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Hydrotalcites Catalyze the Acidolysis Polymerization of Phenolic Acid to Create Highly Heat-Resistant Bioplastics

*Manu Chauzar, Seiji Tateyama, Takanori Ishikura, Keitaro Matsumoto, Daisaku Kaneko, Kohki Ebitani, and Tatsuo Kaneko**

Acidolysis polymerization has been used to prepare phenol-derived polymers such as liquid crystalline (LC) polymers, and is catalyzed by mildly-alkaline salts. The catalytic effects of hydrotalcites (HTs), which are natural alkalescent minerals with controllable basicity, are investigated on the acidolysis copolymerization of coumarates such as *p*-coumaric acid and caffeic acid. As a result, the LC copolymer prepared in the presence of HT with a Mg/Al ratio of 3 shows higher molecular weight values than copolymers prepared in the presence of any other alkalescent salts. On the other hand, the copolymers prepared in the presence of HTs show a clear LC state where the polymer chains are oriented on the surface of the glass fibers. The resin, which is oriented by glass fiber fillers aligning along its longitudinal axis and is annealed at 300 °C for 20 min, shows a softening temperature of 305 °C while keeping a high mechanical strength of 85 MPa and a high mechanical modulus over 1 GPa.

1. Introduction

Bio-based plastics originating from biochemicals, which are produced as metabolites from plant carbon-fixation by photosynthetic activity or are derived from these metabolites by the following reactions, are significant for the establishment of a sustainable society through the carbon-stock inside of their plastics. However, conventional bio-based plastics are generally composed of aliphatic polyesters whose applications have been limited due to their poor thermal and mechanical properties[1]. On the other hand, the introduction of an aromatic component into the polymer backbone is an efficient method to intrinsically improve material performance, since aromatic polyesters such as liquid crystalline (LC) polymers have been used in the engineering of plastics[2]. Most aromatic biochemicals are phenolic compounds obtained by the sikimate biosynthetic pathway[3], and are widely available in various environments.[4] Phenolic compounds are used as building blocks of LC polymers (LCP), but are very easily oxidized. Therefore, they are generally used after acetylation, followed by acidolysis polycondensation to create aromatic polyesters. We have previously developed highly heat-resistant polyesters using acetylated phenolic acids such as *p*-coumaric acid (4-hydroxycinnamic acid; 4HCA) and caffeic acid (3,4-dihydroxycinnamic acid; DHCA); the poly(4HCA-*co*-DHCA) with a copolymer composition of 4HCA/DHCA =60/40 mol/mol showed a glass transition temperature of 156 °C, which is high enough for use as a bio-based engineering plastic[5]. In order to increase the heat-resistance performance to achieve usage as a super-engineering plastic, the development of an efficient and facile method for hybridization with mechanical reinforcing fillers is required.

The acidolysis reaction is catalyzed by mildly-alkaline compounds such as sodium acetate and sodium phosphate[6]. Stronger alkaline catalysts can also promote the acidolysis reaction, but the reverse hydrolysis reaction of the generated polyesters can occur easily. Thus, the development of an appropriate catalyst that can promote the acidolysis chain-propagation without inducing the reverse reaction is required. The alkalescent natural mineral hydrotalcite (HT; $[Mg_6Al_2(OH)_{16}](CO_3)4H_2O$) belongs to the layered-double-hydroxides family as schematically-illustrated in **Figure 1**a[7]. HT has a structure isomorphous to that of brucite, $Mg(OH)_2$, in which magnesium cations (Mg^{2+}) occupy the centers of hydroxide octahedra. These octahedra form a continuous two-dimensional sheet by sharing edges. It has been reported that HT can be used as a heterogeneous catalyst for acetylation using acetic anhydride[7]. The hydroxide groups of HT are important for their catalytic activities, which are proportional to the number and basicity of the interlayer anions. HT derivatives were also reported to be safer, cheaper, and more efficient catalysts than conventional catalysts for poly(alkylene terephthalate) production by the catalysis of the transesterification[8] reaction, which is an intrinsically similar reaction to acidolysis. Furthermore, the structural control of HT is possible; aluminum cations (Al^{3+}) can replace some of the magnesium cations (Mg^{2+}), thus inducing a net positive charge in the cationic sheet, which is counterbalanced by interlayer anions such as carbonate and nitrate anions.

In this study, we investigate the effects of HT as a catalyst on the acidolysis polymerization of acetylated phenolic compounds.

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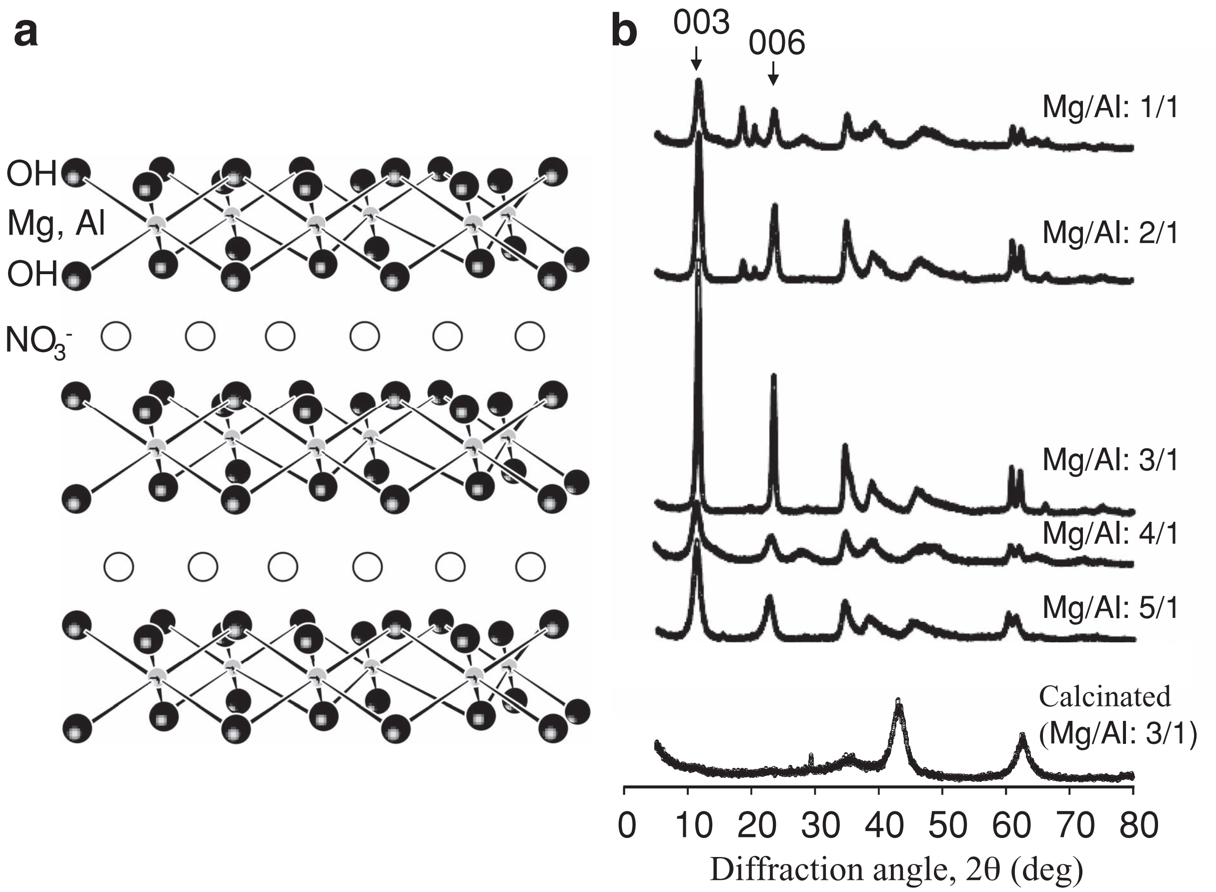


Figure 1. a) Schematic illustrate of representative hydrotalcite structure. b)X-ray diffraction patterns of HT with various Mg/Al ratios.

As a result, we find that HT of a specific composition can be an excellent catalyst to promote the preparation of poly(4HCA-*co*-DHCA) LCP. Consequently, we develop a high-performance resin with a heat-resistance temperature over 300 °C, which is sufficient for use as a bio-based super-engineering plastic.

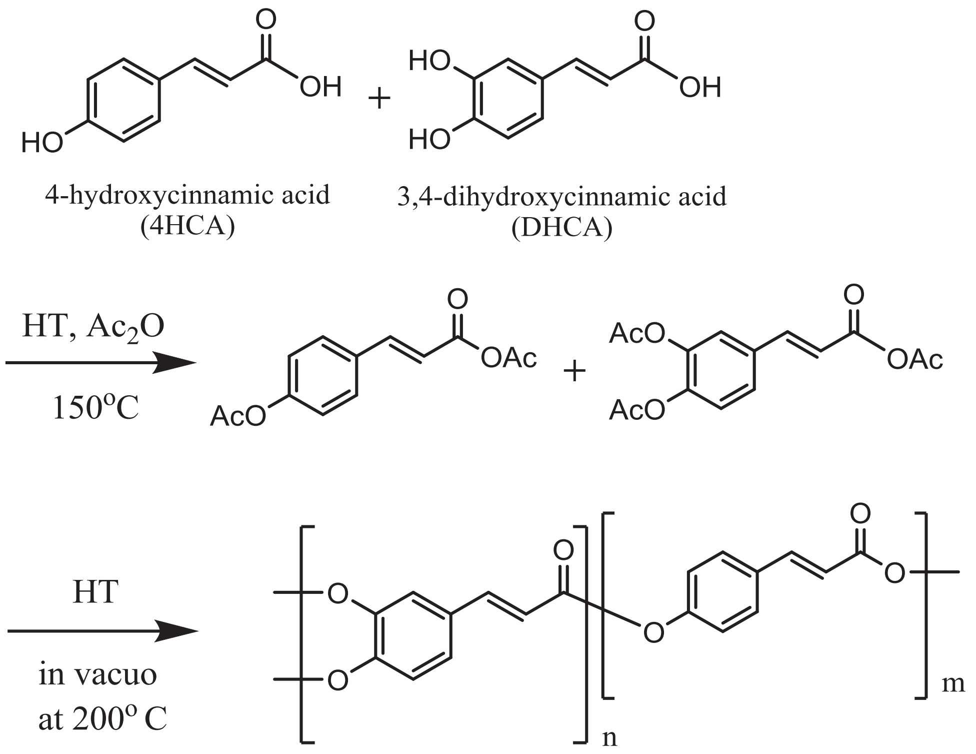
2. Results and Discussion

2.1. Polymer syntheses using various catalysts

The copolymer poly(4HCA-*co*-DHCA) with a 4HCA feed-composition of 60 mol% was prepared in the presence of various alkalescent catalysts (**Scheme 1**). The reaction mixture was treated by acetic anhydride at 150 °C, and was polymerized for 200 °C in vacuo. The excess acetic anhydride was evaporated during polymerization, and gradually increased its viscosity to finally solidify and not allow further agitation. If the reaction speed was high, the polymerization period until solidification became shorter. In particular, polymerization in the presence of HT as a catalyst took 4 hours less than in the other catalysts (6 h).

Figure S1 shows a representative infrared (IR) spectrogram of poly(4HCA-*co*- DHCA)s prepared in the presence of HT. The IR peak at 1728 cm^{-1} indicates the formation of ester bonds from 4HCA and DHCA, and there was also an IR shoulder around 1765 cm^{-1} which could be assigned to the vibration of acetyl groups. In addition, the IR peaks of carboxylic acid detected at 1667 and 1642 cm^{-1} in the spectra of the monomers disappeared in the copolymer spectrogram. These findings support copolymer formation by the acidolysis of acetylated monomers. The copolymers were also characterized by ^{1}H-NMR spectroscopy (Figure S2), and proton signals appeared at δ = 2.20–2.43 ppm (acetyl, $-CH_3$), δ = 6.60–6.82 ppm (α-CH), δ = 7.13–7.82 ppm (aromatic protons), and δ = 7.82–8.18 ppm (β-CH). The detailed assignment of the aromatic protons is shown in the chemical structure. The aromatic protons marked a′ and a″ which are adjacent to the O-substituted carbons of the monomers showed multiple signals, suggesting the coexistence of various ester environments such as a coumaryloyl ester, and 3-O- and/or 4-O-acetyloyl esters unreacted due to steric hindrance.

Various alkalescent catalysts such as NaOAc, Na_2CO_3, NaH_2PO_4, Na_2HPO_4 and HT were used in the copolymerization of 4HCA with DHCA. The molecular weights measured by GPC were summarized in **Table 1**. The copolymers prepared in the presence of HT catalysts showed narrower Mw/Mn values than those in the other catalysts. As shown in the upper chromatogram of Figure S3, the copolymers prepared with the HT catalyst showed only one structureless monomodal



Scheme 1. Syntheses of poly(4HCA-*co*-DHCA)s from acetylated monomers via acidolysis.

Table 1. Molecular weights of poly(4HCA-*co*-DHCA) prepared in the presence of hydrotalcite with different weight contents[a].

Catalysts	Feed ratio to monomers (wt%)	*Mw*	*Mn*	*Mw/Mn*
HT	0.2	24,900	14,400	1.7
	0.4	70,800	51,000	1.4
	0.6	82,300	68,600	1.2
	0.8	54,800	21,100	2.6
	1.0	25,200	12,400	2.4
CH_3COONa	1.0	126,000	24,100	5.2
Na_2CO_3		50,500	8,400	6.0
NaH_2PO_4		64,600	9,800	6.6
Na_2HPO_4		48,000	6,700	7.2

[a] Polymerization was carried out for 2 hrs at 150 °C and for 4 hrs at 200 °C. Molecular weights were estimated by gel permeation chromatography (GPC, eluent DMF) in a polystyrene standard.

peak. On the other hand, the copolymers prepared in the presence of CH_3COONa, Na_2CO_3, NaH_2PO_4, and Na_2HPO_4 showed multimodal GPC peaks as shown in the representative chromatogram in the lower panel of Figure S3. Besides the Mn of the copolymer prepared in the presence of Na_2CO_3, NaH_2PO_4, and Na_2HPO_4 showed low values. These results indicated the presence of various side reactions during the polymerization. Regarding the feed ratio of the monomer to the catalysts, the copolymer in HT at ratios of 0.4 and 0.6 showed high values and narrow molecular weight distributions.

2.2. Polymer Syntheses Using HT

The copolymers were prepared with HT at a content of 0.6 wt% for different polymerization periods (**Table 2**). The molecular weight of the copolymers increased with an increase in the polymerization period, but the molecular weight distribution also increased. Finally, the polymerization liquid was solidified by 240 min. agitation to restrict any further reaction as mentioned above. These results indicate that the inhomogeneous catalyst HT efficiently catalyzed the acidolysis reaction of coumarate carboxylic acid with the acetylated phenol ends of the hyperbranched polymers, even in a melt polymerization

Table 2. Molecular weights of poly(4HCA-*co*-DHCA)s prepared in the presence of HT for different polymerization periods[a].

Polymerization period (min)	*Mw*	*Mn*	*Mw/Mn*
30	16,300	11,500	1.4
90	28,700	16,500	1.7
120	26,800	18,000	1.5
180	36,900	19,600	1.9
210	34,000	19,900	1.7
240	54,800	21,100	2.6

[a] Polymerization was carried out for 2 hrs at 150 °C and for various periods at 200 °C in the presence of HT with a content of 0.8 wt% to monomers. Molecular weights were estimated by gel permeation chromatography (GPC, eluent DMF) in a polystyrene standard.

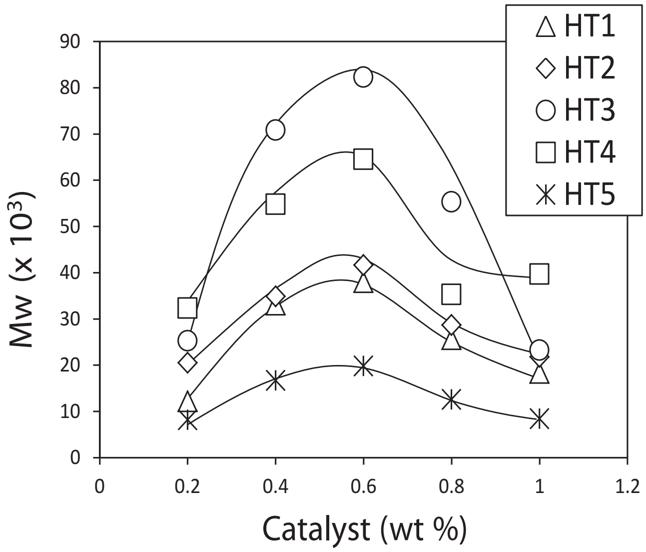


Figure 2. Molecular weights of poly(4HCA-*co*-DHCA)s prepared in the presence of HT with various Al/Mg ratios.

without a solvent. In order to investigate the catalysis in more detail, various HT's were prepared and used for the copolymerization. Figure 1 shows the X-ray diffraction patterns of HT with various Mg/Al ratios, where HT-X was prepared by a Mg/Al ratio of X/1. All HTs showed the XRD patterns characteristic of HT, including the intense diffraction peaks at $2\theta = 11.5°$ (003) and 23.1° (006) (arrows in Figure1) assigned to the layer structure with a spacing of 7.69 Å[9]. When the Mg/Al ratio was increase from 1 to 3, the intensity of the layer diffraction peaks increased, and showed a maximum at the Mg/Al ratio of 3. In addition, the alkalinity of HT should increase with an increase in the Mg/Al ratio according to the literature[10].

The effects of the HT composition change on the Mw of the copolymers were investigated (**Figure 2**). Figure 2 shows the catalyst amount dependence of the Mw, and demonstrated maximum values at 0.6 wt% for all HT compositions. If the hydroxyl ions of HT are present at too high of a composition relative to the monomers, the hydrolysis of the polymer chains may be enhanced. HT-5 has the highest alkalinity of all HTs prepared here and yet showed the lowest *Mw* value, which suggests that this result may be due to the high hydroxyl content of HT. On the other hand, the use of HT-3 gave the highest *Mw* at around 0.6 wt%. Since HT-3 had the highest structural ordering of the layer structure, a layer structure may have a close correlation with the catalysis activity. Moreover, the effects of the increased ordering in the layer structure on the *Mw* increase is higher than the countervail effects of the abovementioned alkalinity increase, because the *Mw* values of HT-3 were higher than those of HT-2 and HT-1.

In order to investigate the layer structure effects on the *Mw* in more detail, we calcinated the HT to lower the layer ordering. As shown in the lowest XRD diagram of Figure 1, the diffraction peaks of the layer structure in the HT-3 XRD diagram disappeared in the XRD diagram of the calcinated HT-3. **Figure 3** shows the *Mw* values of the copolymers prepared in the presence of calcinated HT catalysts with contents of 0.4 and 0.6 wt%. One can observe that calcination reduced the *Mw* values of the copolymers prepared in the presence of HT-1, HT-2, HT-3 and HT-4, although the *Mw* differences were not very dramatic for HT-5, which has a high alkalinity. Thus, the layer structures were effective to catalyze the acidolysis by HT. The polymer chains seem too large to intercalate into the gaps of the HT's. However, the literature on PET preparation has reported that aromatic compounds such as terephthalic acid intercalated efficiently into HT layers, where polymer chains ends can react with them[11]. In the present case, coumarate compounds and a number of acetylated chain ends for the hyperbranched poly(4HCA-*co*-DHCA)s might react around the surface of the layer portions, which can effectively catalyze their acidolysis.

2.3. High-performance Resin Preparation

The copolymers with this monomer composition were liquid crystalline, as previously reported[5], and showed glass transition around 120–140 °C independent of catalysis species (representative DSC chart: Figure S4). We then made liquid

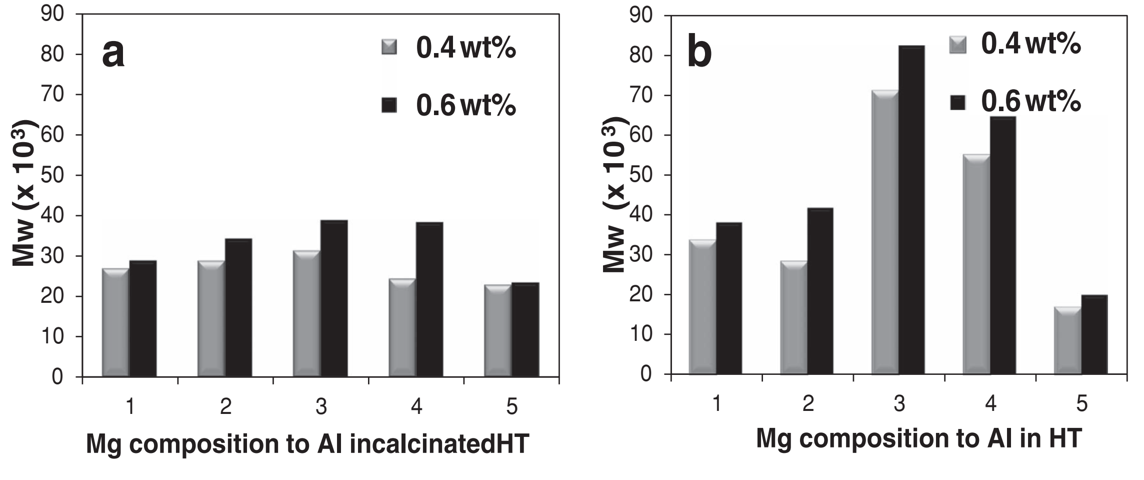


Figure 3. *Mw* values of poly(4HCA-*co*-DHCA) prepared in the presence of calcinated (a) and normal (b) HT catalysts with contents of 0.4 and 0.6 wt%.

crystalline observations of these copolymers. **Figure 4** shows crossed-polarizing microscopic images of the poly(4HCA-*co*-DHCA)s prepared in the presence of various catalysts. The copolymers prepared in NaOAc showed a clear birefringence and fluidity in their melted state, thus demonstrating the formation of the liquid crystalline structure. However, no textures typical of a nematic phase were observed. The copolymers in the other catalysts except for the HT's also gave similar results. On the other hand, the copolymers prepared in the presence of HT's showed some clear threads (Figure 4), where representative threads were marked by arrows in the HT-3, HT-4, and HT-5 images. These results indicate that copolymers prepared in the presence of HT catalysts formed clear interfaces in their orientation domains, which might be induced by the fineness of the copolymer structures.

The fine structure inducing efficient liquid crystallization might also induce good orientation of the copolymer resins. We then tried to prepare oriented resins using the long glass fillers (GF; 3 μm $\varphi \times 5$ mm) set along the longitudinal axes of the molding as shown in the illustration inset in **Figure 5**b. The pictures from Figure 5a are microscopic photos of the GF, taken under cross-nicol polarization using a first-order retardation plate ($\lambda = 530$ nm) inserted into the light path. The left picture showed no light transmission through the GF itself to demonstrate non-orientation. On the other hand, the polymer coating on the GF showed birefringence in the middle and right pictures. From these figures, it was observed that the polymer birefringence was negative, as evidenced by both the subtractive birefringence (blue color) in the GF lying from the upper left to the lower right, and the additive birefringence (orange color) in the fibers lying from the upper right to the lower left. Since the polymers have phenylene vinylene groups in their main chains, the negative birefringence may indicate that the polymer backbones and branches were oriented along the GF axes. If GF was incorporated into the resin in the LC state, the polymer chains should be oriented along the GF. As a result, the mechanical strength (σ) measured by the three-point bending test showed a good correlation with the GF composition, to attain a ca. 140 MPa mechanical strength, which is high enough to use as a super-engineering resin (Figure 5b). If the polymer prepared in the presence of sodium acetate was used, the σ was reduced to around 100 MPa. This high value may be strongly attributed to the LC orientation induced by GF incorporation. Next, the dynamic moduli were measured by dynamic mechanical

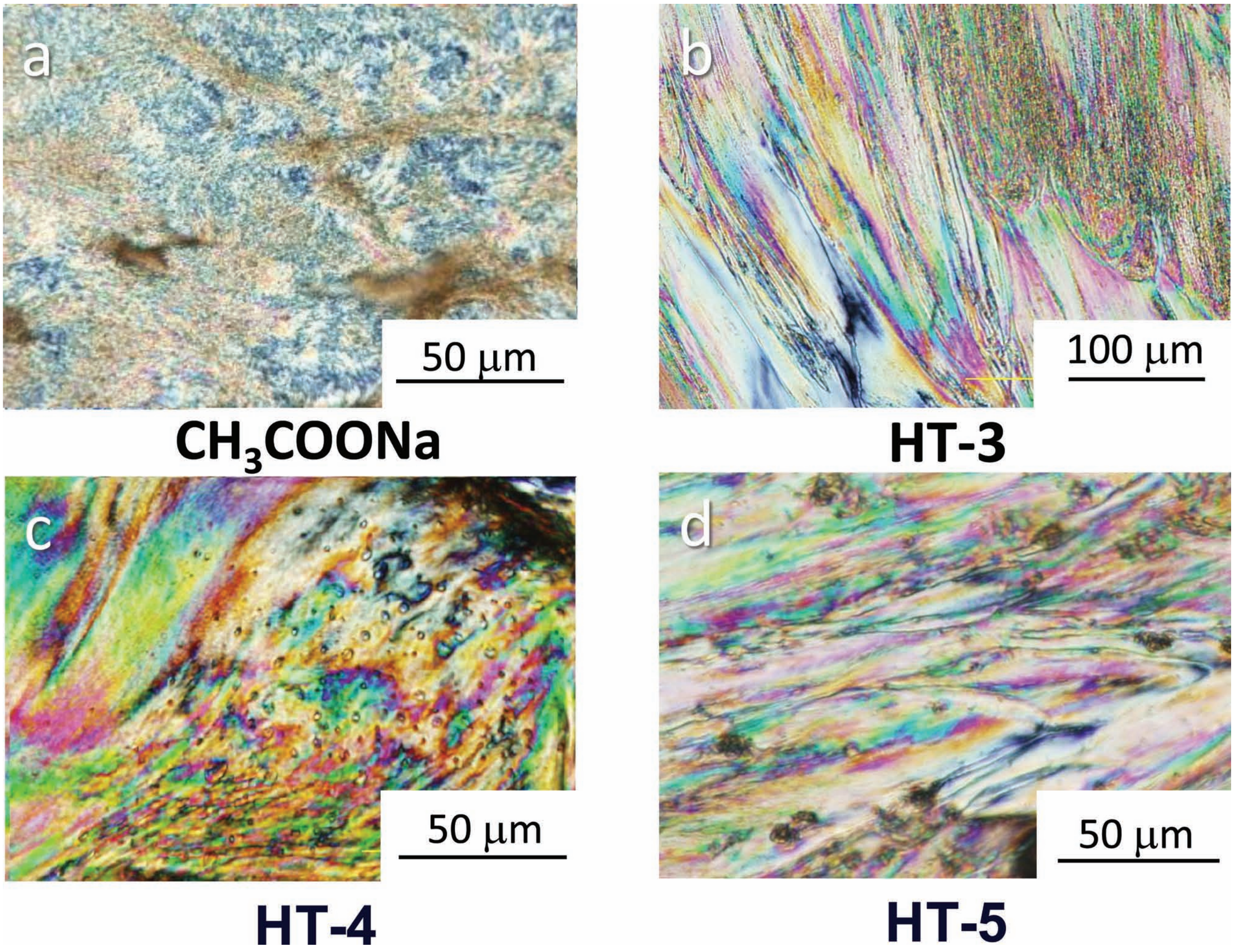


Figure 4. Crossed-polarizing microscopy of poly(4HCA-*co*-DHCA)s prepared in the presence of various catalysts.

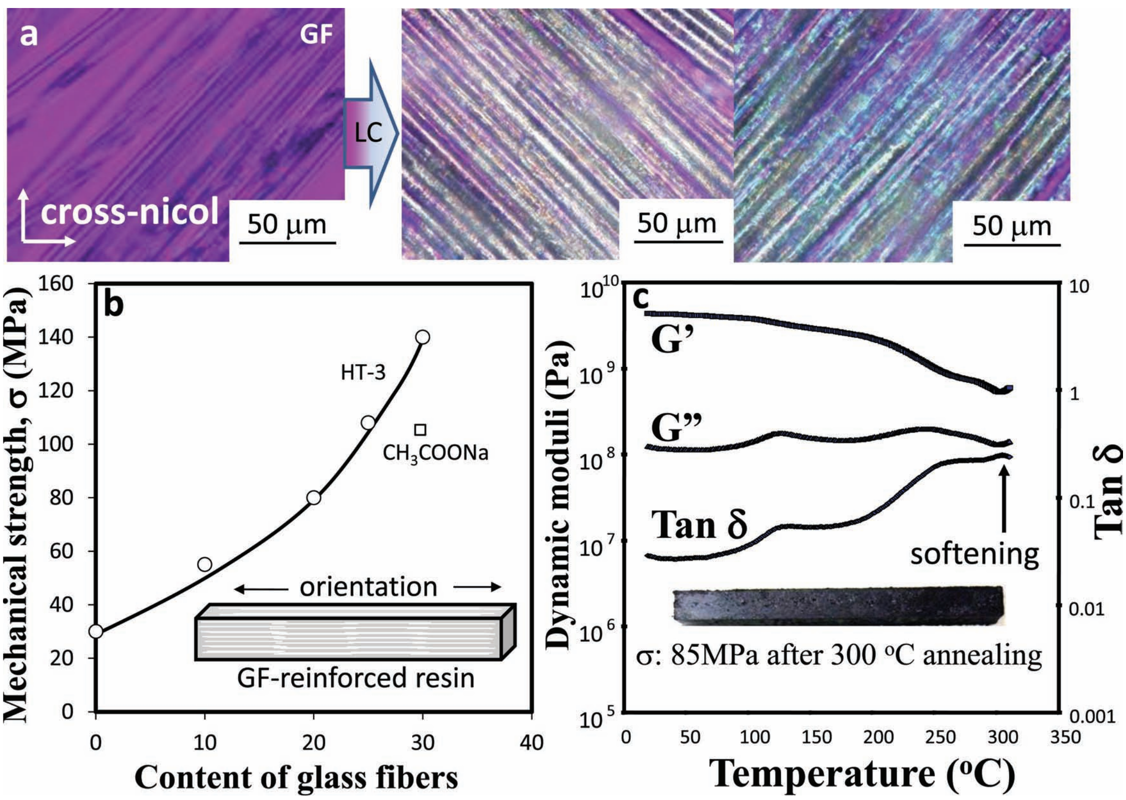


Figure 5. (a) Mechanical strength, σ, at fracture of oriented poly(4HCA-*co*-DHCA) resin reinforced by glass fibers (GF) lying along the orientation direction. (b) Dynamic mechanical analyses of the same resin with GF content of 30 wt% which was annealed at 300 °C for 20 min. The inset picture was the image of the annealed resin whose σ at fracture was kept high 85 MPa.

analyses. The temperature dependence of the storage modulus G′, the loss modulus G″, and the G″/G′ = Tan δ were shown in Figure 5c. The G′ decreased slightly at two steps around 120 and 220 °C with the accompanying G″ peaks, but stayed high (0.6–0.7 GPa) at 300 °C. The G′ values are easily converted into the elastic modulus E' by the Equation 1:

$$E = 2G(1+\gamma) \tag{1}$$

under the assumption of a Poisson's ratio, γ, of 0.2-0.5 (most solids showed this γ range). The resin showed an E' range between 1.3–2.1 GPa at 300 °C, which is also high enough to use as a super-engineering resin. The Tan δ curves showed no peaks at 120 or 220 °C, but a peak at around 305 °C, and thus the softening temperature of the resin was regarded as 305 °C. After this measurement, the resin darkened in color, possibly due to the negative thermal effects on σ. However, the resin showed a high σ value of 85 MPa at room temperature after thermal treatment at 305 °C for 20 min. Thus, we prepared a bio-based resin with high-thermal resistance and high-mechanical properties.

3. Conclusions

We successfully prepared high-performance and functional polymers with rigid and photoreactive phenols, especially poly(p-coumaric acid-co-caffeic acid). Various alkalescent catalysts such as Na_2CO_3, NaOAc, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, and hydrotalcite were used in the copolymerization of 4HCA with DHCA. The copolymer poly(4HCA-co-DHCA) prepared in the presence of HT catalysts showed high molecular weight values and a narrow molecular weight distribution. A 0.6 wt% concentration was considered to be the best ratio for copolymer preparation. On the other hand, the use of HT with a Mg/Al ratio of 3 (HT-3) gave the highest values for the copolymer *Mw* at around 0.6 wt%. Since HT-3 had the highest structural ordering of the layer structure, the layer structure may have a close correlation with the catalysis activity for acidolysis. The copolymers prepared in the presence of HTs showed some clear threads. These results indicate that the copolymers prepared in the presence of the HT catalysts formed clear interfaces in orientation domains, which might be induced by the fineness of the copolymer structures. Cross-polarizing microscopy revealed that the polymer chains were oriented on the surface of glass fibers, and that the resin hybridized by the glass fiber fillers aligning along the longitudinal axis showed a very high mechanical strength. Furthermore, the hybrid resin annealed at 300 °C for 20 min showed a softening temperature of 305 °C while keeping a high mechanical strength of 85 MPa and a high mechanical modulus over 1 GPa. These values were high enough for use as a bio-based super-engineering plastic.

4. Experimental Section

Hydrotalcite Preparation: Mg-Al-NO_3-hydrotalcite (Mg-Al-HT) with 2:1 atomic ratio of Mg to Al was prepared in a nitrogen atmosphere to avoid carbonation in air. Magnesium nitrate hexahydrate (20.5 g, 0.08 mol) and aluminum nitrate nonahydrate (15.0 g, 0.04 mol) were dissolved in 100 mL of deionized water, and sodium carbonate and sodium hydroxide were dissolved in distilled water. The solution of sodium hydroxide and sodium carbonate was then added into the above solution by a peristaltic pump at a rate of 1 ml/min. The resultant slurry was stirred for 2 h under nitrogen at room temperature. The slurries were cooled down to room temperature slowly over 2 h, and filtered under nitrogen to obtain a white powder. The powder was washed with distilled water until the pH reached 7. It was dried under vacuum at 100 °C to obtain Mg-Al-NO$_3$-hydrotalcite. Mg-Al-NO$_3$-hydrotalcites (Mg-Al-HTs) with different atomic ratios of Mg to Al (1:1, 2:1, 3:1, 4:1, 5:1) were prepared in a nitrogen atmosphere to avoid carbonation in air. All of the Mg-Al-hydrotalcites (HT-1, HT-2, HT-3, HT-4, HT-5) were calcinated by incubating them at 450 °C for 4 h.

Polymerization: Poly(4HCA-*co*-DHCA)s were synthesized by a two-step reaction in one bottle by the following procedure (Scheme 1). Monomers of 4HCA (60 mmol) and DHCA (40 mmol) were mixed and mechanically stirred at 150 °C in the presence of acetic anhydride (40 ml) as a condensation reagent plus catalysts such as HT, until the solution became homogeneous (for about 2 hours). The solution was further heated to 200 °C, and the polymerization was carried out for another 4 hours in vacuo. The reaction solution increased its viscosity gradually, and was finally solidified to not allow further stirring. After the reaction was finished by cooling to room temperature, the materials were milled into a powder and purified by washing with acetone (yields: 76–93 wt%).

Resin preparation: The resins were prepared in a casting mold to a length of 50 mm, a width of 6.5 mm and a thickness of 3.5 mm by the following procedure. The polymer powders were placed into the mold, and glass filler-fibers (3 μm $\varphi \times$ 5 mm) of various compositions were set along the longitudinal axis. The mixture was then heated to 200 °C and pressed at 5 MPa, and kept for 5 min.

Measurements: The ^{1}H-NMR spectra of the poly(4HCA-*co*-DHCA) were measured with a NMR spectrometer (JEOL FX 400) at 400 MHz.. The ^{1}H NMR chemical shifts in parts per million (ppm) were recorded downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference using TFA-d/CD$_2$Cl$_2$ as a solvent. The FT-IR spectra of the copolymers were measured at 25 °C on a Perkin Elmer Spectrum One spectropolarimeter between 4000–400 cm^{-1}. The molecular weight of the poly(DHCA-*co*-4HCA)s was determined by gel permeation chromatography (GPC) using a Shodex GPC-101 with a connection column system of 803 and 804 that was calibrated with polystyrene standards (eluant: dimethylformamide). The wide angle X-ray diffraction (WAXD) of hydrotalcite and calcinated hydrotalcite as a catalyst **was** recorded on an X-ray diffractometer (RINT UltraX18) equipped with a scintillation counter, using CuKα radiation (20 kV, 80 mA; wavelength = 1.5418 Å), which was monochromated by a parabolic multilayer mirror using transmission geometry. The thermotropic properties, such as the phase transition, of P(4HCA-co-LCA) was observed by crossed-polarizing microscopy. The samples were sandwiched between two glass plates, and were heated at a rate of 10 °C/min by a METTLER TOLEDO FP82HT Hot Stage (Greifensee, Switzerland). The glass transition temperatures were confirmed by differential scanning calorimetry (DSC) measurement (EXSTAR6100; Seiko Instruments Inc., Chiba, Japan). The three-point bending test was performed using a tensile materials testing machine (INSTRON, Canton City, MA, USA, 3365-L5). The samples were set over two fixtures 30 mm apart, and the center of each sample was pressed from the opposite direction. The fracture strength was defined as the maximum stress in the stress–strain curve.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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