



# Anhydride-cured epoxy resin reinforcing with citric acid-modified cellulose

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## ABSTRACT

Herein, improvement of the mechanical properties of epoxy resin by compositing with citric acid modified cellulose (CAC) was reported. CAC were prepared from carboxyl functionalization with citric acid to increase the adhesion between cellulose and epoxy resin. The epoxy resin composites were prepared using 2,2-bis (4-glycidylphenoxy) propane (BADGE) as component, 4-methylcyclohexane-1,2-dicarboxylic anhydride (MHHPA) as curing agent, and cellulose or CAC as filler. The tensile strength of cellulose/epoxy resin composites were decreased with the content of cellulose increased. On the other hand, the tensile strength of CAC/epoxy resin composites were effectively increased with the content of CAC increased. Moreover, compared with pure epoxy resins and cellulose/epoxy resin composites, the Young's modulus and the toughness of CAC/epoxy resin composites significantly increased with the presence of 10 wt% CAC. SEM images showed that cellulose agglomerated in epoxy resins, in contrast, CAC dispersed uniformly in epoxy resins, determined that the adhesion between CAC and epoxy resins were improved after introduced carboxyl groups to cellulose lead to the mechanical properties improved. CAC was also used to partly replace MHHPA to decrease the usage of toxic curing agent, and the mechanical properties of CAC/epoxy resin composites increased with lower MHHPA content. These results indicated that CAC can partially take place of the conventional curing agent in composite preparation, which may further decrease the production cost and improve the mechanical properties of product.

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## 1. Introduction

Epoxy resins are among the most versatile thermoset polymers, and use as matrixes for high strength composites, corrosion resistant coatings, structural adhesives, such as electronic materials and wind turbines materials, printed circuit boards [1–3]. Bisphenol-A is a generic precursor of epoxy resins due to its high abilities to impart desirable physical and thermal properties [1]. However, its brittleness inhibits further application of the epoxy resins to various industry. Anhydride is one of the general curing agent used to cure epoxy resins with highly cross-linking and three-dimensional network [4,5]. Compared with epoxy resins cured by other curing agents, the anhydride-cure epoxy resins possess lower cure exothermal and smaller cure shrinkage. Moreover, the viscosity of anhydride-cured epoxy resins can be reduced dramatically with the ratio of anhydride increased [2]. This feature makes anhydride-cured epoxy resins suitable for use as matrix in

composites fabrication. Therefore, anhydride-cured epoxy resins have received much attention in the manufacture of epoxy resin composites.

Recently, nanomaterials [3,6,7], liquid-derived resin [8], core-shell nanoparticles [9] have been developed to improve the toughness of epoxy resins. Shibata et al. reported a bio-based epoxy resins composited with chitin- and chitosan-nanofibers. Compared with the original bio-based epoxy resin, bio-based epoxy resins composited with chitin- and chitosan-nanofibers showed higher toughness and modulus. The improvement of toughness and modulus was attained by the fiber-reinforcement effect of chitin- and chitosan-nanofibers [3]. Maiorana et al. reported bio-based epoxy resin toughening with cashew nut shell liquid-derived resin. With the combinations of diglycidyl ether diphenolate methyl ester, a rigid high-viscosity bio-based epoxy resin and a flexible lower viscosity epoxy resin from cashew nut shell liquid, resin viscosity was controlled and important improvements were realized in cured epoxy resin toughness relative to the neat resins [8]. Although these studies improve the toughness of the epoxy resins, many of them adversely affect the glass transition

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temperature ( $T_g$ ) and tensile strength of the cured epoxy resins. Thus, increasing the toughness of epoxy resins with maintaining its mechanical strength and other properties is still a big challenge.

Several studies reported that using cellulose as an excellent filler for composites due to its superior mechanical properties, low density, biodegradability, renewability and low cost [10–12]. Therefore, cellulose is expected to offer significant potential in generating new materials when well dispersed in polymers. However, due to the hydrophilic surface of cellulose, it is hard to be dispersed in resins. Therefore, easy and effective surface modification method for cellulose has been studied. Recently, we reported an effective water-based method to render the cellulose surface with high carboxyl content through the esterification of hydroxyl groups with citric acid in a solid phase reaction without the use of noxious solvents [13]. The modified cellulose was then hydrophobilized by grafting magnesium stearate to the surface. Consequently, the flexural properties of PP composites reinforced by the hydrophobilized cellulose fillers were greatly improved compared to those of composites containing hydrophilic cellulose and pure PP resin. These results considered that modified cellulose has immense potential as a sustainable and cost-effective reinforcing filler for resins.

In this study, to improve toughness of epoxy resins with maintaining its mechanical and thermal properties for using as a hyper branched polymer, cellulose modified with citric acid (CAC) was synthesized and used as a filler. CAC with high hydrophobic properties is expected to improve the dispersion in the epoxy resin composite, and use as a curing agent for epoxy-anhydride system. The effects of adding CAC as a filler on the thermal, mechanical and thermomechanical properties of epoxy resin composites were investigated. Moreover, the effects of the carboxyl groups on the dispersibility in epoxy resin were investigated by compared the CAC/epoxy resin composites with cellulose/epoxy resin composites.

## 2. Material and methods

### 2.1. Materials

2,2-bis(4-glycidyloxyphenyl) propane diglyceryl ether (BADGE), 4-methylcyclohexane-1,2-dicarboxylic anhydride (MHHPA) and citric acid were purchased from Tokyo Chemical Industry (Tokyo, Japan). Acetone, methanol and 0.1 mol/L sodium hydroxide (NaOH) were purchased from Fuji Film Wako Industry (Tokyo, Japan). The cellulose were purchased from Nacalai Tesuque Industry (Kyoto, Japan). All the reagents were used as received without further purification.

### 2.2. Modification and characterization of cellulose

CAC was prepared based on the conventional method [13–16]. Cellulose was dispersed in deionized-water (DI water) with concentration of 0.2 wt/vol%, then 0.1 mol/L NaOH was added into the dispersion with concentration of 0.001 vol%. The dispersion was stirred with magnetic stirring at room temperature for 1 h. Citric acid (3 times equivalent of cellulose) was then added to the

dispersion with magnetic stirring, and the mixture was reacted in a high temperature chamber (ST-110, ESPEC CORP., Osaka, Japan) at 145 °C for 7 h (Fig. 1). Condensation reaction of hydroxyl groups on cellulose and carboxyl groups on citric acid was achieved while evaporating water at 145 °C, and yellow powder obtained. The obtained powder was washed with DI water until the pH changed to 7 to 8, then washed by acetone (200 ml) and methanol (300 ml), continuously, to remove unreacted citric acid. The final product of CAC was dried in vacuum at room temperature. To fibrillate cellulose to nanofiber, CAC dispersion was prepared with DI water with concentration of 0.015 wt/vol%, and fibrillated 10 times using ultra-fine friction grinder (Supermasscolloider, MKCA6-2J, MASUKO SANGYO CO.,LTD., Saitama, Japan), subsequently. The fibrillated CAC dispersion was then freeze-dried to obtain fibrillated CAC powder.

The introduced carboxyl groups were confirmed by Nicolet iS 5 Spectrometer with an iD5 ATR instrument (ATR-IR; Thermo Scientific, MA, USA) at room temperature with the wavenumber range of 450–4000  $\text{cm}^{-1}$ . No baseline correction or other data manipulation techniques were employed. The carboxyl group content of the cellulose was evaluated via conductometric titration (LAQUA F-74, HORIBA, Ltd., Kyoto, Japan) using 0.05 mol/L NaOH. Thermogravimetric and differential thermal analysis (TG/DTA) of cellulose, CAC were performed using a simultaneous thermogravimetric analyser (STA7200RV, Hitachi High-Technologies Co., Tokyo, Japan). The samples weighted approximately 8 mg and were scanned from 100 °C to 500 °C under nitrogen atmosphere with heating rate of 10 °C/min. The fractured surfaces of epoxy resin composites were observed through scanning electron microscopy (SEM; SU8000, Hitachi High-Technologies Co., Tokyo, Japan), operating at 5.0 kV with 3 nm platinum sputter coating.

### 2.3. Preparation and characterization of CAC/epoxy resin composites

Epoxy resins were prepared based on the conventional method (Scheme 1) [17–20]. To prepare CAC/epoxy resin composite, CAC was mixed with BAGDE with contents of 5, 7, 10, 15 and 20 wt% with magnetic stirring at room temperature for 3 h. Then, anhydride curing agent, MHHPA, was added to the mixture with same molar equivalent to BAGDE. The mixture was casted into molds and cured by heating at 80 °C for 3 h and 150 °C for 3hrs. Pure epoxy resin and unmodified cellulose/epoxy resin composites were also prepared.

CAC/epoxy resin composite was also prepared with lower curing agent content. CAC was mixed with BAGDE with contents 10 wt% with magnetic stirring at room temperature for 3 h. Then, anhydride curing agent, MHHPA, was added to the mixture with 0.9 molar equivalent to BAGDE. The mixture was casted into molds and cured by heating at 80 °C for 3 h and 150 °C for 3hrs.

Tensile properties of epoxy resin composites were measured by a table-top material tester (EZ Graph, Shimadzu Corporation, Kyoto, Japan), the compression was also measured at room temperature and the measurement was performed following JIS K 7181 (ISO 604) regulations. The compressing speed is 5 mm/min, the size of the film is 15 mm of length and 1 mm of diameter. The dynamic mechanical properties of epoxy resin composites were performed using dynamic mechanical analysis (DMA; TA Q800, TA Instruments Japan Inc., Tokyo, Japan). A dual cantilever mode with an amplitude of 10  $\mu\text{m}$  was used to determine the storage modulus ( $E'$ ) and glass transition temperature from 0 °C to 200 °C with scanning rate of 2 °C/min. The thermal properties of epoxy resin composites were performed using differential scanning calorimetry (DSC; EXSTAR 6000, Seiko Instruments Inc., Chiba, Japan) with Tzero aluminum pans (TA Instruments Japan Inc., Tokyo, Japan) from 40 °C to 200 under nitrogen atmosphere with scanning rate of 10 °C/min.

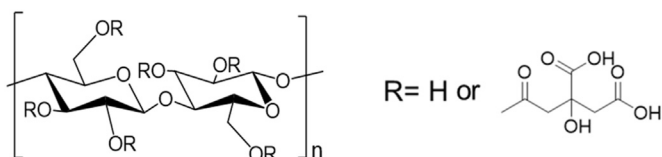
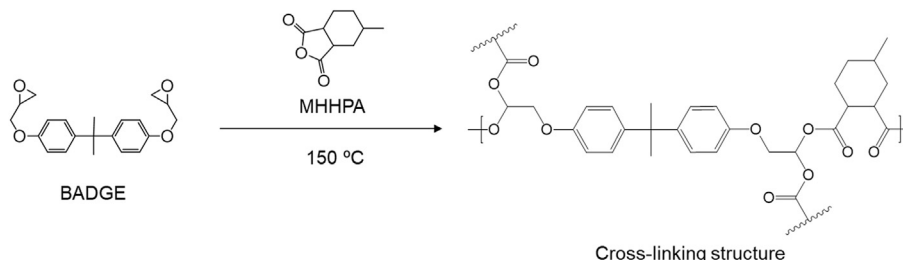


Fig. 1. Structure of citric acid modified cellulose.



**Scheme 1.** Curing reaction of the 2,2-bis(4-glycidyloxyphenyl) propane (BADGE) by 4-methylcyclohexane-1,2-dicarboxylic anhydride (MHHPA).

### 3. Results

#### 3.1. Modification and characterization of cellulose

The surface modification of cellulose was confirmed by ATR-IR. Compared with the characteristic spectrum of cellulose, CAC and fibrillated CAC showed a new absorption peaks around  $1720\text{ cm}^{-1}$  assigned to  $-\text{COO}$  stretching vibration (data not shown). The carboxyl group content of CAC was determined by electric conductivity titration method. The carboxyl groups were introduced to the cellulose surface with a concentration of  $2.1\text{ mmol/g}$ . These results demonstrated that carboxyl groups were introduced successfully to the cellulose.

Decomposition temperature of cellulose and CAC was measured. It was showed that the decomposition temperature of cellulose started at  $263\text{ }^\circ\text{C}$ , and that of CAC started at  $220\text{ }^\circ\text{C}$ . After modified cellulose by citric acid, the stable hydroxyl groups of cellulose are replaced by carboxyl groups, lead the decomposition temperature became lower. Addition, the preparation temperature of epoxy resin is  $150\text{ }^\circ\text{C}$ , therefore, both of cellulose and CAC will not decompose during the curing process of epoxy resin.

When the CAC was composited with resins as a filler, the hydrophobicity and reactive groups of CAC is important, addition, the morphology of the filler is also an important factor. As shown in Fig. 2a and Fig. 2b, the morphologies of cellulose and CAC were both flat, and the diameters of cellulose and CAC fibers are  $17.3 \pm 6.4\text{ }\mu\text{m}$  and  $15.8 \pm 4.6\text{ }\mu\text{m}$ , respectively. There is no significant differences between untreated cellulose and CAC. After CAC fibrillated by Supermasscolloider, the fibers became smaller significantly and the diameters greatly decreased to  $1.8 \pm 1.0\text{ }\mu\text{m}$  (Fig. 2c). Some studies reported that by decreasing the size of the filler, dispersibility of filler to matrix became higher and the mechanical properties of the composites improved [21–23]. Therefore, the fibrillated CAC was used as a filler to prepare the CAC/epoxy resin composites in subsequent experiments.

#### 3.2. Mechanical properties of CAC/epoxy resin composites

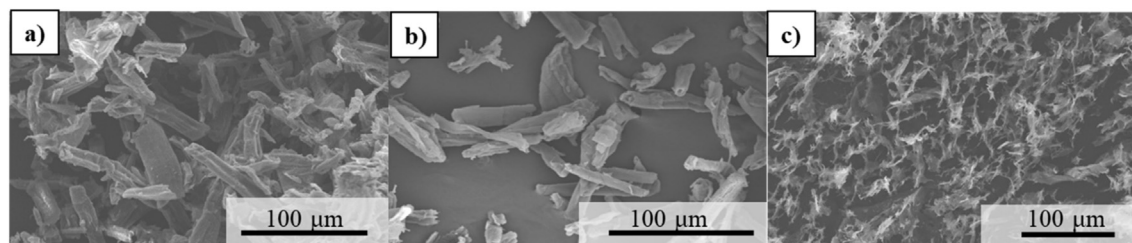
The mechanical properties of the prepared pure epoxy resin, cellulose/epoxy resin composites and CAC/epoxy resin composites

with different contents of cellulose or CAC were determined by uniaxial tensile tests, and the results are shown in Fig. 3. The strain-stress curves show a small deformation at initial elastic region and a large region of plastic deformation until failure (Fig. 3a). Compared to pure epoxy resin and 10 wt% cellulose/epoxy resin composites, 10 wt% CAC/epoxy resin composites showed higher tensile strength and tensile strain. The maximum strength of pure epoxy resin and composites were summarized in Fig. 3b and Table 1. The maximum strength of pure epoxy resins was  $59.7\text{ MPa}$ , and that of cellulose/epoxy resin composites were decreased to  $52.3\text{ MPa}$  with the content of cellulose increased. In contrast, the maximum strength of CAC/epoxy resin composites increased significantly with the content of CAC increased. When the content of CAC was 10 wt%, the maximum strength of the CAC/epoxy resin composite was increased to  $76.2\text{ MPa}$ .

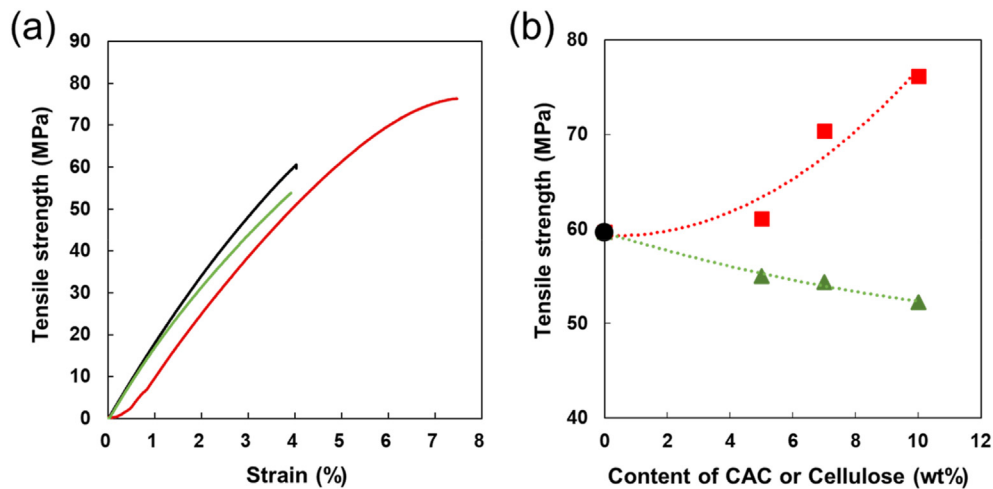
Fig. 5 shows the optical microscopy images of the fracture surfaces of pure epoxy resin, 10 wt% cellulose/epoxy resin composite and 10 wt% CAC/epoxy resin composite after tensile test. The fracture surface of the pure epoxy resin is smooth (Fig. 4a), indicating that pure epoxy resin is brittle and without ductility. In the contrast, the fracture surfaces of the cellulose/epoxy resin composite and CAC/epoxy resin composite are rough (Fig. 4b and c) and both cellulose and CAC showed similar short rod-like features (Fig. 4d and e). The cellulose was agglomerated in the composite lead the tensile strength of the cellulose/epoxy resin composite decreased. In contrast, CAC was dispersed homogeneously in the composite, indicating no phase separated occurred lead the tensile strength of the CAC/epoxy resin composite increased.

Fig. 5a shows the results of compression test of pure epoxy resin and each composites contained 10 wt% cellulose or CAC. Compared to pure epoxy resin and cellulose/epoxy resin composite, the compression stress of CAC/epoxy resin composite significantly increased. The Young's modulus and toughness of pure epoxy resin, 10 wt% cellulose/epoxy resin composite and 10 wt% CAC/epoxy resin composite are summarized in Table 2. The Young's modulus of pure epoxy resin is  $10.7\text{ MPa}$ , and.

CAC/epoxy resin composite shows higher Young's modulus ( $12.1\text{ MPa}$ ) than pure epoxy resin. However, the Young's modulus of the cellulose/epoxy resin composites clearly decreased to  $6.6\text{ MPa}$ . Similarly, the toughness of pure epoxy resin is  $39.3\text{ MJ/m}^3$ , and that



**Fig. 2.** SEM of the a) cellulose, b) CAC, c) fibrillated CAC. The average diameter of cellulose, CAC and fibrillated CAC is  $17.3 \pm 6.4\text{ }\mu\text{m}$ ,  $15.8 \pm 4.6\text{ }\mu\text{m}$  and  $1.8 \pm 1.0\text{ }\mu\text{m}$ , respectively.

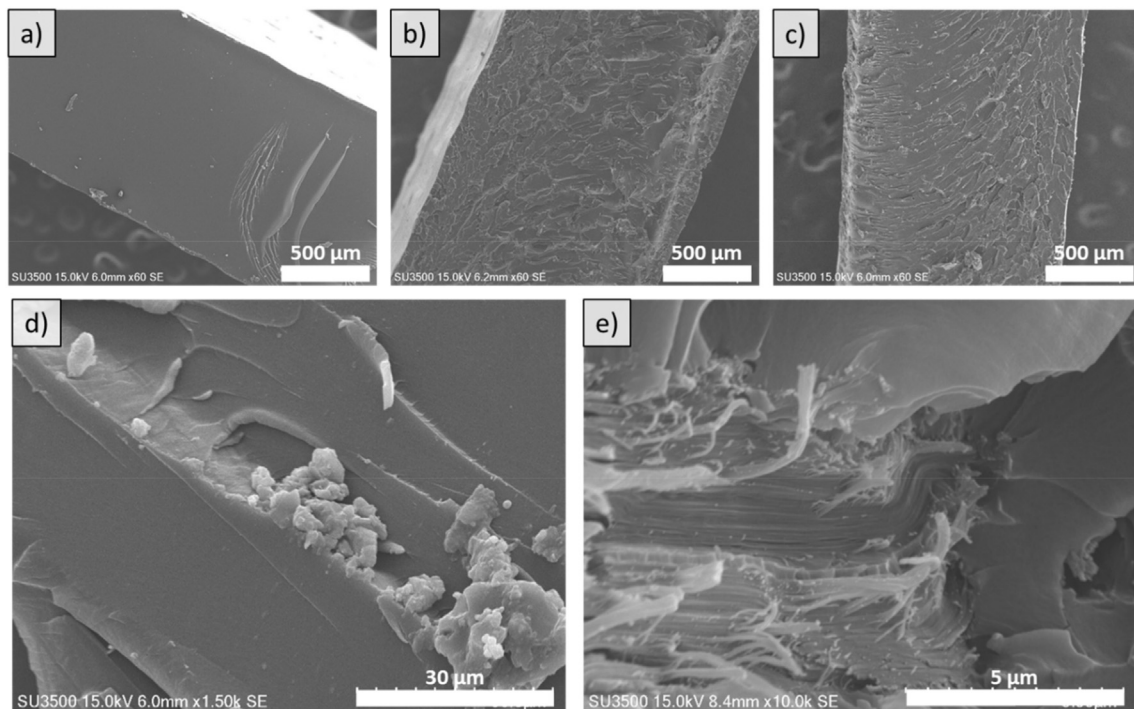


**Fig. 3.** a) Strain-strength curves of pure epoxy resin (black), 10 wt% cellulose/epoxy resin composite (green) and 10 wt% CAC/epoxy resin composite (red), b) maximum tensile strength of pure epoxy resins (●) and epoxy resins compounded with different contents of CAC (■) and cellulose (▲). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 1**

Maximum strength of pure epoxy resin, cellulose/epoxy resins, CAC/epoxy resins by tensile test with different cellulose or CAC content.

	Pure epoxy resin	cellulose/epoxy resins (wt %)			CAC/epoxy resins (wt %)		
		5	7	10	5	7	10
Tensile strength (MPa)	59.7 ± 4.0	55.1 ± 2.9	54.4 ± 3.7	52.3 ± 2.6	61.1 ± 6.9	70.4 ± 3.6	76.2 ± 5.1



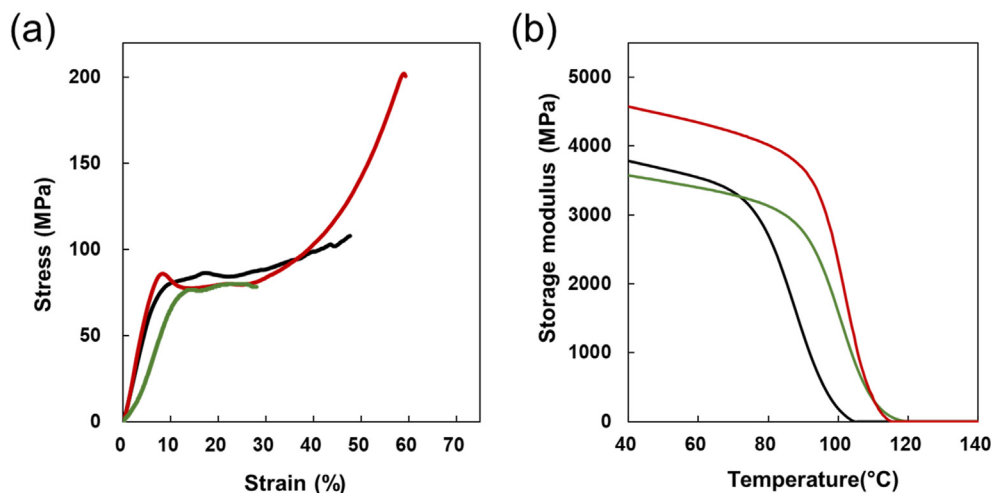
**Fig. 4.** Optical microscopy images of the fracture surfaces observed by SEM. a) pure epoxy resin, b, d) 10 wt% cellulose/epoxy resin composite and c, e) 10 wt% CAC/epoxy resin composite.

of 10 wt% CAC/epoxy resin composite increased to 58.3 MJ/m<sup>3</sup>. In contrast, the toughness of the 10 wt% cellulose/epoxy resin composites decreased to 16.9 MJ/m<sup>3</sup>. Consequently, CAC/epoxy resin composites with the optimized mechanical properties showed

obvious enhancement in both strength and toughness, compared to pure epoxy resins and cellulose/epoxy resin composites.

Fig. 5b shows the storage modulus of pure epoxy resin, 10 wt% cellulose/epoxy resin composite and 10 wt% CAC/epoxy resin





**Fig. 5.** (a) Strain-stress curve, determined by compression test and (b) storage modulus, determined by DMA of pure epoxy resin (black), 10 wt% cellulose/epoxy resin composite (green) and 10 wt% CAC/epoxy resin composite (red). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**

Young's modulus and toughness of pure epoxy, 10 wt% cellulose/epoxy resin composite, 10 wt% CAC/epoxy resin composite.

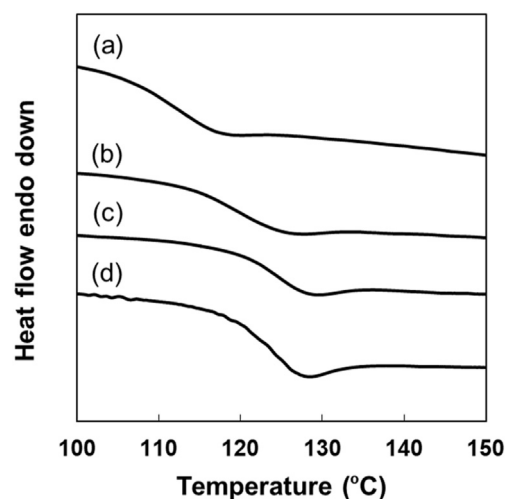
Sample	Young's modulus (MPa)	Toughness (MJ/m <sup>3</sup> )
Pure epoxy resin	10.7 ± 0.7	39.3 ± 9.5
10 wt% cellulose/epoxy resin	6.6 ± 0.9	16.9 ± 2.6
10 wt% CAC/epoxy resin	12.1 ± 1.5	58.3 ± 3.0

**Table 3**

Storage modulus ( $E'$ ) at 50 °C and glass transition temperature ( $T_g$ ) of pure epoxy resin, 10 wt% cellulose/epoxy resin composite, 10 wt% CAC/epoxy resin composite.

Sample	$E'$ at 50 °C (GPa)	$T_g$ (°C)
Pure epoxy resin	3.66 ± 0.16	105
10 wt% cellulose/epoxy resin	3.49 ± 0.14	106
10 wt% CAC/epoxy resin	4.43 ± 0.50	116

composite, measured by DMA. The storage modulus at 50 °C of pure epoxy resin and each composites contained 10 wt% cellulose or CAC are summarized in Table 3. The storage modulus of pure epoxy resins is 3.66 GPa, and that of CAC/epoxy resin composites increase to 4.43 GPa. In contrast, the storage modulus of cellulose/epoxy resin composites decreases slightly to 3.49 GPa. To evaluate the interface between filler (cellulose or CAC) and epoxy resin, glass transition temperature ( $T_g$ ) determined by DMA is a significantly important factor [24]. Both of pure epoxy resin and cellulose/epoxy resin composite showed a value close to 105 °C. In contrast, the storage modulus of CAC/epoxy resin composite was 116 °C, which was significantly higher than that of pure epoxy resin and cellulose/epoxy resin composite. These results indicated that the presence of the carboxyl groups on modified CAC lead an increment of the affinity between filler and the epoxy resin to improve the mechanical properties of composites. The effect of the content of CAC to epoxy resin was confirmed by DSC. As shown in Fig. 6, the  $T_g$  of the CAC/epoxy resin composite is higher than that of pure epoxy resin. Moreover,  $T_g$  increased slightly with the content of CAC increased, indicating that the incorporation of CAC into epoxy resin had a positive influence on the curing reaction of epoxy resin system. Therefore, CAC contains abundant terminal carboxyl groups can act as a hardener and react with the epoxy groups. On the other hand, the carboxyl groups could result in an acceleration of the curing process for epoxy-anhydride system.



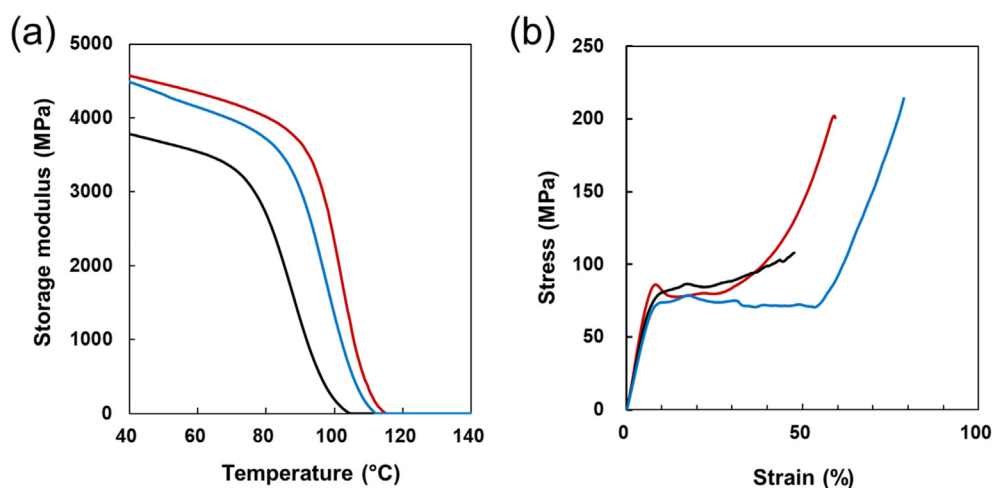
**Fig. 6.** DSC curves of (a) pure epoxy resin, CAC/epoxy resin composites with CAC content (b) 5 wt%, (c) 7 wt%, (d) 10 wt%.

### 3.3. Mechanical properties of CAC/epoxy resin composites

Fig. 7a shows the storage modulus of pure epoxy resin and 10 wt% CAC/epoxy resin composites with different content of MHPA, and the storage modulus at 50 °C are summarized in Table 4. Even.

MHPA/BADGE molar ratio was decreased to 0.9, 10 wt% CAC/epoxy resin composites showed higher storage modulus (4.36 GPa) at 50 °C than pure epoxy resin (3.66 GPa), and was similar with that of 10 wt% CAC/epoxy resin composites with MHPA/BADGE molar ratio of 1 (4.43 GPa). As mentioned in the previous paragraph, the significant improvement of storage modulus attributed to the well dispersed CAC into epoxy resin, lead the reinforcement of CAC/epoxy resin composites.

Fig. 7b shows the strength-strain curves of pure epoxy resins, 10 wt% CAC/epoxy resin composites with MHPA/BADGE molar ratio of 1, and 10 wt% CAC/epoxy resin composites with MHPA/BADGE molar ratio of 0.9, determined by compression test. After reduced MHPA/BADGE molar ratio to 0.9, the compression stress increased to 217 MPa, and the compression strain was higher than pure epoxy resin and 10 wt% CAC/epoxy resin composites with MHPA/BADGE molar ratio of 1. The toughness of each samples were summarized in



**Fig. 7.** (a) Storage modulus, determined by DMA and (b) strain-stress curve, determined by compression test of pure epoxy resin (black), 10 wt% CAC/epoxy resin composite with MHHPA/BADGE molar ratio of 1 (red) and 10 wt% CAC/epoxy resin composite with MHHPA/BADGE molar ratio of 0.9 (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 4**

Toughness and Storage modulus Storage modulus ( $E'$ ) at 50 °C of pure epoxy resin, 10 wt% CAC/epoxy resin composites with different MHHPA content.

	Pure epoxy resin	MHHPA/BADGE	
		1	0.9
Toughness ( $\text{MJ}/\text{m}^3$ ) <sup>a</sup>	39.3 ± 9.5	58.3 ± 3.0	69.7 ± 7.6
$E'$ at 50 °C (GPa) <sup>b</sup>	3.66 ± 0.16	4.43 ± 0.50	4.36 ± 0.36

<sup>a</sup> Determined by compression test.

<sup>b</sup> Determined by DMA.

**Table 4.** The toughness of 10 wt% CAC/epoxy resin composite with MHHPA/BADGE molar ratio of 0.9 increased to 69.7  $\text{MJ}/\text{m}^3$ , which was higher than that of 10 wt% CAC/epoxy resin composite with MHHPA/BADGE molar ratio of 1 (58.3  $\text{MJ}/\text{m}^3$ ). These results indicated that the decrease of the content of MHHPA make the reactivity between CAC and epoxy groups became higher, and filler-to-matrix contact area became larger to improve the mechanical properties.

#### 4. Conclusion

An approach to introduce carboxyl groups onto the cellulose surface by citric acid was presented. The obtained CAC was composited with anhydride cured epoxy resins as filler. Owing to the terminal carboxyl group of CAC, CAC could slightly promote the curing process and avoid phase separation. Compared with pure epoxy resins and cellulose/epoxy resin composites, CAC/epoxy resin composites significantly improved the tensile strength and compression stress with enhancements in maximum strength and the elongation at break. Moreover, CAC/epoxy resin composites showed higher storage modulus and  $T_g$  than pure epoxy resins and cellulose/epoxy resin composites. The enhancements in toughness and strength are because of the incorporation of carboxyl groups having highly reactivity with epoxy resins. After replace 10 wt% MHHPA to CAC, compressing stress, toughness and storage modulus were increased, demonstrated that CAC can not only be used as a filler, but also acted as a curing agent in the epoxy-anhydride system.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRediT authorship contribution statement

**Yu-I Hsu:** Writing - original draft, Writing - review & editing, Validation. **Lulu Huang:** Data curation, Writing - original draft. **Taka-Aki Asoh:** Visualization, Supervision, Writing - review & editing. **Hiroshi Uyama:** Conceptualization, Methodology, Supervision, Writing - review & editing.

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#### References

- [1] C.T. Desire, A. Khodabandeh, T.L. Schiller, R. Wilson, R.D. Arrua, S.A. Bon, E.F. Hilder, Preparation of highly interconnected hydrophilic polymers from emulsion templates with improved mechanical properties, *Eur. Polym. J.* 102 (2018) 56–67.
- [2] G. Sun, H. Sun, Y. Liu, B. Zhao, N. Zhu, K. Hu, Comparative study on the curing kinetics and mechanism of a lignin-based-epoxy/anhydride resin system, *Polymer* 48 (1) (2007) 330–337.
- [3] M. Shibata, J. Fujigasaki, M. Enjoji, A. Shibita, N. Teramoto, S. Ifuku, Amino acid-cured bio-based epoxy resins and their biocomposites with chitin-and chitosan-nanofibers, *Eur. Polym. J.* 98 (2018) 216–225.
- [4] J. Rocks, G.A. George, F. Vohwinkel, Curing kinetics and thermomechanical behaviour of co-anhydride cured aminoglycidyl epoxy resins, *Polym. Int.* 52 (11) (2003) 1758–1766.
- [5] L. Zhang, J. Liu, W. Nie, K. Wang, Y. Wang, X. Yang, T. Tang, Degradation of anhydride-cured epoxy resin using simultaneously recyclable solvent and organic base catalyst, *J. Mater. Cycles Waste Manag.* 20 (1) (2018) 568–577.
- [6] J. Kim, J. Kim, S. Song, S. Zhang, J. Cha, K. Kim, H. Yoon, Y. Jung, K.-W. Paik, S. Jeon, Strength dependence of epoxy composites on the average filler size of non-oxidized graphene flake, *Carbon* 113 (2017) 379–386.
- [7] J.M.L. Reis, R.P. Lima, S.D. Vidal, Effect of rate and temperature on the mechanical properties of epoxy BADGE reinforced with carbon nanotubes, *Compos. Struct.* 202 (2018) 89–94.
- [8] A. Maiorana, L. Ren, G. Lo Re, S. Spinella, C.Y. Ryu, P. Dubois, R.A. Gross, Bio-based epoxy resin toughening with cashew nut shell liquid-derived resin, *Green Mater.* 3 (3) (2015) 80–92.
- [9] X. He, F. Luzi, W. Yang, Z. Xiao, L. Torre, Y. Xie, D. Puglia, Citric acid as green modifier for tuned hydrophilicity of surface modified cellulose and lignin nanoparticles, *ACS Sustain. Chem. Eng.* 6 (8) (2018) 9966–9978.
- [10] V. Heshmati, M.R. Kamal, B.D. Favis, Cellulose nanocrystal in poly (lactic acid)/polyamide11 blends: preparation, morphology and co-continuity, *Eur. Polym. J.* 98 (2018) 11–20.
- [11] J.M. Buffa, G. Mondragon, M.A. Corcuera, A. Eceiza, V. Mucci, M.I. Aranguren, Physical and mechanical properties of a vegetable oil based nanocomposite, *Eur. Polym. J.* 98 (2018) 116–124.
- [12] M.C.G. Saborío, S. Lanzalaco, G. Fabregat, J. Puiggalí, F. Estrany, C. Alemán, Flexible electrodes for supercapacitors based on the supramolecular assembly

- of biohydrogel and conducting polymer, *J. Phys. Chem. C* 122 (2) (2018) 1078–1090.
- [13] X. Cui, T. Honda, T.-A. Asoh, H. Uyama, Cellulose modified by citric acid reinforced polypropylene resin as fillers, *Carbohydr. Polym.* 230 (2020) 115662.
- [14] N.J. Venkatesha, S. Ramesh, Citric acid-assisted synthesis of nanoparticle copper catalyst supported on an oxide system for the reduction of furfural to furfuryl alcohol in the vapor phase, *Ind. Eng. Chem. Res.* 57 (5) (2018) 1506–1515.
- [15] Y.L. Wu, S. Xu, T. Wang, C.F. Wang, Enhanced metal ion rejection by a low-pressure microfiltration system using cellulose filter papers modified with citric acid, *ACS Appl. Mater. Interfaces* 10 (38) (2018) 32736–32746.
- [16] B.A. Noordover, R. Duchateau, R.A. van Benthem, W. Ming, C.E. Koning, Enhancing the functionality of biobased polyester coating resins through modification with citric acid, *Biomacromolecules* 8 (12) (2007) 3860–3870.
- [17] H.K. Jang, B.M. Jung, U.H. Choi, S.B. Lee, Ion conduction and viscoelastic response of epoxy-based solid polymer electrolytes containing solvating plastic crystal plasticizer, *Macromol. Chem. Phys.* 219 (6) (2018) 1700514.
- [18] A. Maiorana, L. Yue, I. Manas-Zloczower, R. Gross, Structure–property relationships of a bio-based reactive diluent in a bio-based epoxy resin, *J. Appl. Polym. Sci.* 133 (45) (2016).
- [19] H.L. Tyan, Y.C. Liu, K.H. Wei, Enhancement of imidization of poly (amic acid) through forming poly (amic acid)/organoclay nanocomposites, *Polymer* 40 (17) (1999) 4877–4886.
- [20] T.L. Li, S.L.C. Hsu, Enhanced thermal conductivity of polyimide films via a hybrid of micro- and nano-sized boron nitride, *J. Phys. Chem. B* 114 (20) (2010) 6825–6829.
- [21] M.V. Maffini, B.S. Rubin, C. Sonnenschein, A.M. Soto, Endocrine disruptors and reproductive health: the case of bisphenol-A, *Mol. Cell. Endocrinol.* 254 (2006) 179–186.
- [22] A. Patel, A. Maiorana, L. Yue, R.A. Gross, I. Manas-Zloczower, Curing kinetics of biobased epoxies for tailored applications, *Macromolecules* 49 (15) (2016) 5315–5324.
- [23] A. Maiorana, A.F. Reano, R. Centore, M. Grimaldi, P. Balaguer, F. Allais, R.A. Gross, Structure property relationships of biobased n-alkyl bisferulate epoxy resins, *Green Chem.* 18 (18) (2016) 4961–4973.
- [24] Y. Xie, D. Kohls, I. Noda, D.W. Schaefer, Y.A. Akpalu, Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) nanocomposites with optimal mechanical properties, *Polymer* 50 (19) (2009) 4656–4670.