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Crack Healing in Polymeric Materials via Photochemical [2+2] Cycloaddition

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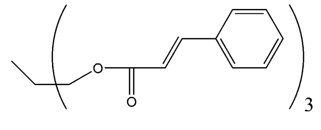
The fatigue in plastics caused by constant or cyclic stress results in microcrack formation and propagation, ultimately leading to significant reduction in mechanical performance of the materials.[1] Recently much attention has been paid to healing of cracks in polymeric matrixes. Crack healing has been accomplished by welding,[2] treatment with small alcohols,[3] incorporating hollow fibers or capsules containing healing monomers,[4,5] and employing a thermally reversible Diels−Alder (DA) reaction.[6] However, so far there has been no report on light-induced crack healing, although photoreactions generally are fast, simple, and environment-friendly.[7] In this paper we describe the first example of photochemical crack healing in a polymeric material.

Photochemical [2 + 2] cycloaddition of cinnamoyl groups was chosen as a healing reaction in this work since the photocycloaddition to form cyclobutane structure[8] and the reversion of cyclobutane to C=C bonds[9] readily occur in solid state. It was expected that the cyclobutane would reverse to original cinnamoyl structure upon crack formation and propagation, and crack healing could be accomplished by the re-cycloaddition of cinnamoyl groups as illustrated in Scheme 1.

A photo-cross-linkable cinnamate monomer, 1,1,1-tris(cinnamoyloxymethyl)ethane (TCE) (Figure 1), was synthesized by reacting 1,1,1-tris(hydroxymethyl)ethane with cinnamoyl chloride.[10] TCE showed an optical absorption peak at 280 nm, and photoirradiation was carried out with UV above 280 nm since the UV of $\lambda <$ 280 nm would induce cleavage of cyclobutane.[11,12] The optical absorbance of TCE at 280 nm decreased with increasing exposure time, indicating the cross-linking of TCE via [2 + 2] photocycloaddition.[13] The irradiated TCE film was hard, transparent, and insoluble in common organic solvents such as chloroform.



TCE

Figure 1. Chemical structure of TCE.

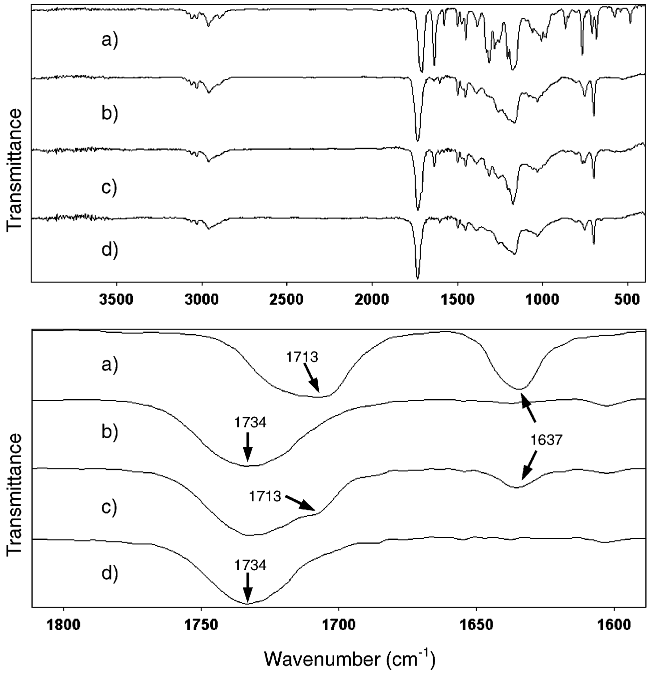


Figure 2. IR spectra of TCE of the whole range (top) and an enlarged range (bottom): (a) before irradiation, (b) after irradiation for 120 s, (c) after grinding, and (d) after re-irradiation for 120 s. The samples for (a) and (b) were films on a KBr disk, and those for (c) and (d) were KBr pellets.

As shown in Figure 2a, a TCE film showed infrared (IR) absorption bands of cinnamoyl C=O and C=C at

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(1) Sauer, J. A.; Hara, M. *Adv. Polym. Sci.* **1990**, *91/92*, 69.

(2) (a) Jud, K.; Kausch, H. H.; Williams, J. G. *J. Mater. Sci.* **1981**, *16*, 204. (b) Kausch, H. H.; Jud, K. *Plast. Rubber Proc. Appl.* **1982**, *2*, 265.

(3) (a) Lin, C. B.; Lee, S.; Liu, K. S. *Polym. Eng. Sci.* **1990**, *30*, 1399. (b) Wang, P.; Lee, S.; Harmon, J. P. *J. Polym. Sci. Part B: Polym. Phys.* **1994**, *32*, 1217.

(4) Dry, C. *Composite Struct.* **1996**, *35*, 263.

(5) White, S. R.; Sottos, N. R.; Geubelle, P. H.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature* **2001**, *409*, 794.

(6) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698.

(7) (a) Arsu, N.; Bowser, R.; Davidson, R. S.; Kahn, N.; Moran, P. M.; Rhodes, C. J. In *Photochemistry and Polymeric Systems*; Kelly, J. M., McArdle, C. B., Maunder, M. J. F., Eds.; Royal Society of Chemistry: London, 1993; p 15. (b) Decker, C. In *Photochemistry and Polymeric Systems*; Kelly, J. M., McArdle, C. B., Maunder, M. J. F., Eds.; Royal Society of Chemistry: London, 1993; p 32.

(8) (a) Paczkowski, J. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; p 5142. (b) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433. (c) Egerton, P. L.; Hyde, E. M.; Trigg, J.; Payne, A.; Beynon, P.; Mijovic, M. V.; Reiser, A. *J. Am. Chem. Soc.* **1981**, *103*, 3859.

(9) Hasegawa, M.; Katsumata, T.; Ito, Y.; Saigo, K.; Iitaka, Y. *Macromolecules* **1988**, *21*, 3134.

(10) 1,1,1-Tris(hydroxymethyl)ethane (0.60 g, 0.0050 mol) and 4-(dimethylamino)pyridine (2.20 g, 0.018 mol) were dissolved in 50 mL of tetrahydrofuran (THF). To the solution was added a solution of cinnamoyl chloride (3.00 g, 0.018 mol) 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%. Elemental analysis: calculated for $C_{32}H_{32}O_6$, C 75.28, H 5.92, O 18.80; found C 74.83, H 6.01. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (s, 3 H, C*H*$_3$), 4.29 (s, 6 H, OC*H*$_2$), 6.45 (d, 3 H, *J* = 16 Hz, phC*H*), 7.33−7.51 (m, 15 H, phenyl), 7.70 (d, 3 H, *J* = 16 Hz, phCH=C*H*). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 17.57 (*C*H$_3$), 39.05 (*C*CH$_3$), 66.46 (O*C*H$_2$), 117.76, 128.32, 129.04, 134.41 (phenyl), 130.57 (ph*C*H), 145.53 (phCH=*C*H), 166.79 (carbonyl).

(11) Chung, C.-M.; Hasegawa, M. *J. Am. Chem. Soc.* **1991**, *113*, 7311.

(12) Photoirradiation was made on an exposure system of Spectra Energy Co. equipped with a 500-W high-pressure mercury lamp (light intensity: 72 mW/cm^2).

(13) Ali, A. H.; Srinivasan, K. S. V. *Polym. Int.* **1997**, *43*, 310.

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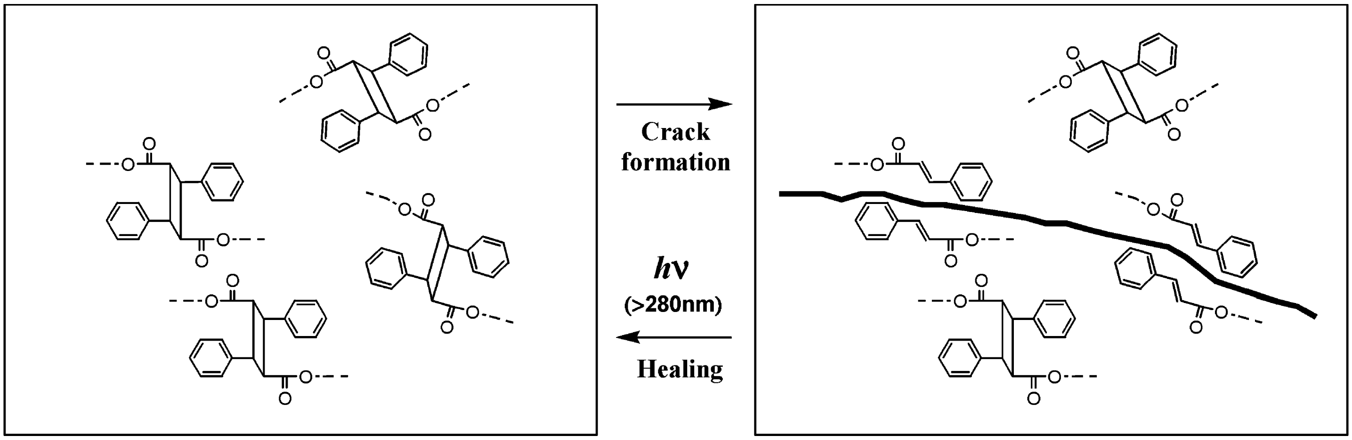
Scheme 1. Schematic Illustration of the Healing Concept in This Study



1713 and 1637 cm^{-1}, respectively. Upon irradiation of the film with UV (>280 nm), the carbonyl absorption shifted to 1734 cm^{-1} and C=C absorption almost disappeared (Figure 2b), which confirmed the photo-cross-linking of TCE.[13,14] The conversion of cinnamoyl groups reached 99% by irradiation for 120 s.[15] Besides the intermolecular cross-linking described above, intramolecular cyclization might also occur since propylene 1,3-dicinnamate undergoes intramolecular cycloaddition.[8c]

Because it is not easy to detect the change in chemical structure of the photo-cross-linked sample upon microcrack propagation, the cross-linked sample was ground in a mortar for 10 min into fine particles. This would help us easily investigate the structural change since a considerable amount of cracks are created when the cross-linked matrix is ground. Both of the cinnamoyl C=O (as a shoulder at 1713 cm^{-1}) and C=C (at 1637 cm^{-1}) bands appeared after grinding (Figure 2c), indicating the reversion of cyclobutane cross-links to the original cinnamate moieties. On the basis of the FT-IR study, 16% of the cyclobutane rings were transformed into cinnamoyl C=C bonds by grinding.[15] A ^{1}H NMR spectrum of the extract from the ground sample also supported the formation of cinnamoyl C=C.[11]

The cinnamate absorption that appeared after grinding (Figure 2c) disappeared again after re-irradiation of the ground sample (Figure 2d). It should be noted that Figure 2d was almost the same as Figure 2b obtained by the first irradiation. First, this suggests that only the cyclobutane cross-links were disconnected (to form cinnamoyl C=C bonds) and the other bonds were almost intact when the sample was ground. The exclusive cleavage of cyclobutane is attributable to its lowest bond strength (due to the high ring strain) compared to that of all the other bonds.[16] It was expected that the cyclobutane would be exclusively cleaved when microcracks formed and propagated in the photo-cross-linked sample. Second, the result implies that [2 + 2] cycloaddition between cinnamoyl C=C bonds occurred again by the re-irradiation. Since the polymer particles were dispersed within a KBr pellet, the cycloaddition reactions might mostly have occurred between adjacent cinnamoyl groups on the surface of each particle. However, this result indicated that re-cycloaddition can occur between cinnamoyl groups formed by cyclobutane cleavage.

Preliminary evaluation of the crack-healing ability of TCE was conducted. Test specimens were prepared using two kinds of methacrylate-based monomers, 1,6-bis(2′-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) and tri(ethylene glycol) dimethacrylate (TEGDMA).[17] TCE, the methacrylates, and camphorquinone (CQ) as a visible-light photoinitiator were mixed to give a viscous paste. The paste was inserted into Teflon molds and irradiated for 10 min with λ > 280 nm. Visible light-induced radical polymerization of the methacrylates and UV-induced [2 + 2] cycloaddition of TCE occurred simultaneously, affording very hard, transparent specimens.[18] It was considered that TCE did not undergo radical reaction since a mixture of TCE and CQ did not show any IR spectral change when irradiated with visible light (λ > 400 nm).[19] This result also implies that CQ did not sensitize the photocycloaddition of TCE while CQ sensitizes the photocycloaddition of conjugated dienes to α-acetoxyacrylonitrile.[20]

Cracks were created in each specimen by inserting it between two stainless steel plates, and by tapping the plates three times using a small hammer. This treatment produced some samples completely broken, which were not used in the healing test. Five cracked samples were randomly chosen and each one was re-irradiated for 10 min with light of λ > 280 nm for crack healing. Measurements of flexural strength were carried out for original, cracked, and healed samples (Table 1).[21] The flexural strength of the original specimens was more

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(14) Pretsch, E.; Buhlmann, P.; Affolter, C. *Structure Determination of Organic Compounds*; Springer: Berlin, 2000; p 292.

(15) The ratios of the calculated areas of the two absorption bands (C=C and C=O as an internal standard) before and after exposure were compared to determine the degree of conversion of the cinnamoyl C=C bonds.

(16) (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structures*; John Wiley and Sons: New York, 2001; p 24. (b) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

(17) Craig, R. G.; Powers, J. M. *Restorative Dental Materials*; Mosby: St. Louis, MO, 2002; pp 191 and 234.

(18) The photocured samples had an average dimension of 25 × 2 × 2 mm. Twenty-five specimens were prepared for each formulation.

(19) Free radical copolymerization of a cinnamate with some vinyl monomers such as methyl methacrylate has been reported to thermally occur in the presence of a peroxide initiator (see Esen, H.; Kusefoglu S. H. *J. Appl. Polym. Sci.* **2003**, *89*, 3882).

(20) Dilling, W. L.; Kroening R. D.; Little, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 928.

(21) Flexural strength was measured with a universal testing machine (Instron 6022) at a cross-head speed of 0.75 mm/min.

Table 1. Flexural Strength and Recovery of TCE-Derived Polymer Specimens

code[b]	UDMA/ TEGDMA (wt %)	TCE (wt %)	Flexural Strength (MPa)[a] original	cracked	healed	recovery (healed − cracked) (MPa)
T40-H	60	40	42.1	3.1	3.2	0.1
T40-P	60	40	42.1	3.1	5.8	2.7
T40-PH	60	40	42.1	3.1	10.9	7.8
T30-PH	70	30	44.3	3.0	9.4	6.4
T20-PH	80	20	45.7	2.9	5.4	2.5
T10-PH	90	10	48.7	3.4	4.9	1.5
T0-PH	100	0	49.6	3.2	3.1	−0.1

[a] Each value was obtained by averaging the strength values for 4−6 specimens. [b] H stands for heating: healing was conducted by heating at 100 °C for 10 min. P stands for photoirradiation: healing was conducted by photoirradiation for 10 min. PH stands for photoirradiation and heating: healing was conducted simultaneously by heating at 100 °C and by photoirradiation for 10 min.

than 40 MPa, which drastically decreased to about 3 MPa when cracks were created. It was demonstrated that TCE acted as a healing agent based on the following results. First, the TCE-derived samples (T40-P, T40-PH, T30-PH, T20-PH, and T10-PH) showed the recovery of flexural strength upon photoirradiation, while T0-PH prepared without TCE had no recovery. Second, as the TCE content was increased, the extent of healing increased (T40-PH, T30-PH, T20-PH, and T10-PH).

When the cracked samples were heated at 100 °C during their photoirradiation, higher recovery was obtained, compared with those only subjected to irradiation: T40-PH exhibited higher recovery than T40-P.[22] However, healing could not be achieved only by heating without irradiation as in the case of T40-H. It was considered that heating the samples might assist low-molar-mass species in diffusing into the void crack areas and the cinnamoyl groups in rearranging for re-photocycloaddition.

In summary, the cross-linking of TCE via [2 + 2] photocycloaddition, reversion of cyclobutane cross-links to original cinnamoyl groups, and re-photocycloaddition of resulting cinnamoyl groups were confirmed by FT-IR spectroscopy. The crack healing using TCE was successfully demonstrated by the measurement of flexural strength of cracked and healed samples. The photochemical healing proceeded very fast,[23] and does not require any catalyst, additive, or severe heat treatment.

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(22) It was confirmed by differential scanning calorimetry and FT-IR spectroscopy that the cyclobutane structure is thermally stable up to 100 °C.

(23) The time periods required for crack healing in the other systems are much longer than that in our system: several hours (refs 3b and 6), 48 h (ref 5), and 8 months (ref 4) compared to 10 min in this work.