Plant Biotechnology 27, 293–296 (2010)

Note

Terminally-catecholized hyper-branched polymers with high performance adhesive characteristics

Daisaku Kaneko, Shougo Kinugawa, Keitaro Matsumoto, Tatsuo Kaneko*

School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923-1292, Japan
* E-mail: kaneko@jaist.ac.jp   Tel: +81-761-51-1631   Fax: +81-761-51-1635

Received June 24, 2009; accepted April 24, 2010 (Edited by K.Igarashi)

Abstract Novel plant-derived, adhesive polymers have been investigated from natural sources as 3,4-dihydroxycinnamic acid (caffeic acid; DHCA) and 4-hydroxycinnamic acid (*p*-coumaric acid; 4HCA) modified by transesterification. These copolymers were found to show strong adhesive characteristics to metal surfaces, which were equivalent to conventional superglues from petroleum resources. This strong adhesive action was due to interactions between catechol groups present at the end of the polymer chains and the metal surfaces.

Key words: Biodegradability, catechols, hyper-branched polymers, plant-derived adhesives.

Recently, for environmental reasons, plant-derived ecoplastics such as poly(lactic acid)s have been investigated. Most of the currently-used ecoplastics are derived from aliphatic polyesters, and are expected to substitute for conventional plastics made from petroleum. However, they have limited applications due to their low fracture strengths and low heat resistance. The reason for these physical weaknesses is the flexible backbones of their polymer chains. The introduction of aromatic components into the polymer backbone has been found to be an efficient method to improve their mechanical and thermal performance. Previously, we have the preparation of wholly aromatic liquid crystalline polyarylates (LCPs) from cinnamoyl monomers such as caffeic acid (3,4-dihydroxycinnamic acid, DHCA) and *p*-coumaric acid (4-hydroxycinnamic acid, 4HCA). Our new plastics were found to have high heat resistance over 150°C. Another characteristic feature of our novel ecoplastics is that they have catechol groups in the chain ends, which are abundant in the hyperbranched architecture of the copolymers. This feature can be expected to produce new functions as adhesives, because it is well known that mussels can adhere strongly to rocks by using an amino acid called "*dopa*" containing the catechol group. Although this phenomenon has been hypothesized to be due to hydrogen bond interactions or covalent bonding between the catechol groups and inorganic surfaces, the precise mechanism has not been elucidated. In this paper, we report an evaluation of the adhesion strength between aromatic copolymers from cinnamates and inorganic materials.

Novel green, adhesive polymers have been investigated from bioavailable sources such as DHCA and 4HCA. The structure of poly(4HCA-*co*-DHCA)s and the reaction formula are shown in Figure 1. The details of the synthesis methods are described in the experimental section. Since the non-acetylated phenolic groups of DHCA and 4HCA show very low direct reactivity with carboxyl groups as compared to the transesterification of acetylated groups, a large amount of cathecols may remained at their chain ends, as shown in the possible structure from Figure 2. This structure was also supported by data from ^{1}H-NMR and FT-IR measurements, and by molecular weight determinations using GPC (data not shown). The presence of catechol groups at the polymer ends could be expected to demonstrate an adhesive action to inorganic surfaces.

To study the possibility of adhesive function, we measured the adhesive force of our new polymers by the T-peel test against stainless steel as illustrated in Figure 3A. The pulling force F of our novel polymer was found to be *c.a.* 1.5 N, which is almost one-half of the value of conventional superglue (Aron alpha, Toagosei Co. Ltd., Japan). In the case of a copper surface, we obtained almost the same data as per stainless steel. This result indicated that our new polymer has strong adhesive action to inorganic surfaces as a green adhesive. After the T-peel test, we observed the fractured surface of the adhesive. Figure 3B shows a snapshot of the fractured surface after the T-peel test. From this picture, it is apparent that the adhesive fractured in its body (cohesive failure), and remained on both surfaces; both stainless

This article can be found at http://www.jspcmb.jp

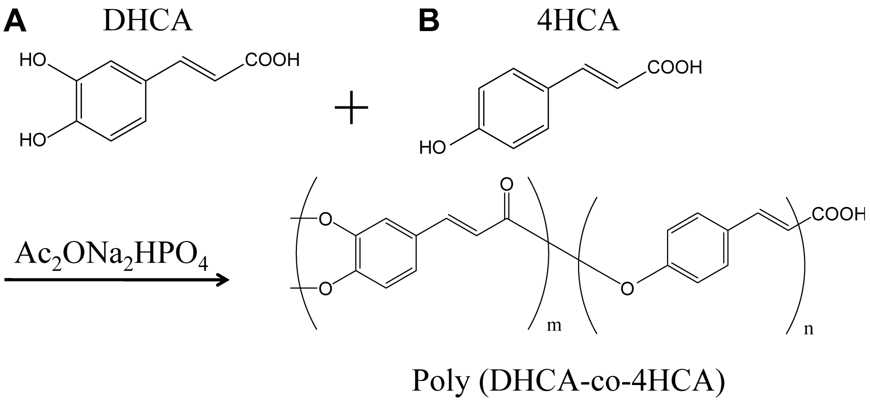

Figure 1. Chemical structure of (A) caffeic acid (3,4-dihydroxycinnamic acid, DHCA) and (B) *p*-Coumaric acid (4-hydroxycinnamic acid, 4HCA). DHCA and 4HCA were copolymerized by a transesterification reaction. DHCA and 4HCA are expected to comprise the straight chains and branching points of polymers, respectively.

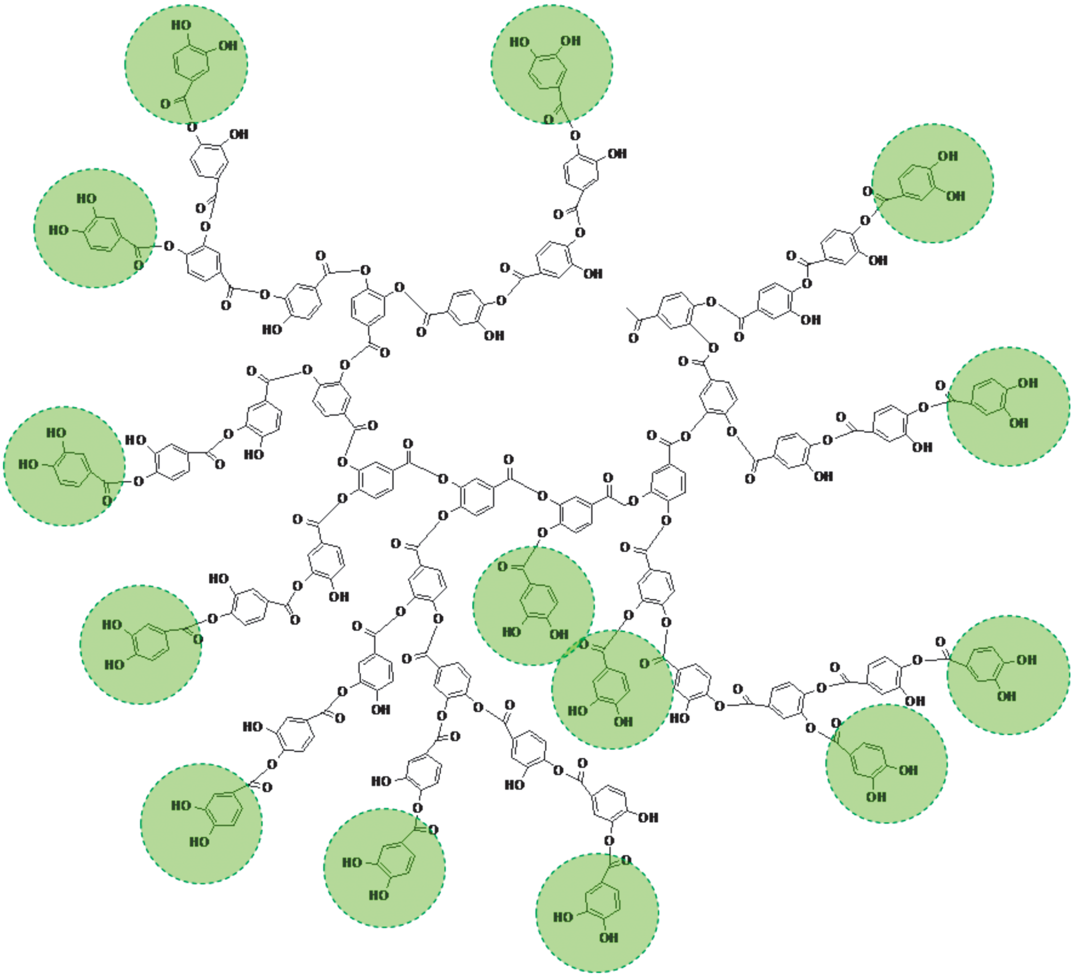

Figure 2. Possible structure of the newly-synthesized adhesive, poly (DHCA-*co*-4HCA), with catechol groups at its polymer ends. The dotted circles in the figure denote the catechol groups at the polymer chain end.

steel surfaces were still completely covered by the adhesive. This result indicates that the adhesion force between the adhesive and the stainless steel surface was sufficiently strong, and that there is a possibility to increase the adhesive force if the bulk strength of adhesive can be enhanced.

For the purposes of enhancing the bulk strength of these adhesives, various composite ratios between DHCA and 4HCA were examined (25%, 33%, 50%, 67% and 75% of 4HCA molar ratios). At this stage, we predicted that an increase in the ratio of 4HCA will enhance the bulk strength of the adhesive, since an

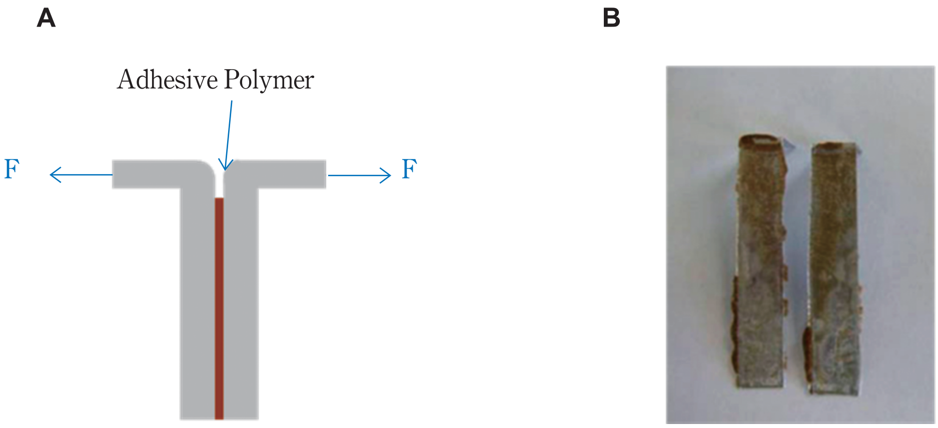

Figure 3. (A) Schematic illustration of the T-peel test. After one pair of stainless steel sheets was glued with some tab space, both tabs were held and pulled in opposite directions. (B) Snapshot of the fractured surfaces after the T-peel test (a pair of stainless steel sheets).

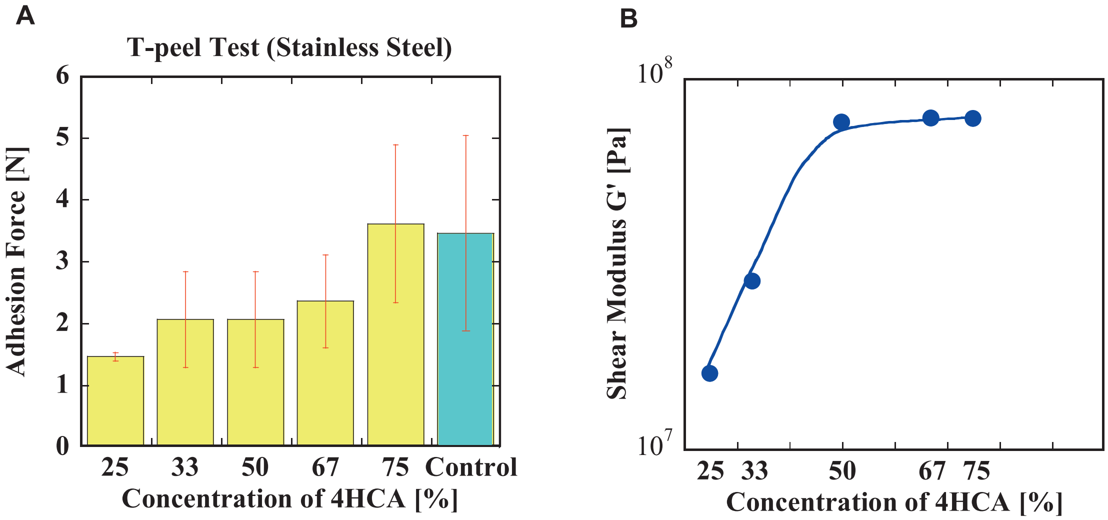

Figure 4. (A) Evaluation of the fracture strength from the T-peel test on stainless steel. Control denotes the results from a conventional superglue tested under the same conditions. (B) Change in the shear modulus of the adhesive depending on the concentration of 4HCA.

increase in the 4HCA content reduces the hyper branched point of the copolymers, leading to excluded-volume interactions between the polymer chains. On the other hand, an increase in the 4HCA ratio is equal to a decrease in the DHCA ratio, thus leading to a reduction in the catechol numbers at the polymer chain end. Although the former effect may increase the adhesion forces by enhancing their bulk strength, the latter may decrease the adhesive interactions at the interface between the adhesive and the metal surface. Thus, we tried to clarify which effects are more pronounced by searching for the optimal conditions.

Figure 4A shows the adhesion forces obtained from T-peel tests as a function of the 4HCA concentration. It was found that the adhesion force increased with increasing 4HCA content. In particular, the adhesion force of the copolymer with a 4HCA composition of 75 mol% became equivalent or was superior to that of a conventional superglue. The fractured surfaces were also observed after the T-peel test to confirm the fracture behaviors at the adhesive bulk. In all cases, it was found that the fracture on the T-peel test occurred in the bulk of the adhesive (cohesive failure). Therefore, the increase in the adhesion force with increasing 4HCA content could be due to the reinforced bulk body of the adhesive, since the bulk shear modulus increased upon increasing the ratio of 4HCA as shown in Figure 4B. These results indicate that copolymers with a low DHCA composition and catechol content still show a stronger adhesive force onto metal surface than the breaking force of the bulk body. Therefore, further increases in adhesion force can be expected if further increases in bulk strength can be achieved.

Since our adhesive polymers were simply constructed from aromatic components, they should have high heat-resistance function. Studies to clarify this are currently in progress.

We synthesized novel, green adhesive polymers from natural sources with catechol groups at their polymer ends. These adhesives demonstrated strong adhesive action with metal surfaces, and were equivalent or superior to conventional superglues. To the best of our knowledge, there have been no reports of this kind of adhesive derived from natural products. Our adhesive polymers have further possibilities in enhancing their adhesion force by reinforcing the bulk body strength, and are expected to have high heat-resistance nature due to the presence of aromatic components.

Monomers of caffeic acid (3,4-dihydroxycinnamic acid, DHCA; Teteyama Kasei, Co. Ltd.) and *p*-coumaric acid (4-hydroxycinnamic acid, 4HCA; Teteyama Kasei, Co. Ltd.) were used as received. Various weight ratios of DHCA and 4HCA (total weight was constant at 16 g) were copolymerized at 150°C in the presence of acetic anhydride (40 mL) as a condensation reagent, plus disodium hydrogen phosphate (trace) as a transesterification catalyst for an hour. The solution was further heated to at 200°C, and incubated at this temperature for six hours in vacuo. After these procedures, dark-brown colored poly (DHCA-*co*-4HCA)s were obtained. These polymers were then milled into a powder, and were then used as adhesive polymers in these experiments. The molecular weight of the adhesive polymers was evaluated by GPC (GPC-101, Shodex), and found to be in the range from twenty thousand to fifty thousand daltons. Structural analysis was performed by H-NMR and IR spectroscopy (data not shown). Poly (DHCA-*co*-4HCA)s was expected to be a hyperbranched structure with catechol groups in the polymer ends, as shown in Figure 1B.

For the T-peel test, the preparation of the test samples was as follows. Stainless steel (or copper) sheets of 0.5 mm thickness were cut into 8.5 mm and 50 mm rectangles in width and length, respectively. A small amount of powder state adhesive was sandwiched between a pair of stainless steel (or copper) sheets, and then pressed by a hot press at 10 MPa and 200ºC in order to exhibit adhesive nature via a hot melting process. The T-peel tests were examined by a tensile materials testing machine (Instron 3365). The shear modulus of the poly (DHCA-*co*-4HCA)s was determined using a rheometer (Physica MCR301, Anton Paar) in oscillation mode.

Acknowledgements

The research was financially supported by the Sakakawa Scientific Research Grant from The Japan Science Society.

References

Kaneko T, Tran HT, Shi DJ, Akashi M (2006) Environmentally-Degradable High-performance Plastics from Phenolic Phytomonomers. *Nat mater* 5: 996–970

Madhavamoorthi P (2004) Vectra liquid crystal polymer fiber. *Synth Fibers* 33: 16–28

Stevens ES (2002) *Green Plastics: An introduction to the new science of biodegradable plastics.* Princeton Univ. Press, New Jersey

Thielemans W, Wool P Richard (2005) Lignin Esters for Use in Unsturated Tehrmosets: Lignin Modification and Solubility Modeling. *Biomacromolecules* 6: 1895–1905

Waite J Herbert (2008) Mussel Power. *Nat Mater* 7: 8–9