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Material Design of Citric Acid-Modified Cellulose Composite Polymeric Materials with Both Tough and Sustainable Enhancement by Multiple Noncovalent Bonds

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Abstract

To achieve a carbon circulation society, petroleum-derived resources must be replaced by cellulose and other bioderived resources. Although cellulose serving as a filler enhances the mechanical properties of polymeric materials upon mixing, it remains a challenge to increase the contents of cellulose fillers while maintaining the enhanced mechanical properties. Regarding mechanical properties, polymer composites containing cellulose fillers can usually be improved by adding a small percentage of cellulose filler. Unfortunately, mixing high amounts of cellulose fillers creates brittle polymer composites. Herein, we report polymer composites containing large amounts of citric acid-modified cellulose. Moreover, the polymeric matrices consist of reversible crosslinks formed by β -cyclodextrin and adamantane and secondary linear polymers. By optimizing the ratios of the reversible crosslinks and the secondary linear polymers, we successfully increase the content of cellulose filler to 10%, which is one order of magnitude higher than the conventional cellulose filler contents, maintaining high toughness and Young's modulus values. In addition, utilizing hydrogen bonds is appropriately advantageous in the reinforcing effect of the citric acid-modified cellulose compared to native cellulose.

Introduction

Recently, sustainability has become a popular topic. The depletion of petroleum-based resources and the abnormal climate have threatened our society. To deal with this crisis, achieving a carbon-neutral society is extremely important. Conventional polymeric materials composed of petroleum-based resources have become necessary in our society due to their advantages, such as their low weight, low cost, and versatility. Despite these advantages, we must reduce the usage of these polymeric materials because they are major reasons for the application of petroleum-based resources.

Carbon circulation is an ideal goal that we must achieve to establish a carbon-neutral society. As a first step towards this goal, reducing the number of petroleum-based components is a simple and easily accessible approach. Cellulose is a plant-based and highly abundant biobased filler. Cellulose has been utilized as a filler for polymer composites by mixing into polymeric matrices. These polymer composites containing various types of cellulose, such as cellulose nanofibers^{1–8}, cellulose whiskers^{9–13}, and cellulose nanocrystals^{14–17} have inspired many scientists to study these polymer composites because of their reinforcement effects. However, polymer composites usually contain small proportions of cellulose fillers, except for a few reported composites^{18,19}. The contribution of cellulose fillers to reducing the use of petroleum-based resources is insufficient. It is difficult to maintain Young's modulus and toughness values while increasing the cellulose contents in polymeric composites.

Another approach for reducing the use of petroleum-based resources is toughening polymeric materials to improve their durability. Polymeric materials can be toughened through energy dissipating mechanisms. Diverse concepts based on supramolecular crosslinks (e.g., hydrogen bonds^{20–23}, ionic bonds^{24,25}, coordination bonds²⁶, and host–guest complexation^{27–32});

topological crosslinks^{33–39}; sacrificial bonds^{40–42}; structural homogeneity^{43–45}; and incorporations of secondary penetrating linear polymers into single cross-network (SC) materials have been utilized to prepare tough polymeric materials⁴⁶.

Herein, we aim to satisfy two properties simultaneously: sustainability and toughness (**Figure 1**). Regarding sustainability, we focus on citric-modified cellulose (CAC) as a cellulose filler because of its good dispersion properties^{47,48}. For toughness, we prepare polymer composites consisting of host–guest complexation among β -cyclodextrin (β CD), adamantane (Ad), and penetrating linear polymers. SC materials penetrated by a secondary liner polymer are called SCPs hereafter. By optimizing the ratios of each component, petroleum-based resources can be replaced at a substitution level that is by one order of magnitude greater than that of previous polymer composites.

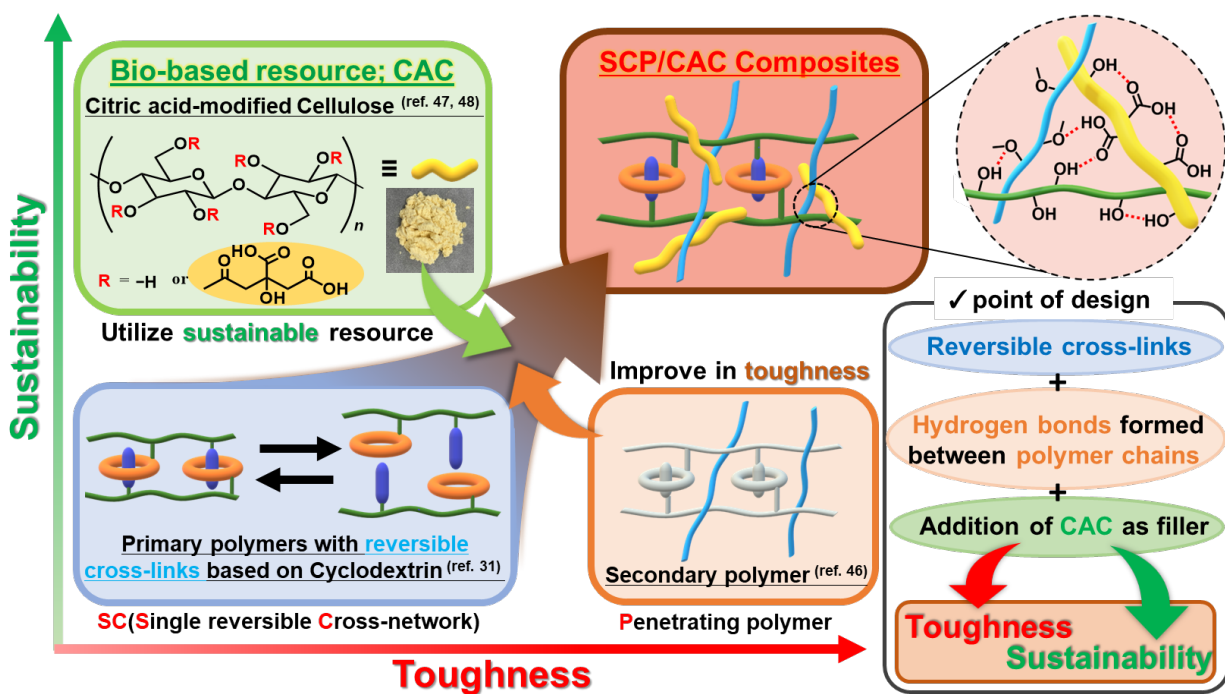


Figure 1. Conceptual design for fabricating polymer composites that simultaneously considers sustainability and mechanical toughness. Reversible host-guest complexes between β CD and Ad, hydrogen bonds in the polymer composites, and CAC represent points of material design.

Materials – preparation of CAC composite materials and their characterization

All the reagents used for the preparation of CAC composite and the conditions of each measurement were described in detail in Supporting Information. CAC was prepared by an esterification reaction between cellulose and citric acid (**Scheme S1 and Figure S1-4**).

Based on the conceptual design shown in **Figure 1** for the polymer composite, we fabricated polymer composites by a two-step polymerization process (SCP(z)/CAC(w); **Figure 2a**, **Scheme S2**, and **Table S1**). Initially, we prepared linear poly(2-hydroxypropyl acrylate) bearing 1 mol% β CD and 1 mol% Ad as reversible crosslinks in dimethyl sulfoxide (DMSO) ($\equiv$ SC(1)) (**Figure 2b**, **Scheme S3**, and **Table S2**). Subsequently, we added 2-methoxyethyl acrylate (MEA) and w wt% of CAC powder into the polymer solution, where w refers to the wt% of CAC against the total amounts of SC(1) and MEA. After mixing them with ball milling, the solution was polymerized to obtain CAC polymer composites. To confirm the impacts of CAC and poly(MEA), we prepared SC(x) without both CAC and poly(MEA), where x refers to the mol% of β CD and Ad. Similarly, we prepared SCP(z) without CAC fed 1 mol% β CD and Ad, where z refers to the mol% of poly(MEA) in SCP(z) (**Figure 2c** and **Table S3**).

First, SCP(z)/CAC(w), SC(x), and SCP(z) were characterized by nuclear magnetic resonance (NMR) measurements to confirm clearly that each component was contained in the obtained materials. ^1H and ^{13}C NMR spectra of SC(0) and SC(1) supported that the desired polymers were obtained (**Figures S5–7**). By comparing the integral values of the proton peaks derived from main chain, β CD, and Ad, we found that SC(1) contained 1.4 and 1.9 mol% β CD and Ad, respectively. Similarly, SCP(20) contained 1.1 and 1.5 mol% β CD and Ad, respectively. (**Figures S8–9**) In addition, we observed the peak derived from poly(MEA) in SCP(20). However, we did not readily detect poly(MEA) from the NMR spectra after adding CAC (**Figures S10–12**).

We performed contact angle measurements as an indirect method to confirm the existence of poly(MEA) in SCP(20)/CAC(*w*)(**Figure S13**). The contact angle of SC(1) was approximately 108°, and it increased to 125° when CAC was added. In contrast, the contact angle of SCP(20)/CAC(10) was approximately 98°, implying more hydrophilicity than SC(1). The contact angle of poly(MEA) was approximately 44°, which indicated hydrophilicity; the hydrophilic component in SCP(20)/CAC(10) seemed to originate from poly(MEA). Based on the contact angle measurements, we concluded that SCP(20)/CAC(*w*) contained poly(MEA), although a quantitative evaluation was missing. From the NMR and contact angle measurements given above, we confirmed that each component was surely incorporated into the prepared materials.

Fourier transform infrared (FT-IR) spectra of the obtained polymer composites were measured and focused on the bands at approximately 3400 cm⁻¹ and 1720 cm⁻¹, corresponding to the OH and C=O groups, respectively, to confirm the formation of hydrogen bonds in polymer composites. The addition of CAC to SC(1) resulted in a blueshift for both bands (**Figure S14a**). When adding poly(MEA) to SC(1), a band at approximately 3400 cm⁻¹ showed a blueshift with increasing amounts of poly(MEA) (**Figure S14b**). In addition, the bands at approximately 1720 cm⁻¹ changed their shapes to that of poly(MEA); Increasing amounts of poly(MEA) in SC decreased the peak intensity at the low wavenumber, which attributed to carbonyl groups formed hydrogen bonds. The addition of poly(MEA) increased the number of carbonyl groups, which are hydrogen bond acceptors. Decreasing the peak intensity at the low wavenumber suggested an increase in the amount of free carbonyl group, which does not form a hydrogen bond. Conversely, when CAC was added to SCP(20) (**Figure S14c**), the round peak at the top of the band at approximately 1720 cm⁻¹ sharpened at low wavenumbers, signifying an increase in hydrogen-bonded carbonyl groups. These peak shift behaviours with increasing the amount of CAC

suggested an increase of hydrogen bonds formed in the polymer composites. In other words, CAC promoted the formation of hydrogen bonds in polymer composites.

Results and discussion

Mechanical properties of polymer composites containing CAC

We investigated the mechanical properties of SC(x) by tensile tests to determine an appropriate number of crosslinks. SC(1) showed the best elongation at break and ultimate strength, which were determined from the strain and stress at the fracture point, respectively (**Figure 3a**). The Young's modulus determined from the initial slope increased with increasing x (**Figure 3b**). This result indicated that β CD and Ad served as supramolecular crosslinks, as previously reported^{28,32}. The toughness defined from the area between the stress–strain curves and strain axis increased with increasing x (**Figure 3c**). Since SC(x) had the largest Young's modulus and toughness values when $x = 1$, we prepared SCP(z) using SC(1).

To determine the appropriate amount of poly(MEA), we prepared SCP(z) with various z values in the range of 0–50 (**Figures 3d and S15**). When $10 < z < 40$, SCP(z) had a longer elongation at break than SCP(0). The Young's modulus value of SCP(z) decreased with increasing z due to the soft features of poly(MEA) (**Figure 3e**). A peak in toughness appeared when $z = 20$ (**Figure 3f**). The well-balanced Young's modulus and elongation at break values resulted in the largest toughness value. In addition, we considered the importance of incorporating poly(MEA) into SC(1) as a secondary polymer to prepare SCP(20). We prepared a copolymer system consisting of the same amounts of hydroxypropyl acrylate (HPA) and MEA to investigate the importance of the network structure of SC and penetrating poly(MEA) (**Figure S16a**). The copolymer system had significantly reduced Young's modulus and toughness values compared to SCP materials (**Figure S16b, c**). This result indicated that incorporating an appropriate amount of poly(MEA) as a secondary polymer, not as a copolymer, into a polymer network could improve its mechanical properties.

After determining the best x and z values, we investigated the impacts of CAC by preparing SCP(20)/CAC(w) with various w values (**Figures 3g** and **S17**). The addition of CAC changed the shapes of the stress–strain curves. The yield point observed in SCP(20) (= SCP(20)/CAC(0)) disappeared and overall tensile strength decreased when CAC was added, regardless of the amount of CAC. That was likely due to the decrease of the relative crosslinking density in SCP/CAC composite. Moreover, the elongation at break increased probably because more hydrogen bonds were formed in the matrix as CAC was added(**Figure S14c**). The Young’s moduli, which were determined from storage moduli, drastically increased when $w > 5$ (**Figure 3h**). This result indicated that CAC began working effectively as a filler when $w > 5$. In general, polymer materials with high Young’s moduli were brittle with low toughness. However, SCP/CAC(w) successfully increased the Young’s modulus while maintaining the toughness at a higher CAC content than that maintained in previous reports^{49,50} (**Figure S18**). We postulated that we should consider the internal structures and interactions between polymeric matrices and CAC, not only the contents of CAC. Unfortunately, it was impossible to obtain any evidence to understand the trends of the Young’s modulus values through scanning electron microscopy (SEM) images (**Figure S19**).

The toughness of SCP(20)/CAC(w) moderately decreased with increasing w (**Figure 3i**). Among the tested specimens, SCP(20)/CAC(5) and SCP(20)/CAC(10) maintained relatively large toughness values. According to the stress–strain curves in **Figure S17**, the improved mechanical properties of Young’s modulus, elongation at break, and fracture stress contributed to the maintenance of high toughness values.

SCP(20) and SCP(20)/CAC(w) exhibited higher Young’s modulus with similar or higher toughness values than versatile rubbers, such as butyl, silicone, latex, and nitrile rubbers. Relative

to polystyrene and other bio-based resource materials, such as bamboo and pine, SCP(20) and SCP(20)/CAC(*w*) exhibited inferior Young's modulus and superior toughness values (**Figure 4**).

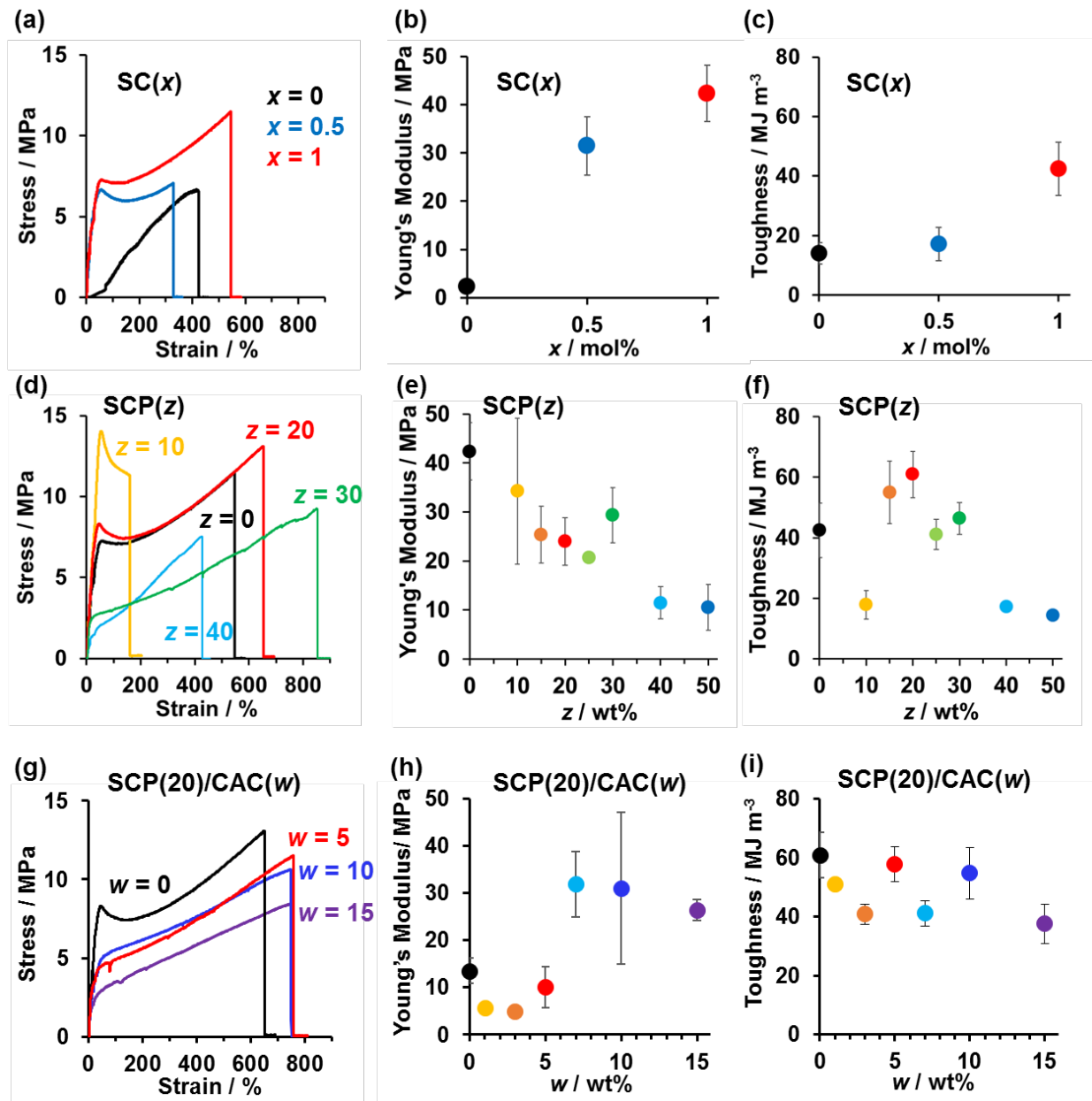


Figure 3. Mechanical properties of (a–c) SC(x), (d–f) SCP(z), and (g–i) SCP(20)/CAC(w): (a, d, g) stress–strain curves, (b, e, h) Young’s modulus values, and (c, f, i) toughness versus x , z , and w , respectively.

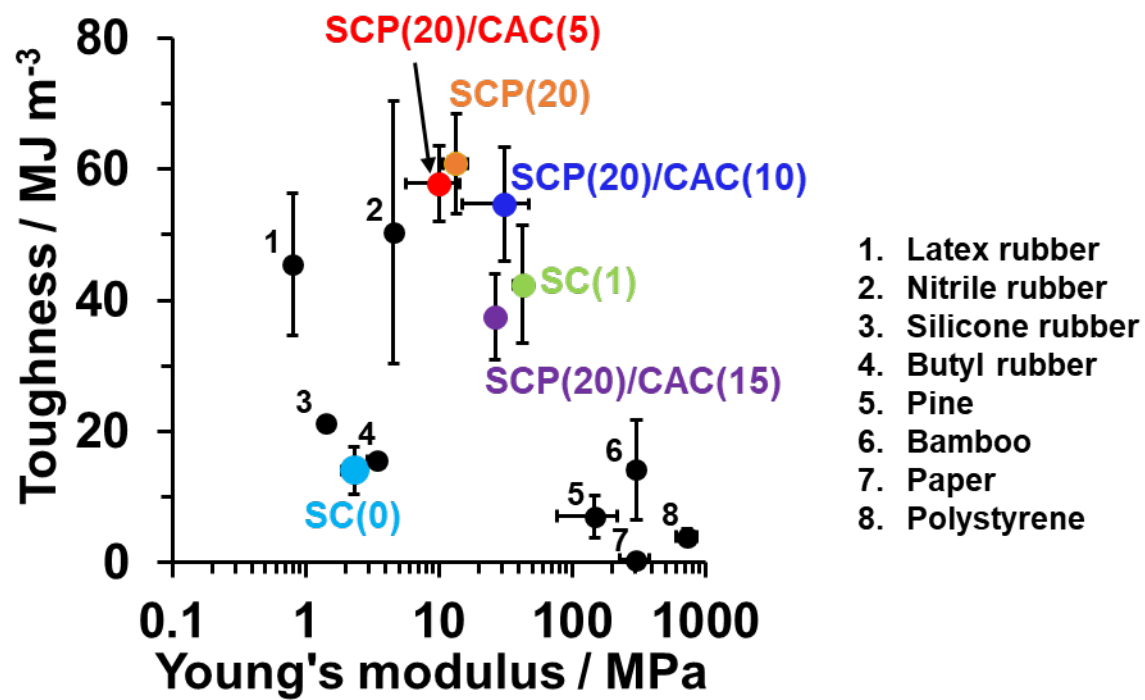


Figure 4. Comparison of the mechanical properties of general-purpose polymers.

Thermal properties of polymer composites containing CAC

We conducted differential scanning calorimetry (DSC) measurements to obtain structural information because spectroscopic data and SEM images did not provide valuable information about their internal structures. SCP(z) had two isolated thermal transitions originating from the glass transition of poly(MEA) and SCP(0) (**Figure 5a** and **Table S4**). When $z = 10$, only one glass transition temperature (T_g) appeared at a high temperature ($T_{g, \text{high}}$). The $T_{g, \text{high}}$ value of SCP(10) was approximately 6 °C higher than that of SCP(0). Subsequently, increasing the z value gradually decreased the $T_{g, \text{high}}$ value. In particular, the $T_{g, \text{high}}$ value of SCP(40) was similar to that of SCP(0). Similarly, the T_g at a low temperature ($T_{g, \text{low}}$) decreased with increasing z . These shifts in T_g could be explained based on the interaction between SCP(0) (=SC(1)) and poly(MEA). With an appropriate amount of poly(MEA), the effective interactions, including hydrogen bonds between OH groups on HPA and acrylic groups on MEA, reduced the free volume of each SCP(0) component and poly(MEA) component, increasing T_g . However, the impacts of the effective interactions between the two components weakened with increasing z due to the dissociation of hydrogen bonds on SCP(0), as shown in **Figure S13b**. Hence, both $T_{g, \text{high}}$ and $T_{g, \text{low}}$ gradually decreased.

SCP(20)/CAC(w) were similarly investigated by DSC measurements (**Figure 5b** and **Table S5**). The $T_{g, \text{high}}$ value gradually decreased with increasing w . Eventually, $T_{g, \text{high}}$ settled at the $T_{g, \text{high}}$ value of SCP(0) shown in **Figure 5a**. In contrast, the $T_{g, \text{low}}$ value of SCP(20)/CAC(w) maintained a relatively high $T_{g, \text{low}}$ value until $w = 3$. We postulated that the increase in $T_{g, \text{low}}$ was attributed to the preference of CAC for forming hydrogen bonds with poly(MEA) over SCP(0). Since CAC preferred to form hydrogen bonds with poly(MEA), the free volume of the SCP(0) component was restored to its pristine state with increasing w . The hydrogen bonds formed

between CAC and poly(MEA) maintained a relatively high $T_{g, \text{ low}}$ value at approximately $-24\text{ }^{\circ}\text{C}$. Moreover, increased levels of CAC ($w > 3$) could result in increased interactions, limiting the chain mobility of poly(MEA). This phenomenon could be the reason for the disappearance of the $T_{g, \text{ low}}$ value and the difficulty of detecting poly(MEA) in the NMR spectra.

As shown in **Figure S13c**, OH and C=O groups formed hydrogen bonds according to the FT-IR spectra of SCP(20)/CAC(w). The hydrogen bonds of OH groups were formations of intrachain hydrogen bonds because SCP(20) contained hydrogen bonding-free moieties, as shown in **Figure S13b**. Conversely, the shift regarding C=O groups should originate from the formation of hydrogen bonds between CAC and poly(MEA). These peak shifts in the FT-IR spectra supported the explanation of the DSC thermograms. Consequently, the high toughness of SCP(20)/CAC(10) shown in **Figure 3i** was attributed to the synergistic effect with host–guest crosslinks between β CD and Ad in SC and effective hydrogen bonds between CAC and poly(MEA).

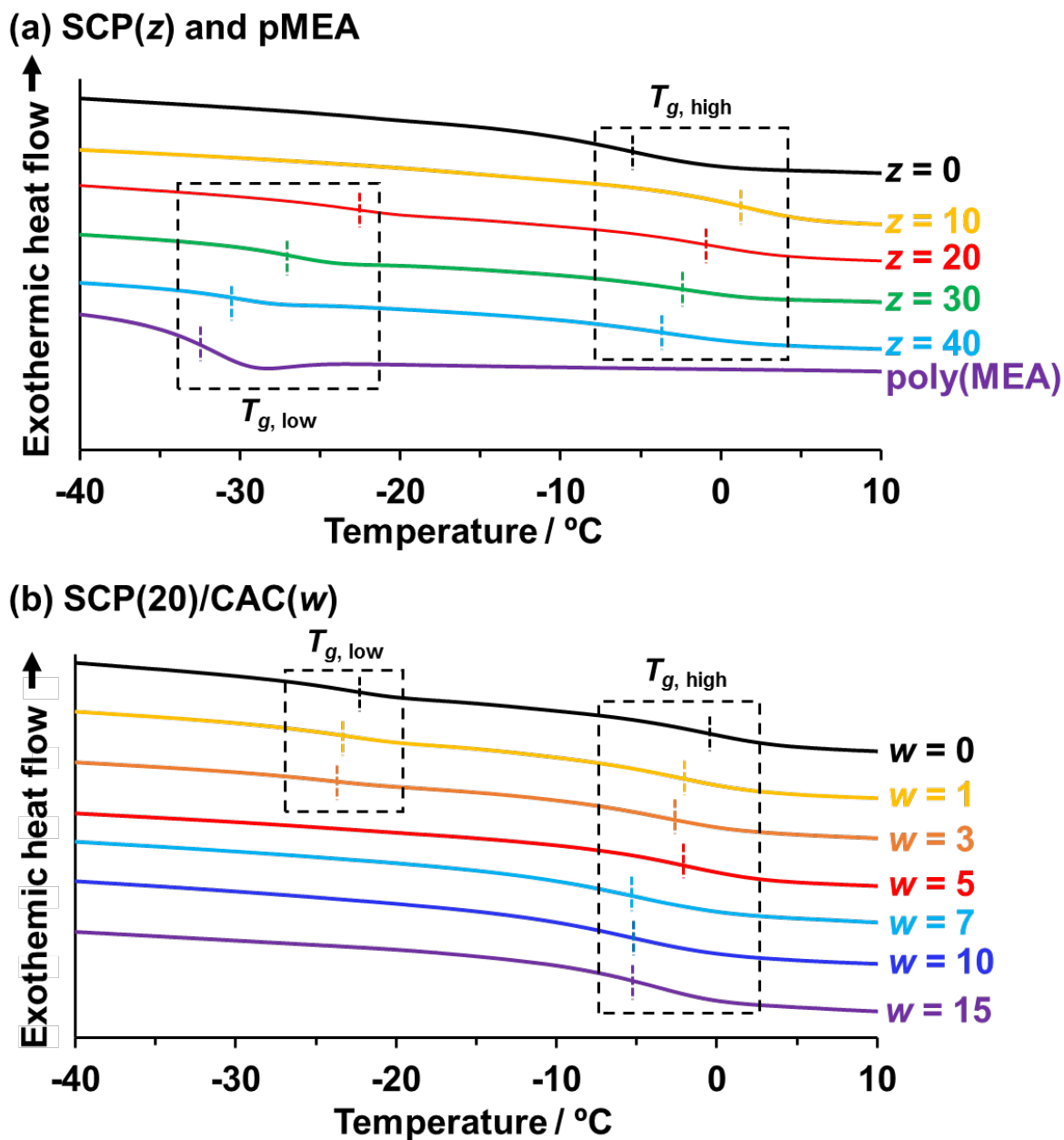


Figure 5. DSC thermograms of (a) SCP(z) with various z values and poly(MEA) and (b) SCP(20)/CAC(w) with various w values.

X-ray scattering studies on polymer composites containing CAC

In addition to DSC measurements, we conducted X-ray scattering measurements to comprehensively understand the internal structures of the polymer composites. The polymer composites underwent ultrasmall angle X-ray scattering (USAXS) and small angle X-ray scattering (SAXS) measurements. Then, the two types of profiles that we obtained were combined to continuously overlook scattering vector q from 5×10^{-3} to 2 nm^{-1} .

The SAXS profiles of SCP(z) changed with changing z values (**Figure 6a**). The SAXS profile of SCP(10) exhibited a shoulder peak at $2 \times 10^{-1} \text{ nm}^{-1}$, implying a phase separation with an approximately 30 nm domain spacing size. This small phase separation structure seemingly contributed to the large yield stress shown in **Figure 3d** because of the large interface area. In contrast, the SAXS profile of SCP(40) showed larger scattering intensities than other profiles when $q < 10^{-2} \text{ nm}^{-1}$ (**Figure S20**). The relatively large phase separation in SCP(40) resulted in poor mechanical properties. Except for these two profiles, the SAXS profiles of SCP(20) and SCP(30) nearly overlapped. This finding indicated that the difference in interactions observed in DSC measurements mainly affected the mechanical properties of SCP(20) and SCP(30), not the phase structures.

The internal structures of SCP(20)/CAC(w) were similarly investigated with USAXS and SAXS measurements (**Figure 6b**). With the addition of CAC, the peak at approximately $1.5 \times 10^{-2} \text{ nm}^{-1}$ disappeared, and additional peaks appeared at approximately $2.5\text{--}3.5 \times 10^{-1} \text{ nm}^{-1}$. The newly appeared peaks shifted to relatively large q values with increasing w , indicating the formation of small phase separation structures. By considering the toughness values in **Figure 3i**, we found that an appropriate domain spacing size of SCP(20)/CAC(10) and the synergistic effects between the host–guest crosslinks and hydrogen bonds were seemingly important factors.

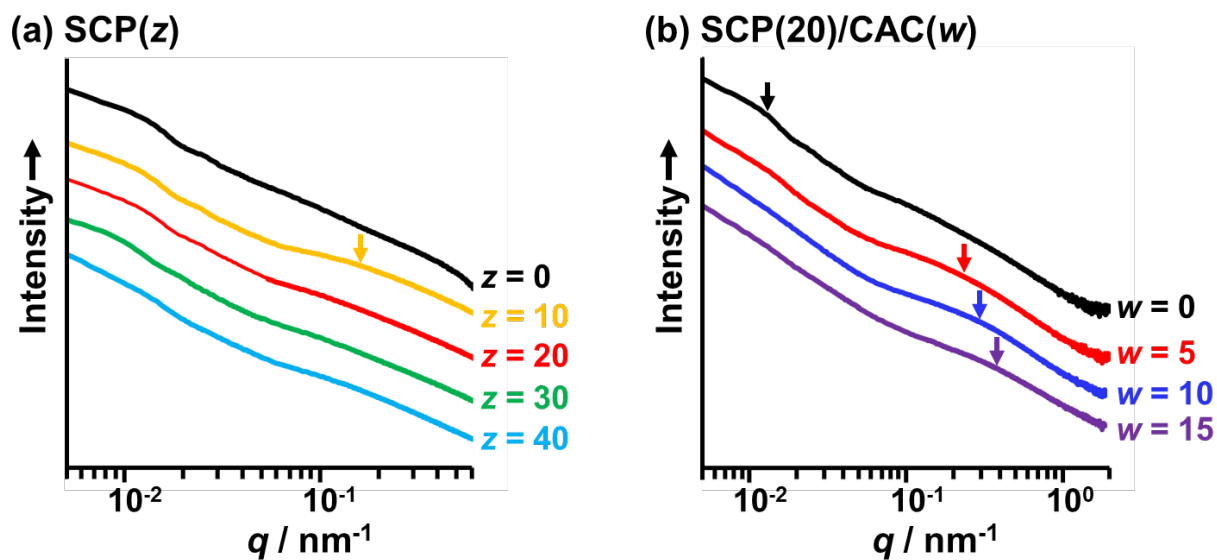


Figure 6. Combined X-ray scattering profiles of (a) SCP(z) with various z values and (b) SCP(20)/CAC(w) with various w values.

Comparison between polymer composites containing CAC or cellulose

Although we found that CAC filler could effectively enhance mechanical properties, it is not yet clear if citric acid modification is necessary. To clarify the effects of citric acid groups on CAC, we prepared polymer composites containing 10 wt% cellulose without any chemical modification (Cellulose(10)) in the same manner described in **Figure 2a** and **Scheme S1** to compare with SCP(20)/CAC(10) (CAC(10)). According to the stress–strain curves of tensile tests, CAC effectively enhanced the mechanical properties (**Figure 7a**). Regarding toughness, CAC was approximately two times more effective than cellulose (**Figure 7b**). In contrast, SCP(20) with cellulose fillers had weaker mechanical properties than SCP(20) without cellulose fillers.

To discuss the reason why CAC composite materials exhibited better mechanical properties than non-modified cellulose composite materials, we observe the surface of each composite material through SEM images (**Figure S21**). Compared to pure cellulose composites (**Figure S21c**), CAC composites seemed to have smoother surfaces (**Figure S21b**). This suggested that CAC had better compatibility with SCP materials due to citric acid-modification. Thus, well-dispersed CAC could form more hydrogen bonds in the composite materials, which had a good influence on their mechanical properties.

We also investigated the structures of Cellulose(10) through DSC and X-ray scattering measurements (**Figure 7c** and **7d**). CAC(10) had one T_g value that was lower than the $T_{g, \text{high}}$ value of SCP(20), as previously mentioned. Conversely, Cellulose(10) had two T_g values. Moreover, the $T_{g, \text{low}}$ value of Cellulose(10) was lower than that of SCP(20), while $T_{g, \text{high}}$ value was higher than that of SCP(20). On this basis, as described in the previous section, the cellulose in Cellulose(10) seemed to prefer to form hydrogen bonds with SC(1) rather than poly(MEA). By comparing the FT-IR spectra of CAC(10) and Cellulose(10), we found that Cellulose(10) exhibited band

separation (**Figure S22**). A band at a large wavenumber of approximately 1730 cm^{-1} indicated the presence of poly(MEA) without the formation of hydrogen bonds. An additional shoulder band appeared at approximately 1710 cm^{-1} , suggesting a significant redshift of the band originating from SC(1). A blueshift at approximately 3400 cm^{-1} seemed to occur due to the presence of free OH groups that initially formed hydrogen bonds with poly(MEA). These FT-IR spectra supported the formation of hydrogen bonds between SC(1) and cellulose, as described by the DSC results (**Figure 7c**). In addition, the combined X-ray scattering profile of Cellulose(10) exhibited a broad peak at approximately $5 \times 10^{-1}\text{ nm}^{-1}$, indicating a domain spacing size of approximately 10 nm (**Figure 7d**). The hydrogen bonds between cellulose and SC(1) and the very small phase separation structure could not enhance the toughness. Citric acid modification improved the mechanical properties and compatibility levels of SCP and CAC, introducing hydrogen bonds between penetrated poly(MEA) and the CAC filler (**Figure 7e**).

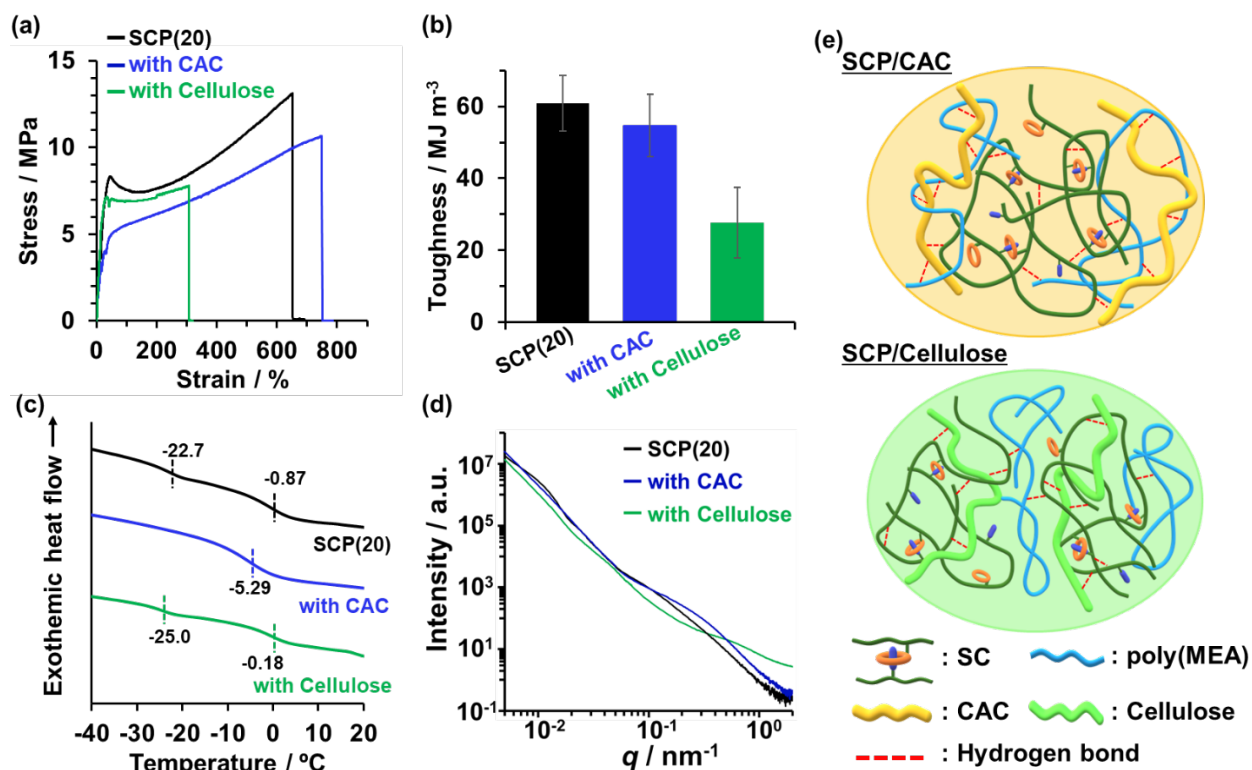


Figure 7. Comparison of CAC and conventional cellulose without chemical modification as a filler. (a, b) Mechanical properties, (c) DSC curves, and (d) USAXS and SAXS profiles of SCP(20), SCP(20)/CAC(10), and SCP(20)/Cellulose(10). (e) Proposed internal structures of SCP/CAC and SCP/Cellulose composites.

Conclusions

We proposed that the citric acid modification of cellulose filler promoted the formation of hydrogen bonds in polymer composites, resulting in better mechanical properties of obtained elastomers. We successfully prepared tough polymer composites with high cellulose contents (10 wt%) by introducing two types of noncovalent interactions such as host-guest complexation and hydrogen bonds. CAC composite elastomers indicated greater mechanical properties than general-purpose polymers and other bio-based polymers. We found that the formation of hydrogen bonds between CAC and poly(MEA), secondary linear polymers, was key to enhancing the mechanical toughness values of the polymer composites. In addition, an appropriate phase separation structure, such as domain spacing, was a considerable factor influencing the high mechanical toughness. Based on these two factors, we concluded that CAC is a better cellulose filler than conventional cellulose.

Cellulose is a promising bio-based filler because it can create a carbon circulation society. One remaining challenge with cellulose filler is its low content. Even though certain cellulose fillers can enhance mechanical properties, they cannot be utilized practically without sufficiently high contents. In this report, we suggested an approach for increasing the cellulose content while maintaining the reinforcement effect. We believe that our material design provides an additional step for carbon circulation.

Associated content

Supporting information

List of abbreviation, experimental details including materials, methods, and conditions of each measurement, preparation and characterization of CAC and CAC composite materials, ^1H and ^{13}C NMR spectra of all compounds, FT-IR spectra, mechanical properties, SEM images, thermal properties, and X-ray scattering profiles of composite materials (PDF).

List of abbreviations

CAC	citric acid-modified cellulose
CD	cyclodextrin
$\beta\text{CDAAmMe}$	mono-6O-acrylamidomethyl- β -cyclodextrin
AdAAm	adamantane acrylamide
HPA	2-hydroxypropyl acrylate
MEA	2-methoxyethyl acrylate
DMSO	dimethyl sulfoxide
SC	single cross-network
SCP	single cross-network with penetrating polymer
NMR	nuclear magnetic resonance
ATR-FT-IR	attenuated total reflection Fourier-transform infrared
DMA	dynamic mechanical analysis
SEM	scanning electron microscope
DSC	differential scanning calorimetry
USAXS	ultra-small angle X-ray scattering

SAXS

small angle X-ray scattering

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