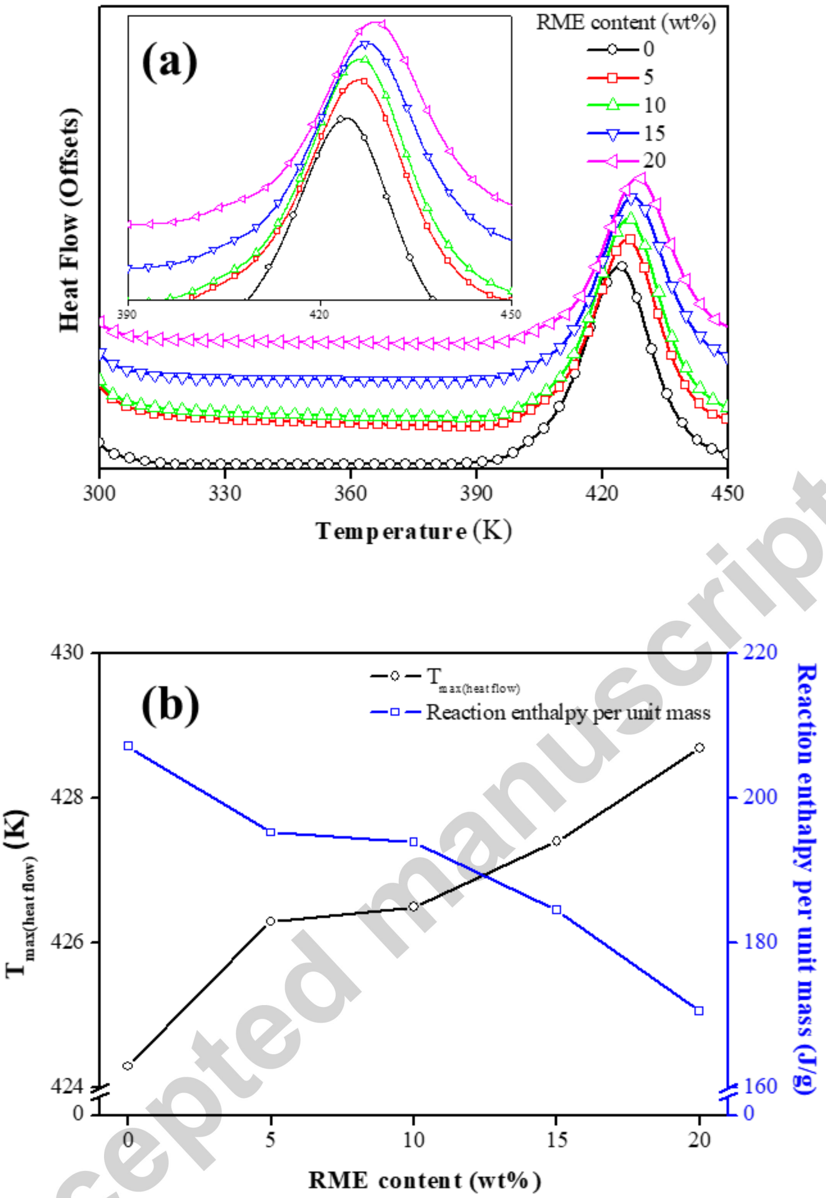
(a)
Heat Flow (Offsets)
RME content (wt%)
0
5
10
15
20
390
420
450
300
330
360
390
420
450
Temperature (K)
(b)
$T_{max(heat flow)}$
Reaction enthalpy per unit mass
430
428
426
424
0
220
200
180
160
0
$T_{max(heat flow)}$ (K)
Reaction enthalpy per unit mass (J/g)
0
5
10
15
20
RME content (wt%)

Fig. 3

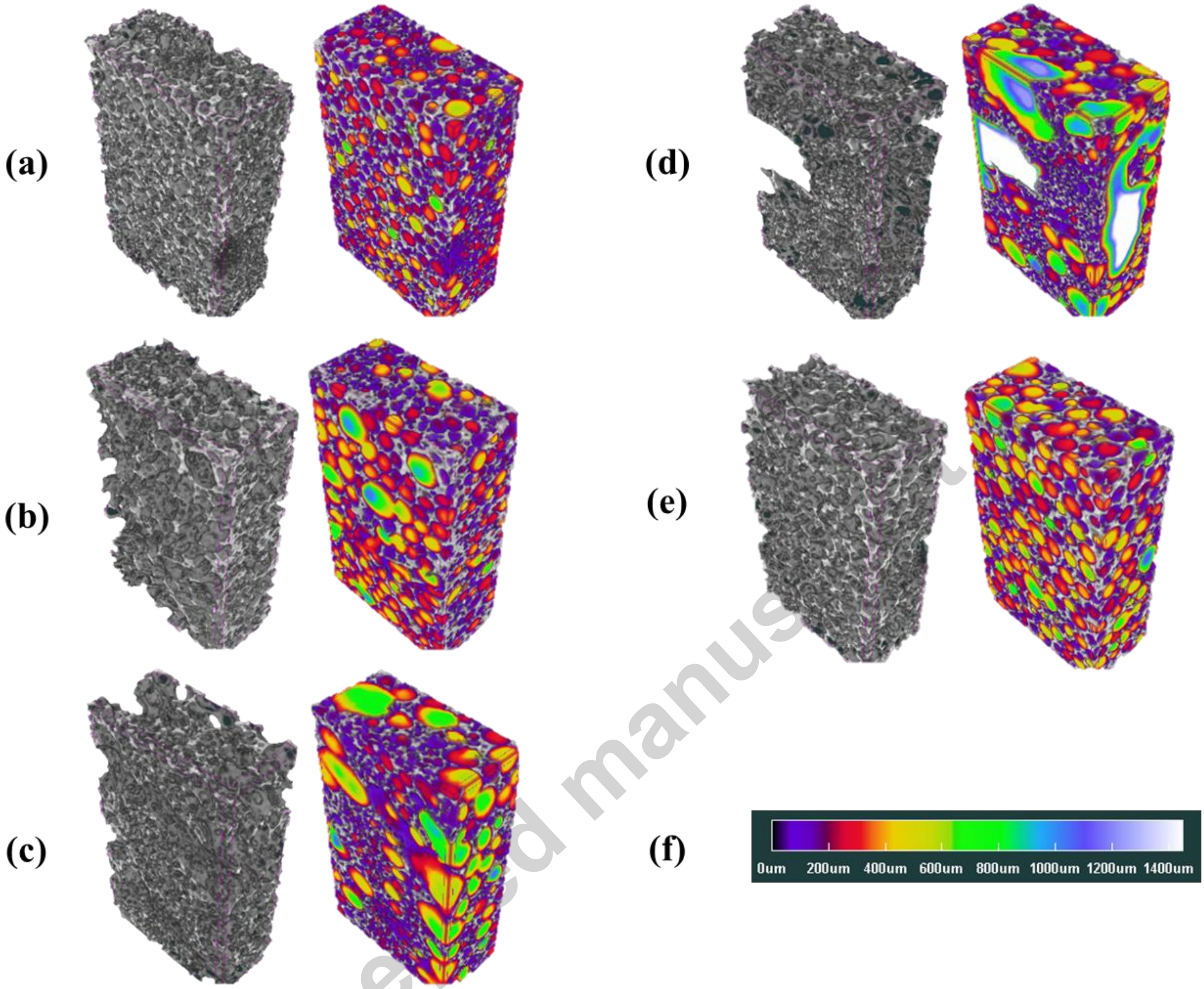

Fig. 4

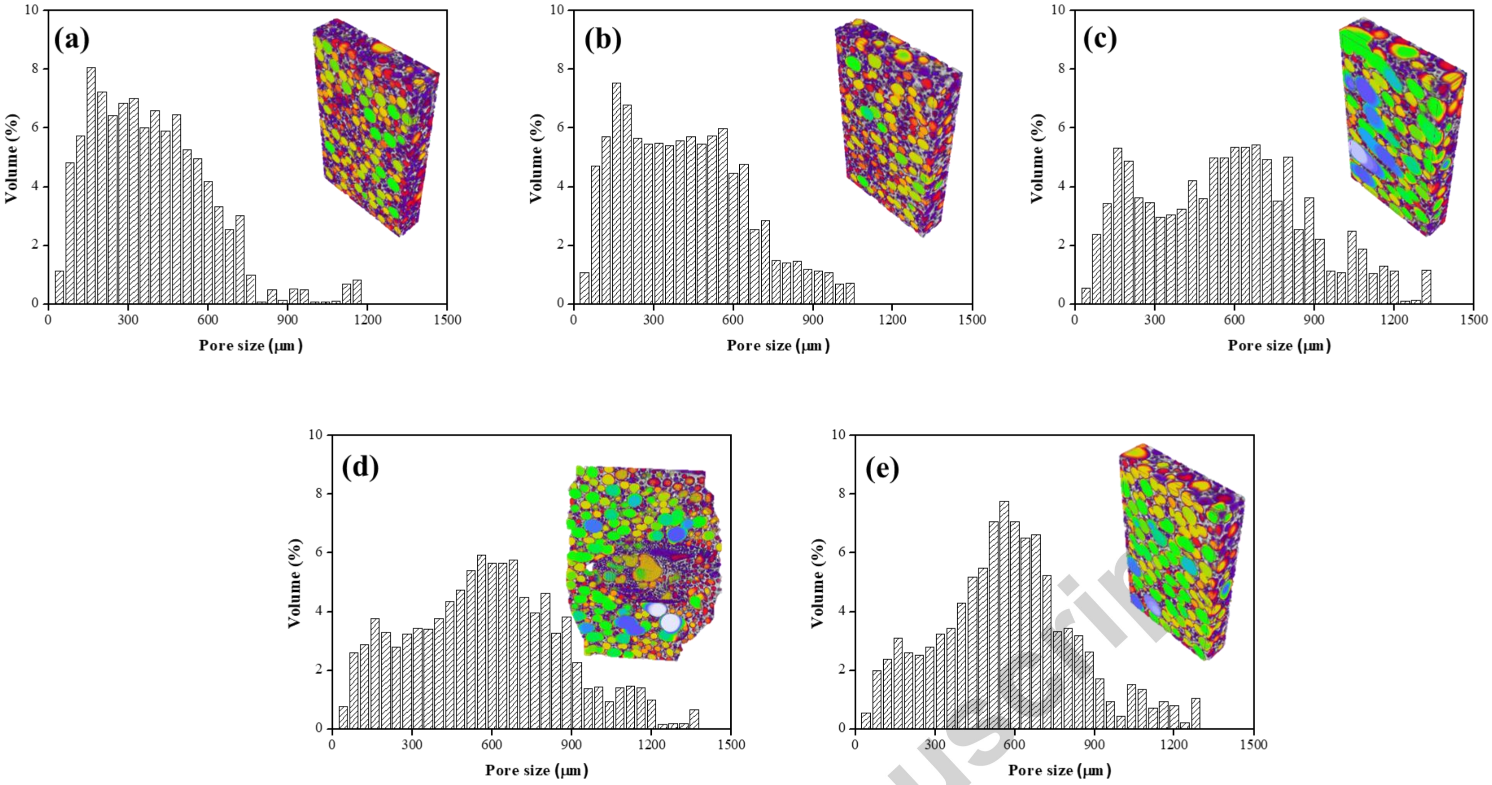

Fig. 5

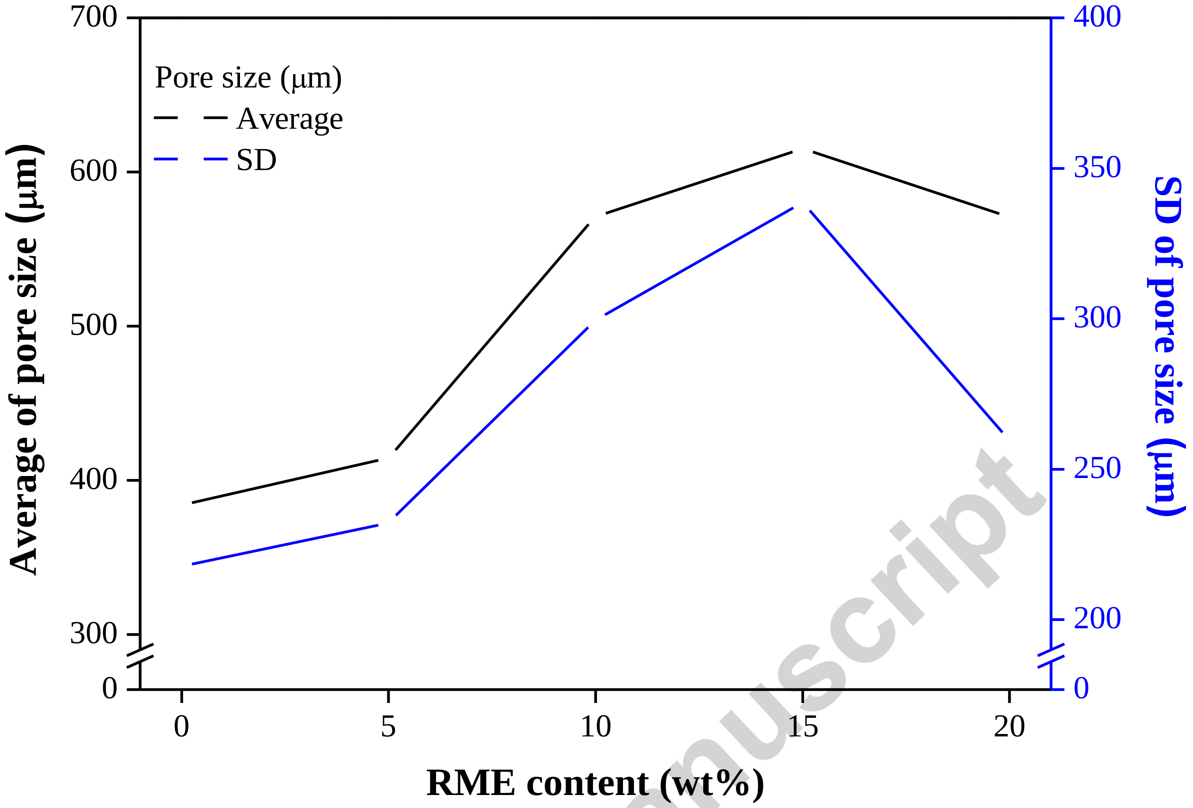
700
600
500
400
300
0
400
350
300
250
200
0
Pore size (μm)
Average
SD
Average of pore size (μm)
SD of pore size (μm)
0
5
10
15
20
RME content (wt%)

Fig. 6

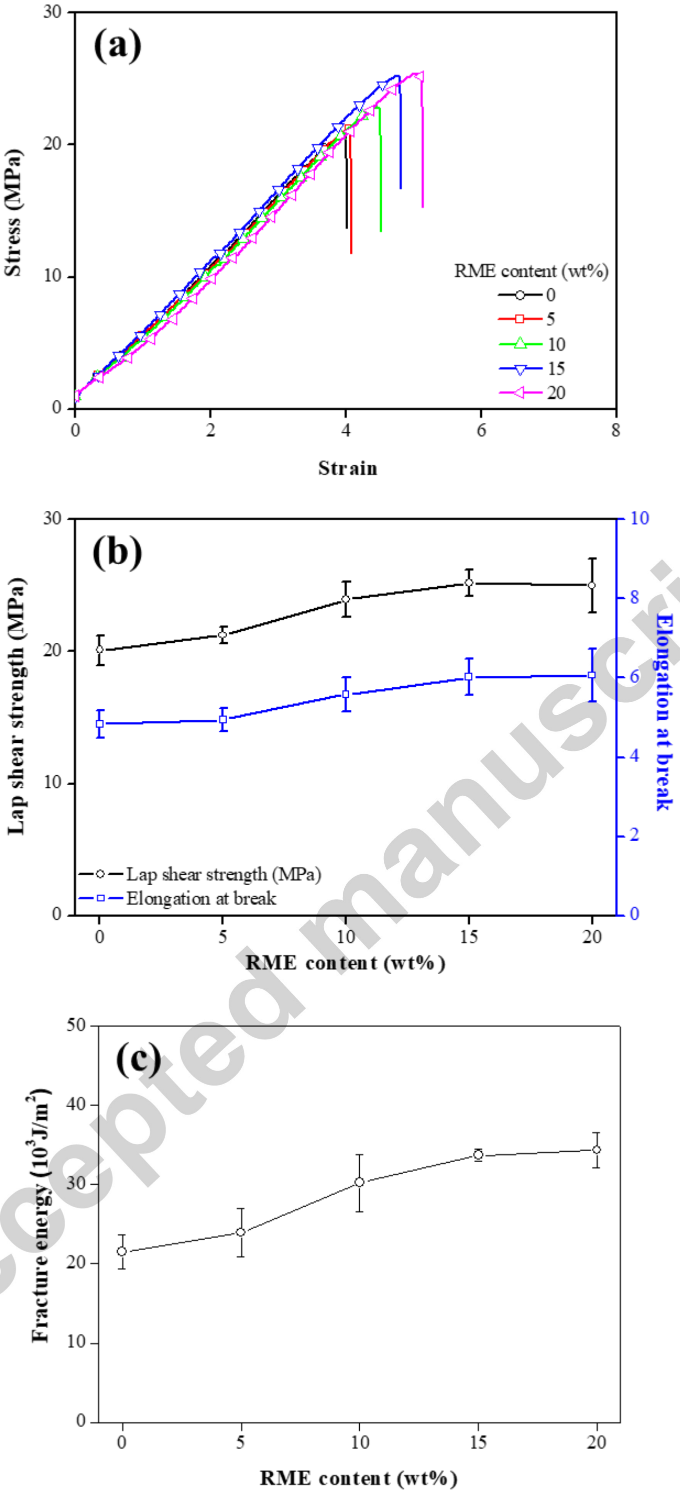
(a)
Stress (MPa)
Strain
30
20
10
0
0
2
4
6
8
RME content (wt%)
0
5
10
15
20
(b)
Lap shear strength (MPa)
Elongation at break
RME content (wt%)
30
20
10
0
10
8
6
4
2
0
0
5
10
15
20
Lap shear strength (MPa)
Elongation at break
(c)
Fracture energy (10³J/m²)
RME content (wt%)
50
40
30
20
10
0
0
5
10
15
20

Fig. 7

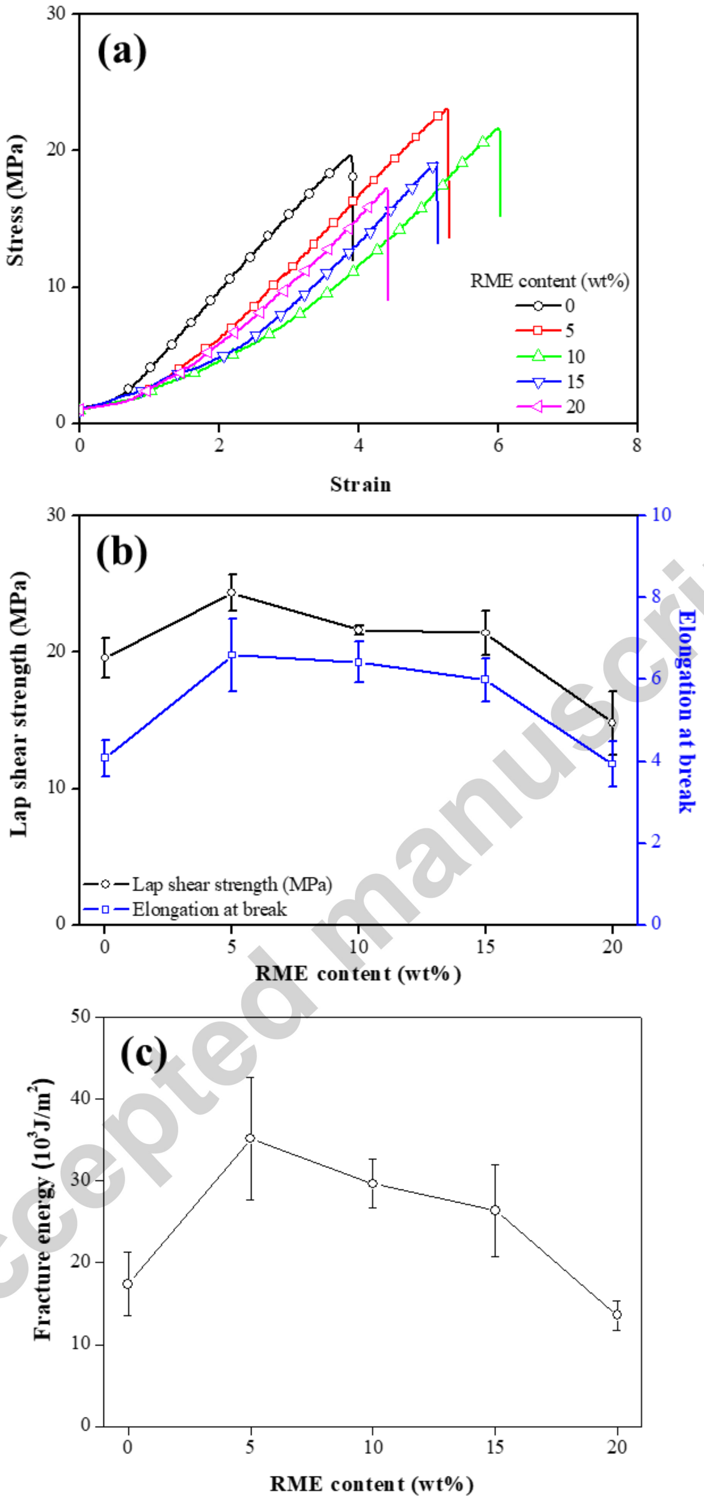
(a)
Stress (MPa)
Strain
0
10
20
30
0
2
4
6
8
RME content (wt%)
0
5
10
15
20
(b)
Lap shear strength (MPa)
Elongation at break
RME content (wt%)
0
10
20
30
0
2
4
6
8
10
0
5
10
15
20
Lap shear strength (MPa)
Elongation at break
(c)
Fracture energy (10^3J/m^2)
RME content (wt%)
0
10
20
30
40
50
0
5
10
15
20

Fig. 8

Table 1. Materials for epoxy composites

Materials	Composition	Abbreviation	Equivalent weight (g)
Epoxy (Base resin)	Bisphenol-A diglycidyl ether type	BPA-E	187
	Silane-modified epoxy (Silane 2 wt%)	SME	205
	Rubber-modified epoxy (Rubber 29 wt%)	RME	300
Amine (Curing agent)	Dicyandiamide	CA-1	30
	Substituted urea	CA-2	3
Chemical foaming agent	Sodium bicarbonate	CFA	-
Filler	Calcium carbonate	-	-

Table 2. Composition of epoxy and epoxy-foam adhesives

Sample		SME (wt%)	RME (wt%)	CA-1 (wt%)	CA-2 (wt%)	Filler (wt%)
Epoxy adhesives	RME 00	40	0	7.92	0.64	35.44
	RME 05	35	5	7.88	0.61	35.52
	RME 10	30	10	7.55	0.60	33.45
	RME 15	25	15	7.24	0.59	36.17
	RME 20	20	20	7.21	0.56	36.24
Epoxy-foam adhesives	RME 00/Foam	40	0	7.92	0.64	33.04
	RME 05/Foam	35	5	7.88	0.61	33.12
	RME 10/Foam	30	10	7.55	0.60	33.45
	RME 15/Foam	25	15	7.24	0.59	33.77
	RME 20/Foam	20	20	7.21	0.56	33.84

* BPA-E (wt%) = 16

* CFA (wt%): for epoxy adhesives = 0; for epoxy-foam adhesives = 2.40

Table 3. Porosity and expansion ratio of epoxy-foam adhesives

Sample	Porosity (%)	Expansion ratio (%)
RME 00/Foam	60.7	254.6
RME 05/Foam	59.3	245.7
RME 10/Foam	69.6	329.1
RME 15/Foam	70.7	340.8
RME 20/Foam	71.0	344.4