

Development of High-Performance Hybrid Resin of Lignin-Mimetic Polymers with Celluloses

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The hybrid resins of poly(4HCA-co-DHCA) copolymers with kenaf nanofibers were prepared by polymerization simultaneous hybridization. The kenaf fibers were milled into the nanofibers by a ceramic pestle, and were cinnamoylated. The hybridization had some effects on improving the performance of resins; 1) mechanical strength, 2) glass transition temperature, 3) dynamic moduli in torsion. On the other hand, the hybridization with cinnamoylated celluloses increased the softening temperature restraining an increase of melt viscosity.

Key words: bio-base polymers, high-performance polymers, lignin, cellulose, biomimetics

1. INTRODUCTION

Ecoplastics which are developed under the concept of earth environment protection showed a degradation into natural molecules. Almost all the ecoplastics are bio-base aliphatic polyesters from naturally-occurring molecules [1]. However, the application of the aliphatic polyesters has been limited due to their low thermal and mechanical properties [2]. The introduction of aromatic component into the polymer backbone is an efficient method to intrinsically improve the material performance, as aromatic polyesters were used in the engineering of plastics [3,4]. We have previously reported the preparation of wholly aromatic liquid crystalline polyarylates (LCPs) with performance as high as an engineering plastic derived from cinnamoyl monomers [5]. The cinnamic acid family includes some natural materials, which has a photosensitive phenylenevinylene and a polymerizable hydroxylcarboxylic acid group [6]. These molecules exist in various plants with a lignin biosynthesis pathway or in microbial metabolites, and can be used as "phytomonomers". The obtained LCP showed degradability, high processability, high heat-resistance. In addition, the LCP showed high-mechanical properties in the molecularly-oriented state, while non-oriented LCP did not show mechanical properties high enough to use in engineering field. Then an increase in their mechanical properties in non-oriented state is required for actual use. One possible method is the use of fillers reinforcing the LCP resin. The chemical structure of the LCP (Fig.1) is very similar with that of lignin which is hyperbranched and composed of many aromatic rings [7]. In bark, lignin showed a quite high affinity with cellulose, then we can imagine the cellulose may be an excellent filler efficiently reinforcing the LCP.

In this study, we hybridized the LCP with celluloses from kenaf fibers and investigated the effects of cellulose on performance of resins.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

p-Coumaric acid {4-hydroxycinnamic acid, 4HCA; Teteyama Kasei, Co. Ltd.} and caffeic acid

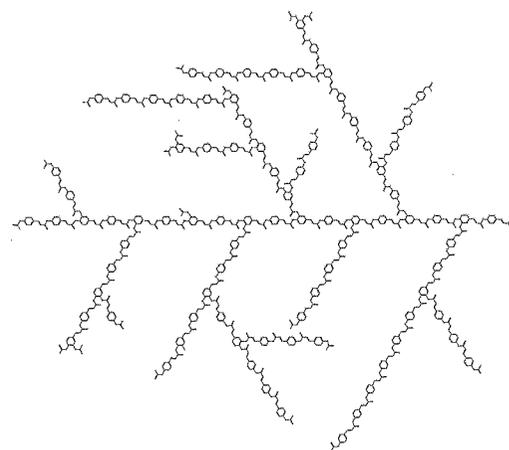


Fig.1. Chemical structure of poly(*p*-coumaric acid-co-caffeic acid) whose monomers are polyphenolic chemicals available in plant cell walls.

(3,4-dihydroxycinnamic acid, DHCA; Teteyama Kasei, Co. Ltd.) were used as monomers, and were used as received. The acetic anhydride (Wako Pure Chemical Industries, Ltd.) and sodium acetate (Wako Pure Chemical Industries, Ltd. used for polymerization were used as received. Kenaf fibers were used as received.

2-2 Preparation of hybrids

Hybrids of poly(4HCA-co-DHCA)s with celluloses were prepared during polymerization from monomers as follows. Monomers of 4HCA (8.0-0.0 g) and DHCA (0.0-8.8 g) were mixed with celluloses from kenaf fibers and mechanically stirred at 150 °C in the presence of acetic anhydride (40 mL) as a condensation reagent plus sodium acetate (trace) as a transesterification catalyst (for about an hour). The solution was further heated to 200 °C, and the polymerization was carried out in vacuo for another six hours. The reaction solution increased its viscosity gradually, and became dark brown. After the reaction was finished and cooled to room temperature to give resins. The resins were milled into powder and

processed in a brass template by hot press.

2.3 Stress-strain measurement.

Young's modulus, mechanical strength at break, and strain at break of resins were measured by three-points bending test of the rectangular samples ($0.3 \times 5.0 \times 25 \text{ mm}^3$). All tests were carried out at $25 \text{ }^\circ\text{C}$ using a fixed nominal displacement rate of $1 \text{ mm}\cdot\text{min}^{-1}$. The data of at least three samples were averaged.

2.4 Dynamic mechanical analyses.

Dynamic mechanical analyses (DMA) of hybrid resins were performed on the rectangular samples ($0.3 \times 5.0 \times 15\text{-}25 \text{ mm}^3$) with an Anton Paar MCR301 with SRF 92 torsion module. Samples were subjected to a 1-Hz cyclic torsion deformation while the temperature was increased from room temperature to $300 \text{ }^\circ\text{C}$ at a rate

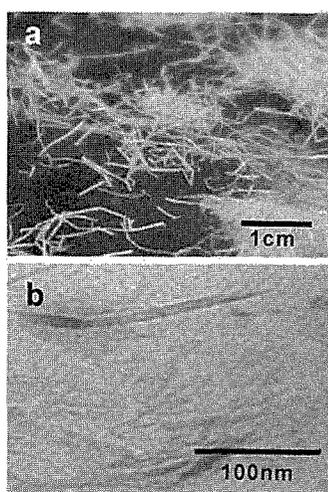


Fig.2. Images of Kenaf fibers. a) Digital image of as-received sample. b) Scanning electron microscopic image of milled fibers by a ceramic pestle.

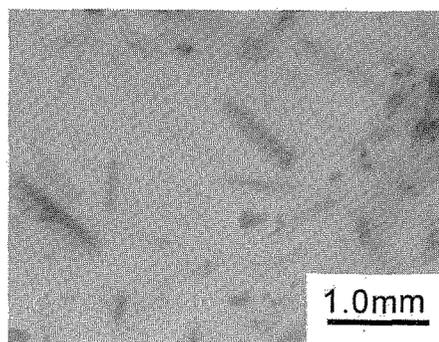


Fig.3. Microscopic image of surface of hybrid resin of poly(4HCA-co-DHCA) with kenaf fibers.

of $5 \text{ }^\circ\text{C}/\text{min}$. The mechanical data were converted to yield storage (G') and loss (G'') moduli as well as loss tangent ($\tan \delta = G''/G'$) versus temperature plots.

3. RESULTS AND DISCUSSION

Poly(4HCA-co-DHCA)s were hyperbranch polymers which have many bulky branches rigid-rod to make difficult to hybridize with other macromolecules. Then we made a polymerization-simultaneous hybridization, i.e. 4HCA and DHCA were copolymerized in the presence of celluloses. Here the feed composition of

4HCA/DHCA was fixed at 60/40 mol/mol. The reaction solution increased its viscosity gradually and became dark brown. The color was darker than the resins prepared without celluloses, presumably due to the impurities such as lignins contaminating celluloses. However infrared (IR) analyses demonstrated that ester linkages between 4HCA and/or DHCA was successfully formed.

Kenaf fibers were very stiff and too long and thick to hybridize with the copolymers as shown in the picture of Fig.2a. Millimeter-scaled broken pieces of kenaf fibers dispersed over the resins after polymerization-simultaneous hybridization (Fig.3). The dispersion gave inhomogeneity functioning as mechanically-weak points bad for performance of hybrid and in fact the mechanical strength of resins was decreased after hybridization using this type of kenaf fibers. Then we milled kenaf hybrids before use. Since the fibers were very stiff, it was difficult to reduce their size using mechanical mill with some blades even if liquid nitrogen was used for freezing the fibers. Using a ceramic pestle gave one of the best methods for grinding down the kenaf fibers into nanometer-scaled fibers. Scanning electron microscopic image illustrated the existence of nanofibers 1-5 nm in thickness and 20-200 nm in length. In this study, the nanofibers were used for fillers reinforcing the copolymer resins. Moreover we tried to cinnamoylation of cellulose fiber aiming to increase the miscibility of the fiber with the copolymers. The chemical reaction used for cinnamoylation was shown in Fig.4. The ground fibers were dispersed into dimethylacetamide (DMAc), and then cinnamoyl chloride was added. The reaction mixture was stirred overnight to give dark-brown powdery nanofibers. The cinnamoylation of the nanofiber surface were confirmed by IR analyses and here abbreviated as c-kenaf.

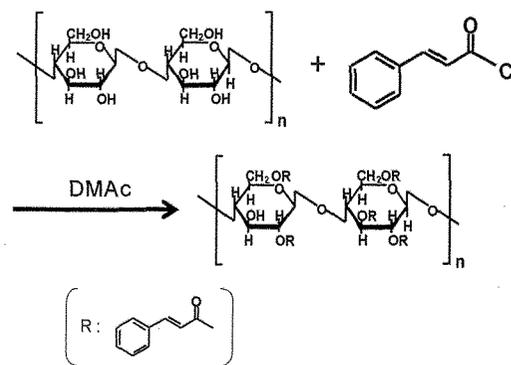


Fig.4. Reaction root of cinnamoylation to cellulose derived from Kenaf fibers.

Effects of hybridization of the copolymers with the nanofibers were investigated in terms of mechanical properties and melting behaviors. The hybrids were successfully processed into rectangular compacts in brass template by hot pressing. The mechanical strength of the resins was measured by three-points bending tests. The mechanical strengths of the copolymer resins without the fillers were 31 MPa which increased to 41 MPa by hybridization using the kenaf nanofiber (10 wt%). The kenaf nanofibers have a reinforcing effect on the hyperbranching copolymers. We tried to prepare the

hybrids just by mixing the melting copolymer with the nanofibers. However, the mechanical strengths were not increased through the hybridization methods. These results indicated that the hyperbranching chains were difficult to interact with the celluloses as imagined above, while the chains might entangle with the celluloses during the propagating of the copolymer chains from monomers.

Dynamic mechanical properties were measured in order to determine the softening temperature of the resins as well as the viscoelasticity. The copolymer resins and every hybrid showed two peaks of $\tan \delta$ around -50 and 150°C (Fig.5a). One at lower-temperature can be assigned to local relaxation and the other at higher-temperature can be assigned to glass transition. While the relaxation at around 50°C did not change regardless of hybridization, softening temperature increased from 139 to 154°C with increasing the composition of kenaf nanofibers up to 10 wt.%. This result indicated that the cellulose directly interact with the hyperbranch copolymers on the molecular level e.g. cross-linking physically. The interaction may be based on hydrogen and/or π -hydrogen interaction of phenols with hydroxyls of sugar units. However, kenaf nanofibers aggregated through their own strong interchain interaction to form apparent nanofiber networks, which reduced miscibility of copolymer chains with nanofibers to show the left shoulders of $\tan \delta$ peaks. The softening temperature of the hybrid with the c-kenaf nanofiber was slightly higher than that of the corresponding hybrid with normal nanofiber. The cinnamoylation can increase the interaction of the nanofibers with hyperbranch polymers, as expected, presumably due to the high compatibility between cinnamoyl groups of nanofibers and copolymers. Moduli in torsion and complex viscosities at room temperature increased by hybridization, presumably due to the reinforcement by kenaf networks. However, one can see the difference in complex viscosity in the melt state (around 200°C) between kenaf and c-kenaf hybrids, as shown in Fig. 5b. From these

results, we can summarize the effects of cinnamoylation of kenaf nanofibers; the cinnamoylation could enhance the interaction of the copolymers with kenaf nanofibers to increase the softening temperature, while it could weaken the kenaf interchain interactions to reduce moduli and viscosities of hybrids.

4. CONCLUSION

The hybrid resins of poly(4HCA-co-DHCA) copolymers with kenaf nanofibers were prepared by polymerization simultaneous hybridization. The kenaf fibers were milled into the nanofibers by a ceramic pestle before use, and we prepared other type of nanofibers by cinnamoylation of the kenaf cellulose. The hybridization had some effects on improving the performance of resins; 1) bending test showed an increase in mechanical strengths, 2) dynamic mechanical analyses in torsion mode showed an increase in softening temperatures and 3) in dynamic moduli and viscosities. On the other hand, the hybridization with cinnamoylated celluloses increased the softening temperature restraining an increase of melt viscosity, which has an advantage in melt processing. Thus the hybridization of the non-oriented copolymer resins with kenaf nanofibers is one of the methods for improving the performance. In order to create the resins with a performance high enough to use actually, further studies using other fillers were required, which are currently progressed.

Acknowledgements

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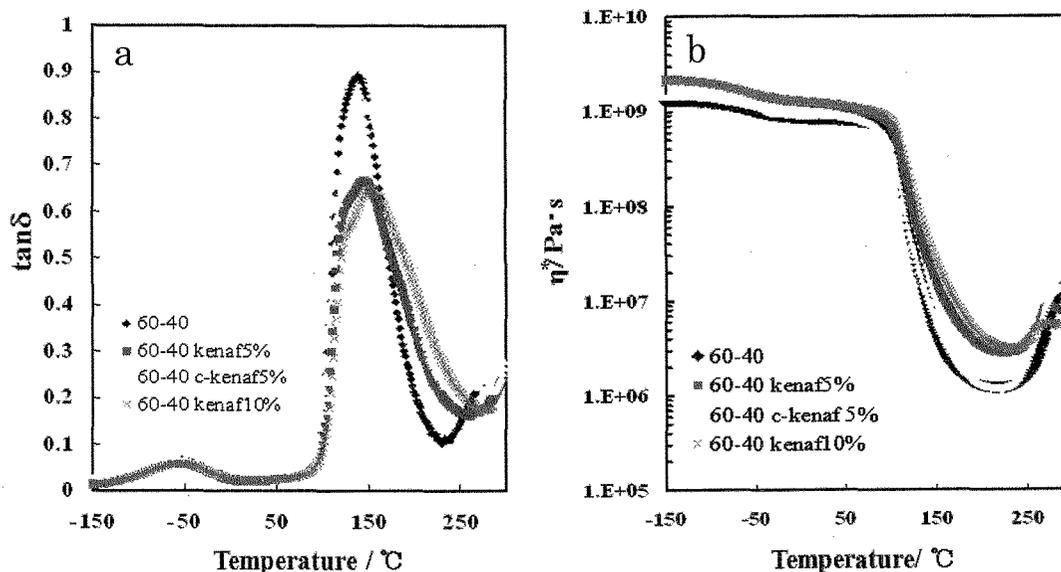


Fig.5. Dynamic mechanical analyses of rectangular compacts of poly(4HCA-co-DHCA) (60/40) hybrids with kenaf cellulose. a) Temperature dependence of loss tangent, $\tan \delta$. b) Temperature dependence of complex viscosities, η^* .

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