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Photochemical Crack Healing in Cinnamate-Based Polymers

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Four kinds of cinnamate-type monomers were synthesized as healing agents. Photoirradiation of the monomers gave cyclobutane-containing crosslinked polymers via [2+2] cycloaddition. Cyclobutane cleavage upon cracking of the crosslinked polymers and re-cycloaddition of the cracked polymers were investigated by FT-IR spectroscopy. Photochemical crack healing was demonstrated by measurement of flexural strength of crosslinked, cracked, and healed polymers. It was observed that microcracks with width of 200 nm to 2 μm were healed by photoirradiation.

Keywords: Photocycloaddition, Crack Healing, Cinnamate, Cyclobutane.

1. INTRODUCTION

Polymeric materials are used in a variety of applications, but they are susceptible to damage induced by various physical and chemical factors. This results in microcrack formation and propagation, ultimately leading to significant reduction in mechanical performance and other desired properties of the materials.[1,2]

Recently, much attention has been paid to crack healing in polymeric matrixes.[3,4] Crack healing in thermoplastics resulted from the interdiffusion of polymer chains and formation of entanglements by heating a cracked sample above its glass transition temperature (T_g).[5] Crack healing induced by small molecules such as methanol and ethanol has also been reported for thermoplastics.[6,7] A self-repair system was developed by incorporating hollow fibers into a polymer composite, so that the fibers can be broken when cracks propagate, releasing repair chemicals.[2] Autonomic healing was accomplished by incorporating microcapsules or microvascular networks from which a healing monomer is released upon crack intrusion and polymerizes by contact with an embedded catalyst within a polymer matrix, bonding the crack faces.[8,9] A re-mendable polymeric material employed a thermally reversible Diels-Alder (DA) reaction.[10] We reported the first example of photochemical crack healing in a polymeric material.[11]

Photochemical [2 + 2] cycloaddition of cinnamoyl groups was chosen as a healing reaction in our work since it readily occurs in the solid state. As part of the backbone or pendant groups in a polymer, cinnamate structure has been used to obtain cyclobutane-type crosslinked polymers via its [2+2] photocycloaddition.[12] Poly(vinyl cinnamate) is one of the best known examples that undergo crosslinking through the photocycloaddition in the film state.[13]

One of the major concerns in the development of our healing system was that the cyclobutane-containing crosslinks should reverse to the original cinnamate structure upon crack formation and propagation so that crack healing can be accomplished by the re-cycloaddition of cinnamoyl groups as illustrated in Scheme 1. First, it is necessary that the cleavage of the cyclobutane structure should be preferred over nonreversible breaking of the other bonds when cracks form and propagate. The exclusive cleavage of cyclobutane was expected based on the fact that the bond energy of cyclobutane C–C is known to be lower than that of the other bonds such as C–O and the other C–Cs because of the high ring strain of cyclobutane.[14,15] Second, it is required that mechanical cleavage of cyclobutane should produce original cinnamoyl groups. The reversion of cyclobutane to original C=C bonds is known to occur photochemically or thermally.[16]

The object of this work is to develop a photochemically mendable polymeric system in which cracks can be readily healed by photoirradiation. Cinnamate-type healing monomers were synthesized, and the applicability of their photocycloaddition to crack healing was investigated. Preliminary evaluation of crack-healing ability of the cinnamates was carried out by flexural strength testing.

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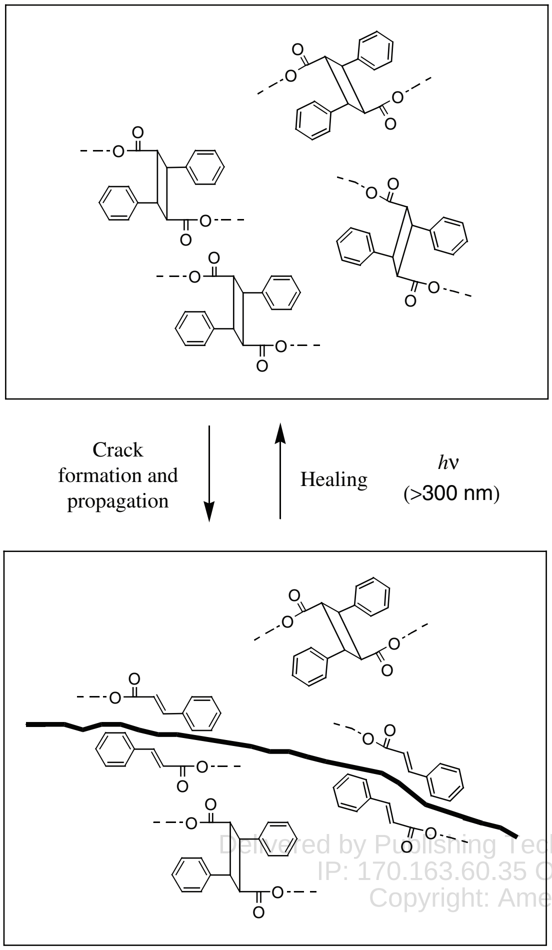


Scheme 1. Schematic illustration of the healing concept in this study.

2. EXPERIMENTAL DETAILS

2.1. General Methods

Cinnamoyl chloride, 1,1,1-tris(hydroxymethyl)ethane, 1,1,1-tris(hydroxymethyl)propane, 2,2-bis(hydroxymethyl)-1,3-propanediol, 2-hydroxyethyl methacrylate, 1,6-bis(2′-methacryloyloxyethoxycarbonylamino)-2, 4, 4-trimethylhexane (UDMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and camphorquinone (CQ) were purchased from Aldrich Chemical Co., and used without purification.

^{1}H and ^{13}C-NMR spectra were taken on a Varian Gemini spectrometer (300 MHz) in deuteriochloroform using tetramethylsilane as an internal standard. Infrared (IR) spectra of the samples were recorded on a Genisis Fourier transform infrared (FT-IR) spectrometer (Mattson Instrument Co.). Elemental analysis was done with an EA 1108 CHNS-O (Fisons Instrument). UV-vis spectroscopy was conducted using a Hewlett-Packard 8453-A. A Sciencetech 500-W high pressure mercury lamp (light intensity: 72.4 mW/cm^2) was used for photoirradiation in conjunction with a UV cut off filter (<300 nm, Optosigma Co). 3-Point flexural test was performed with a universal testing machine, DTU-900MHA (DT&T), at a cross-head speed of 0.75 mm/min according to ISO 4049. A microscope BX-51 (Olympus) was used to take pictures of cracked surfaces.

2.2. Synthesis of 1,1,1-Tris(cinnamoyloxymethyl) Ethane (TCE)

1,1,1-Tris(hydroxymethyl)ethane (0.60 g, 5.0 mmol) and 4-(dimethylamino)pyridine (2.20 g, 18 mmol) were dissolved in 50 mL of tetrahydrofuran (THF). To the solution was added a solution of cinnamoyl chloride (3.00 g, 18 mmol) in THF (15 mL). The resultant solution was refluxed for 5 h. Purification by column chromatography afforded TCE as a viscous oil in a yield of 70%. ^{1}H NMR (CDCl$_3$): δ 1.17 (s, 3H, $C\underline{H}_3$), 4.29 (s, 6H, $OC\underline{H}_2$), 6.45 (d, 3H, $J = 16$ Hz, phC$\underline{H}$), 7.33–7.51 (m, 15H, phenyl), 7.70 (d, 3H, $J = 16$ Hz, phCH=C$\underline{H}$). ^{13}C NMR (CDCl$_3$): δ 17.57 ($\underline{C}H_3$), 39.05 ($\underline{C}CH_3$), 66.46 ($O\underline{C}H_2$), 117.76, 128.32, 129.04, 134.41 (phenyl), 130.57 (ph$\underline{C}$H), 145.53 (phCH=$\underline{C}$H), 166.79 (carbonyl). Elementary analysis: calculated for $C_{32}H_{30}O_6$, C 75.28, H 5.92, O 18.80; found C 74.83, H 6.01.

2.3. Synthesis of 1,1,1-Tris(cinnamoyloxymethyl) Propane (TCP)

To a solution of 1,1,1-tris(hydroxymethyl)propane (0.67 g, 5.0 mmol) in 50 mL of THF was added 4-(dimethylamino)-pyridine (2.38 g, 20 mmol), and the resultant solution was stirred for 10 min. To the solution was added a solution of cinnamoyl chloride (3.25 g, 20 mmol) in THF (15 mL). The resultant solution was refluxed for 24 h. After workup with a saturated aqueous NaHCO$_3$ and then a saturated brine, purification by column chromatography (ethyl acetate: n-hexane = 1:6 in volume) afforded TCP as a pale yellow gum in a yield of 81% (2.12 g). ^{1}H NMR (CDCl$_3$) δ 1.00 (t, 3H, $J = 7.4$ Hz, CH$_3$), 1.66 (q, 2H, $J = 7.4$ Hz, CCH$_2$C), 4.32 (s, 6H, OCH$_2$), 6.45 (d, 3H, $J = 15.9$ Hz, phCH=), 7.33–7.52 (m, 15H, phenyl), 7.70 (d, 3H, $J = 15.9$ Hz, =CHC=O). ^{13}C NMR (CDCl$_3$) δ 7.61 ($\underline{C}H_3$), 23.56 ($C\underline{C}H_2CH_3$), 41.17 ($\underline{C}CH_2CH_3$), 64.60 ($O\underline{C}H_2$), 117.69, 128.20, 128.91, 134.27 (phenyl), 130.43 (ph$\underline{C}$H), 145.35 (phCH=$\underline{C}$H), 166.65 (carbonyl). Elemental analysis: Calcd. for $C_{33}H_{32}O_6$: C 75.55, H 6.15, O 18.30; Found: C 75.23, H 6.24.

2.4. Synthesis of Tetra(cinnamoyloxymethyl) Methane (TECE)

2,2-Bis(hydroxymethyl)-1,3-propanediol (3.40 g, 25 mmol) reacted with cinnamoyl chloride (21.66 g, 0.13 mol) in THF (370 mL) at 90 °C for 48 h. After workup with a saturated NaHCO$_3$, a 5% HCl solution, and a saturated brine, purification by column chromatography (ethyl acetate: n-hexane = 1:6 in volume) afforded TECE as pale yellow powders in a yield of 78% (12.80 g). ^{1}H-NMR ($CDCl_3$): δ 4.31 (s, 8H, $OC\underline{H}_2$), 6.47 (d, 4H, $J = 16$ Hz, $phC\underline{H}$), 7.23–7.52 (m, 20H, phenyl), 7.72 (d, 4H, $J = 16$ Hz, $phCH{=}C\underline{H}$). ^{13}C-NMR ($CDCl_3$): δ 40.07 ($\underline{C}CH_2$), 65.21 ($O\underline{C}H_2$), 118.21, 127.29, 129.10, 135.31 (phenyl), 130.59 ($ph\underline{C}{=}C$), 145.75 ($phC{=}\underline{C}$), 166.63 (carbonyl). Elemental analysis: Calcd. For $C_{41}H_{36}O_8$: C 74.98, H 5.53, O 19.49; Found: C 75.23, H 5.41.

2.5. Synthesis of 2-Methacryloyloxyethyl Cinnamate (MCE)

2-Hydroxylethyl methacrylate (2.60 g, 20 mmol) reacted with cinnamoyl chloride (3.33 g, 20 mmol) in the presence of triethylamine (2.23 g, 22 mmol) in dichloromethane (10 mL) at room temperature for 3 h. After workup with water and an aqueous NaOH, MCE was obtained as a pale yellow oil in a yield of 93% (4.60 g). ^{1}H-NMR ($CDCl_3$): δ 1.95 (s, 3H, $C\underline{H}_3$), 4.44 (s, 4H, $C\underline{H}_2C\underline{H}_2$), 5.51 (s, 1H, $CC\underline{H}_2$), 6.14 (s, 1H, $CC\underline{H}_2$), 6.45 (d, 1H, $J = 16$ Hz, $phCH{=}C\underline{H}$), 7.30–7.57 (m, 5H, phenyl), 7.71 (d, 1H, $J = 16$ Hz, $phC\underline{H}{=}CH$). ^{13}C-NMR ($CDCl_3$): δ 21.8 ($\underline{C}H_3$), 64.6 ($\underline{C}H_2\underline{C}H_2$), 118.96 ($phC{=}\underline{C}$), 128.92, 129.09 (phenyl), 134.11 (phenyl and $CH_3\underline{C}{=}CH_2$), 132.21 ($CH_3C{=}\underline{C}H_2$), 147.21 ($ph\underline{C}{=}C$), 164.53 (carbonyl in cinnamoyl), 165.12 (carbonyl in methacryloyl). Elemental analysis: Calcd. For $C_{15}H_{16}O_4$: C 69.22, H 6.19, O 24.59; Found: C 68.86, H 6.35.

2.6. Crack-Healing Experiment

Photocurable pastes were formulated using a mass ratio of a cinnamate:UDMA:DMAEMA:CQ of 40:57:2:1. The mixtures were stirred for 1 h, and placed under vacuum to remove interior bubbles. Each solution was inserted into a mold made of stainless steel and Teflon. The open end of the mold was covered with a polyethylene film and the solution was photoirradiated for 20 h. The photocured samples had an average dimension of 25 × 2 × 2 mm. About twenty specimens were prepared for each formulation. Cracks were generated with a universal testing machine by pressing the center part of a specimen to a given extent. A part of the cracked samples were photoirradiated to induce healing reaction. Flexural strength was measured for crosslinked, cracked, and healed samples using the universal testing machine. About five specimens were used to obtain an average strength value.

3. RESULTS AND DISCUSSION

Chemical structures of the cinnamate monomers used in this work are shown in Figure 1. TCE and TCP were prepared by reacting cinnamoyl chloride with 1,1,1- tris(hydroxymethyl)-ethane and 1,1,1-tris(hydroxymethyl)propane, respectively.[11,17] Tetrafunctional TECE was synthesized by reaction of cinnamoyl chloride with 2,2-bis(hydroxymethyl)-1,3-propanediol. MCE was prepared from cinnamoyl chloride and 2-hydroxyethyl methacrylate. The chemical structures of the monomers were confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analysis.

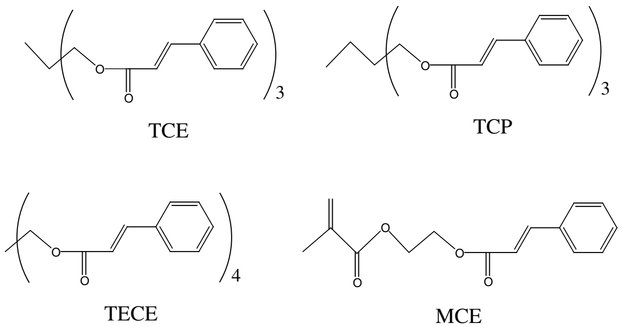


Fig. 1. Structures of the cinnamate monomers.

The cinnamates showed optical absorption peaks around 280 nm, and photoirradiation was carried out through a filter that cuts off UV below 300 nm since the UV of $\lambda < 300$ nm would induce cleavage of cyclobutane ring. As exposure time was increased, absorbance of the cinnamates decreased at 280 nm (Fig. 2). This implied that cinnamoyl C=C bonds underwent [2+2] cycloaddition to form cyclobutane crosslinks.[18] It was confirmed by FT-IR spectroscopy that radical polymerization of cinnamates did not occur under those conditions.[19] The photoreaction was almost completed within 30 min and gave hard, transparent films. The crosslinked films were insoluble in common organic solvents such as chloroform and acetone while the original monomers were quite soluble in those solvents.

The photocrosslinking of the cinnamates was also verified by FT-IR spectroscopy. As shown in Figure 3(a), TCP (coated on a KBr disk) showed absorption bands of cinnamoyl C=O and C=C at 1713 and 1637 cm^{-1}, respectively. Upon irradiation with UV (>300 nm), the carbonyl absorption shifted to 1734 cm^{-1} and C=C absorption almost disappeared (Fig. 3(b)), indicating the photocycloaddition of cinnamoyl groups. The photocycloaddition conversion of the cinnamates was measured based on the ratios of the areas of the two absorption bands (C=C and

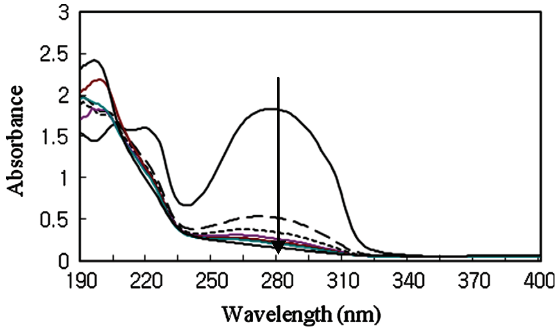


Fig. 2. UV spectral change of a TCE film upon photoirradiation for 0, 20, 40, 60, 80, 100, and 120 s.

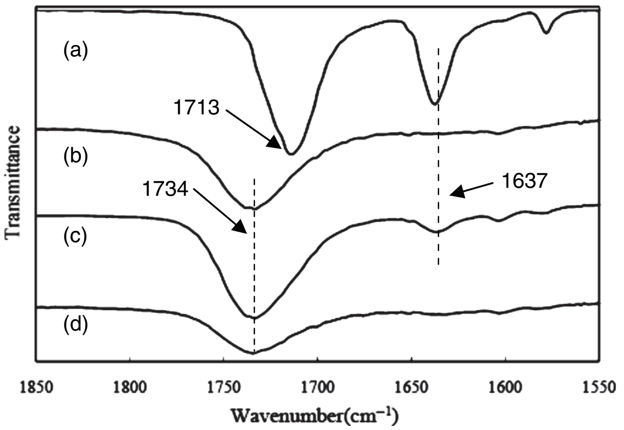


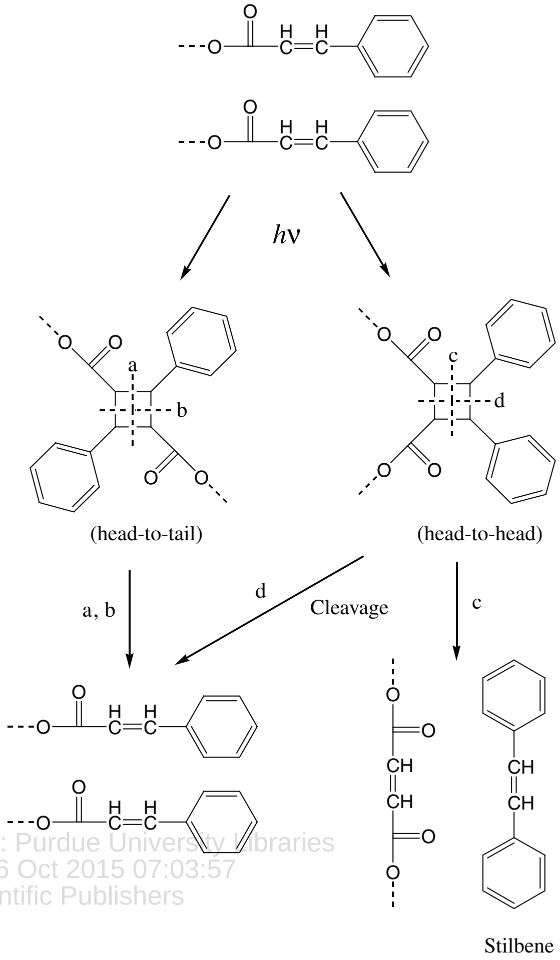
Fig. 3. IR spectra of (a) TCP, (b) a TCP polymer obtained by irradiation, (c) a ground TCP polymer, and (d) a ground TCP polymer after re-irradiation.

C=O as an internal standard) before and after exposure.[11] The conversion of TCE and TCP reached almost 100%, but TECE and MCE showed much lower conversion values (62 and 52%, respectively). Because TECE is somewhat powdery in room temperature, TECE molecules inside a particle or at bottom of a film might have not been exposed enough to light because of light scattering. In the case of MCE, both the methacryloyl C=C and cinnamoyl C=C bonds showed absorption at 1637 cm^{-1}. The low conversion (52%) of MCE is due to the methacryloyl group that is unreactive under the experimental conditions.

Structural change of the cinnamate polymers upon cracking was studied by FT-IR spectroscopy. A TCP polymer was ground into fine particles to create 'a large amount of cracks' for easy detection of structural change. A KBr pellet containing the powders showed reappearance of the cinnamoyl C=C band at 1637 cm^{-1} (Fig. 3(c)). This indicated that the cyclobutane crosslinks were cleaved to reverse to the original cinnamate moieties.

As illustrated in Scheme 2, the [2 + 2] cycloaddition of cinnamoyl groups might give two types of cyclobutane product, head-to-tail and head-to-head adducts.[20,21] Cleavage of the head-to-tail adduct would generate two cinnamate groups (routes a and b). The head-to-head type, on the other hand, would be cleaved to form either two cinnamate groups (route d) or unsaturated ester and stilbene (route c).[21] The IR spectrum of Figure 3(c) showed no band for unsaturated ester C=C (1644 cm^{-1}) or stilbene (1600 cm^{-1}), implying that route c does not occur upon crack propagation. This was also supported by ^{1}H NMR spectroscopy and thin-layer chromatography (TLC): the ground polymer particles were extracted with $CDCl_3$, and stilbene was not detected from the extract.

When the ground sample was re-irradiated, the C=C absorption completely disappeared (Fig. 3(d)), implying that [2 + 2] cycloaddition between cinnamoyl C=C bonds occurred again. Since the polymer particles were dispersed inside a KBr pellet, the cycloaddition reaction might have mostly occurred between adjacent cinnamoyl groups on the surface of each particle. This result, however, indicated that re-cycloaddition can occur between cinnamoyl groups formed by cyclobutane cleavage.



Scheme 2. Formation and cleavage of cyclobutane.

Preliminary evaluation of the crack-healing ability of the cinnamates was conducted. Test specimens were prepared by adding a dimethacrylate monomer, UDMA. In the presence of a radical photoinitiator system (CQ + DMAEMA), UDMA undergoes crosslinking; thus, it has been used as a photocurable monomer, especially in restorative dental composites.[22] A photocurable paste was prepared by mixing a cinnamate, UDMA, DMAEMA and CQ. Upon photoirradiation ($\lambda > 300$ nm), visible light-induced radical polymerization of the methacrylate and UV-induced cycloaddition of a cinnamate occurred simultaneously, and very hard, transparent specimens were obtained. Microcracks were generated in each specimen using a universal testing machine. Cracked specimens were photoirradiated to induce re-cycloaddition of cinnamoyl groups. It was observed that microcracks with width of 200 nm to 2 μm (Fig. 4, left) were healed by photoirradiation for several minutes (Fig. 4, right). Flexural strength was measured for original, cracked, and healed specimens and the results are

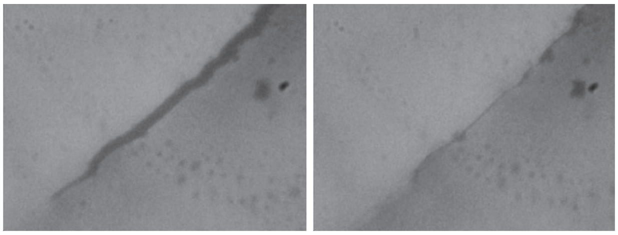


Fig. 4. Microscopic images of a TCP-based sample after crack formation (left) and after healing by re-irradiation (right).

Table I. Flexural strength and healing efficiency of cinnamate-based polymer specimens.

Monomer	Flexural strength (MPa) Original	Cracked	Healed	Healing Efficiency (%)[a]
TCE	42.1	3.1	5.8	13.8
TCP	46.1	1.5	8.2	17.8
TECE	26.0	1.2	2.0	7.7
MCE	54.1	1.7	3.5	6.5

[a] Healing efficiency = healed/original.

summarized in Table I. The flexural strength of the photocrosslinked specimens drastically decreased when cracks were created. The cracked samples showed recovery of flexural strength upon re-irradiation, while a control sample containing no cinnamate showed no recovery. TECE-based samples showed the lowest strength and a very low healing efficiency. This might be due to a higher tendency of TECE to undergo intramolecular cycloaddition because of larger number of cinnamoyl groups in TECE molecule compared to the other cinnamates.[20] The highest flexural strength of MCE-based samples can be ascribed to methacryloyl group in MCE capable of binding to the polymer network through radical polymerization. But the MCE-containing samples showed the lowest healing efficiency probably due to more nonreversible breaking of bonds upon cracking associated with the lowest concentration of cinnamoyl groups in the matrix, compared to the other samples.

4. CONCLUSION

Novel cinnamate-type monomers, TCE, TCP, TECE, and MCE, were synthesized and their photochemical crack-healing ability was demonstrated. The crosslinking of the monomers via $[2+2]$ photocycloaddition, reversion of cyclobutane crosslinks to original cinnamoyl groups, and re-photocycloaddition of resulting cinnamoyl groups were confirmed by FT-IR spectroscopy. The crack healing using the cinnamates was successfully demonstrated by flexural strength testing and optical microscopy. The trifunctional TCE and TCP showed greater crack-healing ability than TECE and MCE. The photochemical healing proceeded very fast, and does not require any catalyst, additive, or severe heat treatment. Our results could give material chemists a valuable insight into the development of efficient polymeric healing systems.

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