View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Journal of
Materials Chemistry

Cite this: *J. Mater. Chem.*, 2012, **22**, 1380

www.rsc.org/materials

PAPER

Fluorescence sensing of microcracks based on cycloreversion of a dimeric anthracene moiety†

Young-Kyu Song, Kwang-Hun Lee, Woo-Sung Hong, Sung-Youl Cho, Hwan-Chul Yu and Chan-Moon Chung*

Received 2nd August 2011, Accepted 27th October 2011
DOI: 10.1039/c1jm13709c

Novel fluorescent crack sensors have been developed based on dimeric anthracene moiety-containing polymers. Two anthracene derivatives, 9-anthraldehyde (AA) and 9-anthracenecarboxylic acid (AC), were photodimerized to obtain cyclooctane-type dimers. Crack-sensing polymers (Poly-AA and Poly-AC) were prepared by crosslinking of poly(vinyl alcohol) by using the dimers as crosslinkers. The polymers afforded transparent, hard coatings. Upon cracking, the polymers exhibited strong optical absorption and fluorescence emission while the uncracked original polymers did not. This was explained by regeneration of the anthracene moiety by mechanochemical cycloreversion of the cyclooctane dimer structure. It was found that the crack planes emitted fluorescence having emission maxima in the range of 500–600 nm when excited with 330–385 nm UV light. Absolute fluorescence quantum yield measurements indicated that the polymers could have good capability of fluorescence crack sensing. Preliminary evaluation of the crack-sensing ability of Poly-AA and Poly-AC was performed with the polymer films, and fluorescence emission was clearly observed along the crack planes upon excitation with 330–385 nm UV light. Poly-AA and Poly-AC are promising as fluorescent crack sensors because the anthracene moiety regenerated upon cracking has relatively long excitation and emission wavelengths as well as strong fluorescence.

Introduction

All hard materials, especially structural materials, are susceptible to degradation, and the long-time degradation process leads to microcrack formation and propagation. Microcracking can severely reduce the mechanical properties and the load carrying capability of the structure. Thermal, electrical, and acoustical properties have also been shown to change as matrix cracks initiate and grow.[1] If cracks can be detected in the initial stage, healing or replacement of the cracked materials can be performed before their complete destruction, which could lead to lifetime extension of the materials and enhancement of public safety.

Because of the importance of crack sensing in the materials field, a variety of approaches to crack sensors have been reported. Ultrasonic sensing, acoustic emission monitoring, and infrared thermograph have been developed to detect and monitor cracks.[2–4] Piezoelectric films were developed to monitor crack initiation and growth based on change in output voltage signals from the sensors.[5–7] Change in electrical resistance of a carbon powder-glass fiber reinforced plastic sensor was measured for crack detection.[8] Optical fiber-type sensors have been developed for structural condition monitoring.[9–14] However, only a few studies have been done on fluorescent crack sensing[15–17] in spite of the fact that fluorescent sensors generally offer the advantages of high sensitivity and ease of detection of exact crack position. Although crack inspection by applying fluorescent dye penetrants on cracked surfaces has been studied,[18,19] this type of dye cannot be included in a class of crack sensors.[15] Recently fluorescence sensing of structural deformation in polymeric materials has been reported.[20,21]

In previous papers we reported on fluorescent crack sensors based on styrylpyrylium salt and alkyl cinnamate compounds.[15,16] Upon cracking, cyclobutane-containing dimeric structures of the compounds were cleaved to generate the corresponding monomeric structures that emit fluorescence. The crack sensors, however, have some limitations in application. The cyclobutane-containing dimeric form of the styrylpyrylium salt is unstable during its synthesis.[22] The cinnamates absorb light at relatively short wavelengths below 330 nm and have absorbance maxima at 280 nm, and such short-wave UV light can induce photodamage to the sensor materials.[23] In addition, the cinnamates have relatively short emission wavelengths: they showed a maximal emission band at 495 nm when excited with 330–385 nm UV light.[15] It is desirable for a fluorescent sensor to emit fluorescence at a longer wavelength because the long wavelength emission can offer the advantages of the use of naked

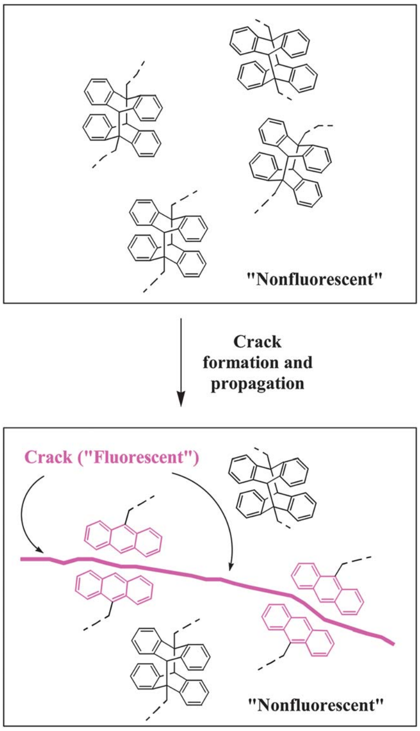
---

Department of Chemistry, Yonsei University, Wonju, Gangwon-do, 220-710, Republic of Korea. E-mail: cmchung@yonsei.ac.kr; Fax: +82-33-760-2182; Tel: +82-33-760-2266

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of Di-AA and Di-AC; UV-vis spectra of AA, AC, Di-AA, and Di-AC; results of the control experiment; and emission spectra of AA, Di-AA, AC, and Di-AC. See DOI: 10.1039/c1jm13709c

eye detection or the use of inexpensive optics, relatively long lived excited states, high quantum yields, low scattering, and deep penetration.[24,25] Therefore, it is necessary to develop an advanced fluorescent crack sensor system having longer excitation and emission wavelengths as well as improved stability.

In this study, novel fluorescent crack sensors were developed based on cycloaddition of anthracene derivatives and cycloreversion of the adducts. It has been reported that anthracene derivatives undergo $4\pi + 4\pi$ photocycloaddition to give cyclooctane-type dimers.[26,27] We thought that if the dimers would return to the original monomers through mechanochemical bond cleavage of the cyclooctane moiety, fluorescence sensing of microcracks could be achieved because the monomer and dimer structures would have quite different fluorescence properties. Our crack-sensing concept is illustrated in Scheme 1. When a crosslinked polymer containing the cyclooctane-type crosslinks undergoes crack formation and propagation, the cyclooctane is mechanochemically cleaved to afford the original anthracene structure that is capable of strong fluorescence emission. Recently mechanochemistry has attracted much attention as a new tool to generate chemical reactivity and the mechanochemistry of polymeric materials has been reviewed in detail in recent literatures.[28,29]



Scheme 1 The crack-sensing concept in this study.

Experimental section

Materials and instruments

9-Anthraldehyde (AA), 9-anthracenecarboxylic acid (AC), poly(vinyl alcohol) (PVA) (M_w = 31 000–50 000 g mol^{-1}), *p*-toluenesulfonic acid monohydrate (*p*-TSA), and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich and used without purification. *N*-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker 400 MHz spectrometer in DMSO-d_6 using tetramethylsilane as an internal standard. The melting point was measured with a Shimadzu DSC-60 at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. IR spectra were recorded on a Spectrum one B Fourier transform infrared (FTIR) spectrophotometer (Perkin-Elmer). UV-vis spectroscopy was conducted using a Lambda 25 UV/Vis spectrometer (Perkin-Elmer). Fluorescence spectra were taken on a LS 55 fluorescence spectrometer (Perkin-Elmer). A fluorescence microscope BX-51 (Olympus) was used to take pictures of cracked surfaces. A UV/Vis spectrometer (EPP2000C, StellarNet) was equipped to the microscope to obtain fluorescence spectra of crack planes. Photoirradiation was conducted with an exposure system (Sciencetech 201-100) equipped with a 500 W high-pressure mercury lamp (light intensity: 72 mW cm^{-2}) in conjunction with a UV cutoff filter of OptoSigma Co.

Synthesis of Di-AA and Di-AC

AA (1.00 g) was dissolved in 20 mL of THF under nitrogen atmosphere. The solution was photoirradiated through a 300 nm cutoff filter for 40 h. A precipitate formed, which was filtered and washed with THF. The solvent was removed in vacuo, and 9-anthraldehyde dimer (Di-AA) was obtained as a pale-yellow powder in a yield of 39%. A photodimer of AC (Di-AC) was prepared in a similar fashion and obtained as a white powder in a yield of 66%. The structures of Di-AA and Di-AC were confirmed by ^{1}H and ^{13}C NMR spectroscopy (see Fig. S1 and S2†).

Synthesis of Poly-AA and Poly-AC

To a solution of Di-AA (0.093 g, 0.225 mmol) in DMF (15 mL) was added 4.00 g of a NMP solution containing 5 wt% PVA. To the solution, *p*-TSA (0.092 g, 0.485 mmol) was added, and the resultant solution was subjected to heating at 60–70 °C for 24 h to induce crosslinking *via* acetalization reaction. During the reaction some precipitate formed. The reaction mixture was concentrated to approximately one-half volume. THF was added to the mixture, and the precipitated Poly-AA was filtered and washed with THF. IR (KBr, cm^{-1}): 1234, 1095, 815.

To a solution of Di-AC (0.100 g, 0.225 mmol) in DMF (15 mL) was added 4.00 g of a NMP solution containing 5 wt% PVA. To the solution, *p*-TSA (0.092 g, 0.485 mmol) was added, and the resultant solution was subjected to heating at 60–70 °C for 24 h to induce crosslinking *via* esterification reaction. During the reaction some precipitate formed. The reaction mixture was concentrated to approximately one-half volume. THF was added to the mixture, and the precipitated Poly-AC was filtered and washed with THF. IR (KBr, cm^{-1}): 1716, 1250, 1110.

Preparation, grinding, and heating of polymer films

50 mg of Poly-AA (or Poly-AC) was dissolved in 2 mL of NMP. In the case of the control experiments using BPO, 20 mg of BPO was additionally dissolved in the solution. Each solution was

filtered with a syringe filter and applied on a slide glass. The solvent was removed at 45 °C for 12 h under atmospheric pressure to obtain a film. In a grinding experiment, the film specimen was vigorously ground in a mortar for 1–4 h at room temperature. The ground samples were dissolved in NMP (2 mL) and the resultant solutions were applied on quartz plates to obtain films for UV-vis and fluorescence spectroscopy. For the ^{1}H NMR study, DMSO-d$_6$ solutions of the ground samples were used. In a heating experiment, the film specimens were heated at 85 °C for 4 h in an oven. Samples for UV-vis and ^{1}H NMR spectroscopy were prepared in a similar fashion as described above.

Determination of absolute fluorescence quantum yield

A DMF (10 mL) solution containing 5 wt% poly(methyl methacrylate) was prepared. To the solution, 1.0×10^{-6} mol of AA, AC, or ethyl cinnamate was added and completely dissolved. In the case of their dimers, 5.0×10^{-7} mol was used. Each solution was applied on a quartz plate and the solvent was removed in vacuo. Absolute quantum yields were measured using a 325 nm He–Cd laser, a 6 inch diameter integration sphere, and a monochromator with a photomultiplier tube (PMT). Powder and film samples were used in the case of ground and unground polymers, respectively.

Crack-sensing test

10 mg of Poly-AA (or Poly-AC) was dissolved in NMP (0.5 mL) at 50–60 °C, and the solution was applied on a surface of a plastic substrate. The solvent was removed at 75 °C for 12 h to obtain a film, and the plastic was slightly bent to generate cracks in the film. The cracks formed were observed using the fluorescence microscope by exposure of the film to UV or white light.

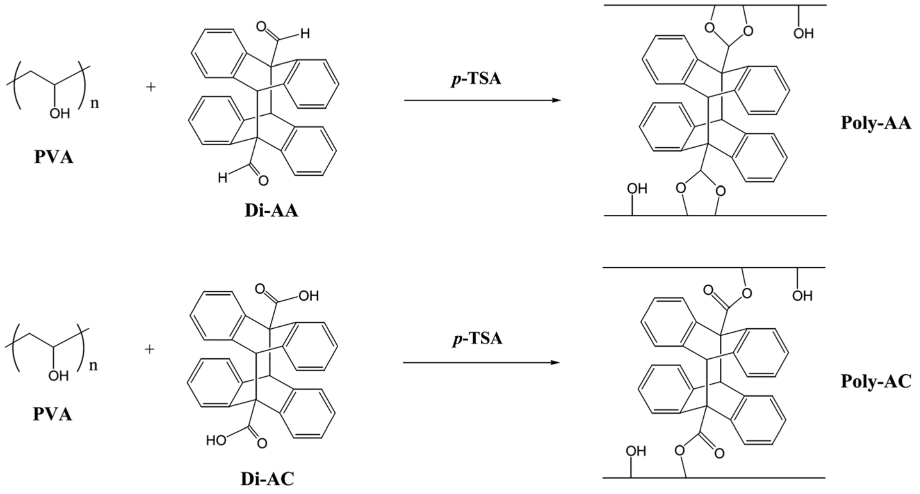
Results and discussion

9-Substituted anthracenes are known to form cyclooctane-type dimers upon irradiation with light of $\lambda > 300$ nm under inert atmosphere.[27] It was reported that 9-anthracenecarboxylic acid (AC) gives mainly a head-to-tail dimer along with a small amount of a head-to-head dimer.[30] NMR spectroscopic studies showed that the dimer of AC (Di-AC) prepared in this work has only a head-to-tail structure (see Fig. S1†).[31] A dimer of 9-anthraldehyde (AA), Di-AA, was also prepared by photoirradiation of AA and confirmed to have a head-to-tail structure by NMR spectroscopy (see Fig. S2†). Di-AA and Di-AC were stable under usual synthetic conditions, and their melting points were measured to be 189 °C and 226 °C, respectively.

Two types of crosslinked polymers, Poly-AA and Poly-AC, were prepared using Di-AA and Di-AC, respectively (Scheme 2). Poly-AA was prepared *via* acetalization between hydroxyl groups in PVA and formyl groups in Di-AA in the presence of *p*-toluenesulfonic acid (*p*-TSA). The formation of Poly-AA was confirmed by FT-IR spectroscopy (Fig. 1). After the reaction, the absorption peak due to the formyl C=O bonds (1727 cm^{-1}) disappeared, and new peaks due to the acetal groups appeared at 1234 ($\nu_{C\text{–}O}$), 1095 ($\nu_{C\text{–}O\text{–}C}$), and 815 cm^{-1} (skeletal vibration of acetal ring) (Fig. 1(a) and (b)). On the other hand, Poly-AC was synthesized through esterification between hydroxyl groups in PVA and carboxyl groups in Di-AC in the presence of *p*-TSA. The IR study indicated that absorption peaks at 1716 cm^{-1} ($\nu_{C=O}$) and 1250 and 1110 cm^{-1} ($\nu_{C\text{–}O}$) newly appeared, while the carboxyl C=O peaks at 1698 cm^{-1} disappeared after the esterification reaction, implying the formation of Poly-AC (Fig. 1(c) and (d)). The crosslinked polymers afforded transparent, hard coatings.

In order to investigate the mechanochemical cycloreversion of the dimeric anthracene moiety upon cracking, Poly-AA (or Poly-AC) coating specimens were ground into fine particles in a mortar to create 'a considerable number of cracks'. It was found that each ground sample (50 mg) was completely dissolved in NMP (2 mL) at room temperature to form a clear solution. In contrast, when the original polymers (50 mg) were put in NMP (2 mL), a small amount of insoluble portion (10–20 wt%) was observed. A NMP solution containing the ground sample was applied on a quartz plate for UV-vis spectroscopy. As shown in Fig. 2(a), the coating of the ground Poly-AA showed optical absorption in the range of 325 to 475 nm. In contrast, Poly-AA itself exhibited only weak absorption above 325 nm (Fig. 2(a)). Poly-AC showed a similar tendency upon grinding; the ground Poly-AC showed strong optical absorption (Fig. 2(b)). The results imply the regeneration of the anthracene moiety upon grinding of the polymers. This can be supported by the comparison of optical absorption of dimeric and monomeric forms of AA: Di-AA shows practically no absorption while AA shows strong absorption due to its highly conjugated structure (see Fig. S3(c) and (a)†, respectively). A similar tendency was observed in UV-vis spectra of AC and Di-AC (see Fig. S3(b) and (d)†, respectively).

It has been reported that dimeric anthracene derivatives cyclorevert to monomeric ones photochemically or thermally.[24] In this work all the samples were carefully treated in a dark place, so there would be no possibility of photochemical cycloreversion of the dimeric anthracene moiety. In order to rule out the possibility of the thermal cycloreversion, several control experiments were conducted. Especially, there was concern that local hot spots may be created by grinding and the thermal cycloreversion may be induced by thermal energy. Benzoyl peroxide (BPO), a well-known initiator for radical polymerization, was employed as a kind of 'temperature indicator'. When heated at 85 °C for 4 h in solution, BPO completely decomposed (see Fig. S4†). It was reported that BPO decomposes below 100 °C in the film and the rate and product of decomposition vary depending on the structure of the matrix material.[32] In this study, a transparent film of Poly-AC (or Poly-AA) containing BPO was prepared and subjected to heating at 85 °C for 4 h in an oven. After the thermal treatment of the film, BPO almost decomposed (see Fig. S5†). We did not perform the analysis of the decomposition product of BPO because it is beyond the scope of this work. On the other hand, the Poly-AC (or Poly-AA) film containing BPO was ground vigorously in a mortar for 4 h at room temperature. Fig. S6† shows that BPO did not decompose during the grinding. This indicates that the sample temperature does not rise up to 85 °C during the grinding. When a Poly-AC (or Poly-AA) film was heated at 85 °C for 4 h in an oven, practically no increase in optical absorption was observed (see Fig. S7 and S8†) while a significant increase in absorbance was induced by grinding the polymers (Fig. 2). Based on these results from the control experiments, thermal cycloreversion of the dimeric



Scheme 2 Preparation of Poly-AA and Poly-AC.

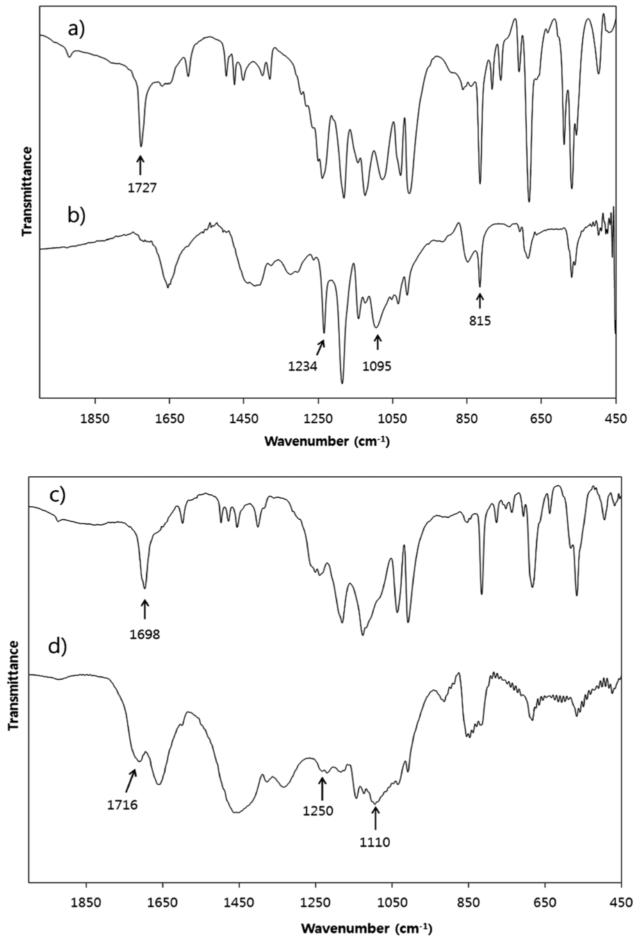


Fig. 1 IR spectra of (a) a mixture of Di-AA, PVA, and *p*-TSA; (b) Poly-AA; (c) a mixture of Di-AC, PVA, and *p*-TSA; and (d) Poly-AC.

anthracene moiety to a monomeric one did not occur by grinding.

The results of the grinding study of Poly-AA and Poly-AC, in conjunction with the results of the control experiments, imply the following two facts. First, the grinding of Poly-AA and Poly-AC resulted in mechanical cleavage of the crosslinks, leading to the greater solubility of the ground polymers than that of the unground ones. Second, the anthracene moiety was regenerated by the cleavage of the crosslinks (*i.e.*, mechanochemical cycloreversion of the dimeric adducts) (Scheme 1). The grinding study confirmed the cycloreversion of the dimeric anthracene moiety to a monomeric one upon cracking. On the other hand, grinding of Di-AA and Di-AC did not induce any change of their chemical structure (see Fig. S9†). This indicates that the dimers need to be bound to a polymer matrix in order for them to undergo the cycloreversion.

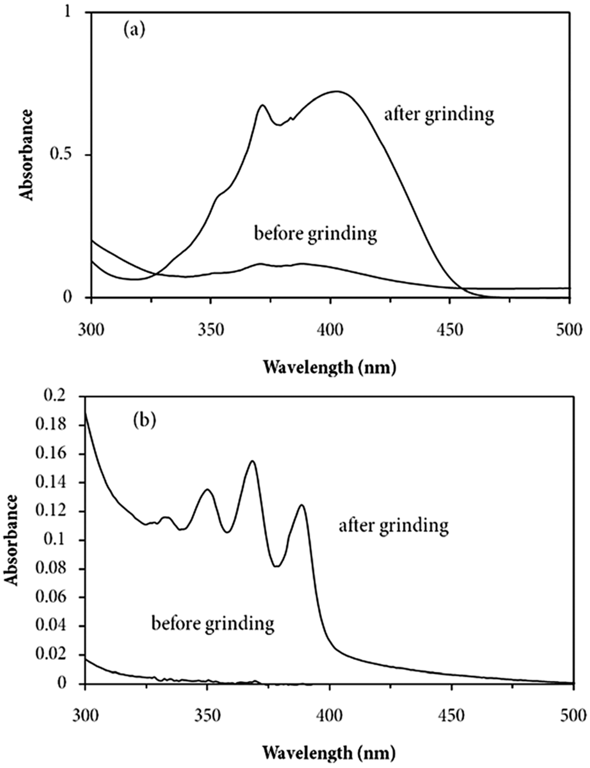


Fig. 2 UV-vis spectra of the polymers before and after grinding: (a) Poly-AA and (b) Poly-AC.

To the best of our knowledge, our result is the first example of mechanochemical cycloreversion of the cyclooctane-type dimeric anthracene moiety to a monomeric one. As a similar case, the cycloreversion of cyclobutane-type dimers of cinnamates has been known to occur upon cracking.[15,33] The cleavage of the cyclobutane was preferred over breaking of the other bonds in a polymer matrix when cracks form and propagate. This is attributable to the lowest bond strength of the cyclobutane C–C bond (due to the high ring strain of cyclobutane) compared to that of all the other bonds. On the other hand, in a crosslinked polymer containing a Diels–Alder (DA) adduct, its retro-DA reaction is the major reason for crack propagation because the bond strength between diene and dienophile of the DA adduct is much lower than that of all the other covalent bonds.[34,35] Recently it has been reported that ultrasound induces mechanochemical cycloreversion such as retro [4 + 2] or [2 + 2] cycloaddition reactions and 1,3-dipolar cycloreversions.[36–38] In our present study, the cycloreversion of the anthracene adducts might be due to lower bond strength between the anthracene moieties compared to that of the other covalent bonds. Another possible driving force of the cycloreversion might be the restoration of the anthracene aromaticity.

Fluorescence spectroscopy was conducted for the ground polymers. As shown in Fig. 3, the ground Poly-AA and Poly-AC showed fluorescence emission while the unground original polymers showed only weak emission. The fluorescence emission from the ground polymers is probably due to the regenerated anthracene structures upon grinding. This can be supported by the comparison of emission from dimeric and monomeric forms of AA (or AC): Di-AA (or Di-AC) shows practically no emission while AA (or AC) shows strong emission (see Fig. S10 and S11†, respectively). On the other hand, in order to investigate the fluorescence emission from crack planes, some cracks were generated in the coatings of Poly-AA and Poly-AC. Using a fluorescence microscope equipped with a UV-vis spectrometer, the emission spectra of the crack planes were obtained by detecting fluorescence emitted from areas along the crack lines (Fig. 4). The crack planes emitted strong fluorescence having maxima in the range of 500–600 nm when excited with 330–385 nm UV light. In contrast, the coating surfaces without crack showed much lower emission (Fig. 4). This suggests that the original anthracene moiety was regenerated upon cracking as supported by the grinding study, and Poly-AA and Poly-AC could be used as "turn-on" type fluorescent crack sensors.

It should be noted that the regenerated anthracene structures in Poly-AA and Poly-AC coatings have the wavelengths of maximum emission of 568 and 527 nm, respectively, which are longer than that of alkyl cinnamates (495 nm) when excited with 330–385 nm UV light (Fig. 4). In addition the anthracene structures absorb light above 325 nm (Fig. 2) while the absorption of the alkyl cinnamates is very weak in the same range. These relatively long excitation and emission wavelengths of the new

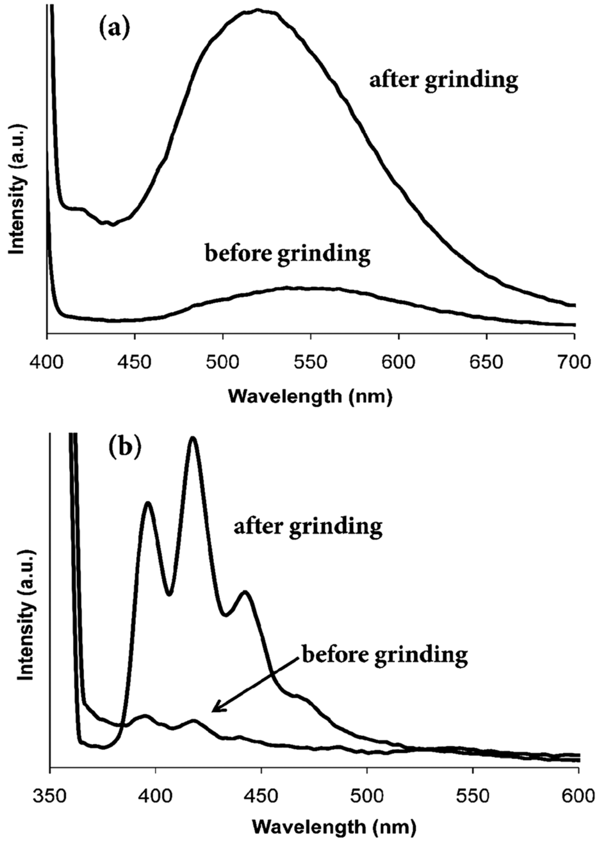


Fig. 3 Emission spectra of the polymers before and after grinding: (a) Poly-AA and (b) Poly-AC. Excitation wavelengths were 380 nm for (a) and 350 nm for (b).

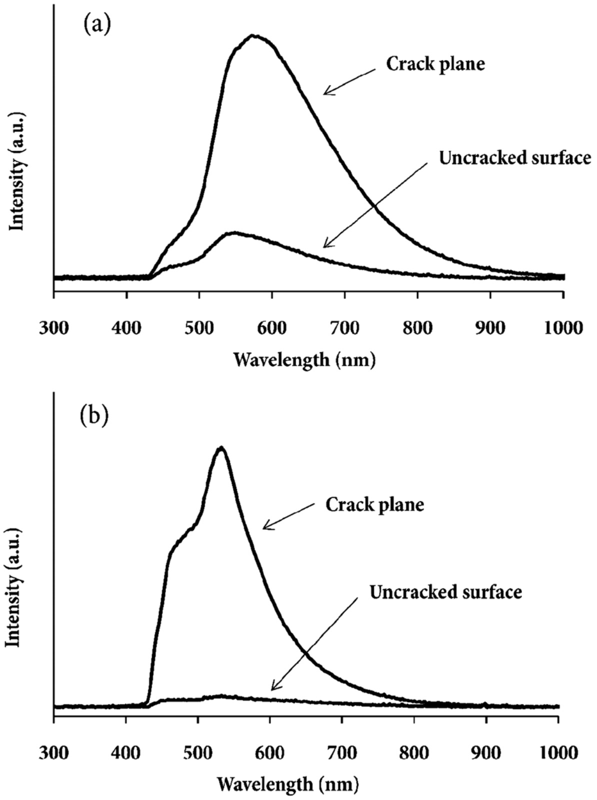


Fig. 4 Emission spectra of crack planes and uncracked surfaces of (a) Poly-AA and (b) Poly-AC. The spectra were obtained using a fluorescence microscope equipped with a UV-vis spectrometer by excitation with 330–385 nm UV light.

Table 1 Absolute fluorescence quantum yields of AA, AC, Di-AA, Di-AC, Poly-AA, Poly-AC, ethyl cinnamate, and its photodimer

Compound	Quantum yield (%)	Compound	Quantum yield (%)
AA	5.49	Di-AA	1.46
AC	15.70	Di-AC	1.53
Ethyl cinnamate	1.42	Ethyl cinnamate dimer	0.21
Poly-AA (after grinding)	0.58	Poly-AA (before grinding)	0.19
Poly-AC (after grinding)	8.36	Poly-AC (before grinding)	0.40

fluorescent crack sensors could provide several advantages as stated in the Introduction.

Absolute fluorescence quantum yields of AA, AC, and their dimers were measured using poly(methyl methacrylate) films containing the compounds with a 325 nm He–Cd laser (Table 1). The quantum yield values of the monomers (5.49% for AA and 15.70% for AC) were much higher than those of their dimers (1.46% for Di-AA and 1.53% for Di-AC). It was found that AA and AC showed higher quantum yield values than ethyl cinnamate under the same conditions. As expected, the ground polymers showed even higher quantum yields than the original polymers.

Preliminary evaluation of the crack-sensing ability of Poly-AA and Poly-AC was performed. A NMP solution of Poly-AA (or Poly-AC) was applied on a surface of a plastic substrate. The solvent was removed to obtain a film, and the plastic was slightly bent to generate cracks in the film. The cracks formed were observed under white light to have widths below 10 μm (Fig. 5(a)). As shown in Fig. 5(b), strong fluorescence emission was clearly observed along the cracks upon excitation with 330–385 nm UV light. Our fluorescent crack sensors could provide an important advantage of facile detection of exact crack position compared to the other types of crack sensors.

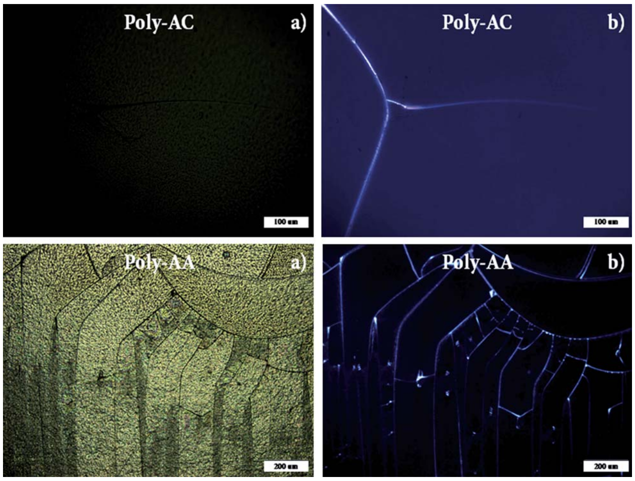


Fig. 5 Photographs of the cracks formed in films of Poly-AC and Poly-AA. The photographs were obtained using a fluorescence microscope equipped with a CCD camera (a) under white light and (b) under 330–385 nm UV light.

Conclusions

The fluorescence-based crack sensing could be accomplished by using Poly-AA and Poly-AC containing the dimeric anthracene moiety. It was demonstrated that, upon cracking, the polymer films underwent the cleavage of the cyclooctane-type dimer structure, leading to regeneration of the anthracene moiety having strong fluorescence. Because the anthracene moiety is regenerated along propagating cracks, our system could easily detect the exact position of cracks. Di-AA and Di-AC are very useful because they can be used to crosslink many polymers that can react with formyl or carboxyl groups to obtain a variety of crack-sensing polymers. Poly-AA and Poly-AC are very promising as fluorescent crack sensors because the anthracene moiety regenerated upon cracking has relatively long excitation and emission wavelengths as well as strong fluorescence.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0077531). This work was also supported in part by the Yonsei University Research Fund of 2009.

References

1 C. Dry, *Compos. Struct.*, 1996, **35**, 263–269.
2 A. A. Shah, Y. Ribakov and S. Hirose, *Mater. Des.*, 2009, **30**, 775–782.
3 S. Degala, P. Rizzo, K. Ramanathan and K. A. Harries, *Constr. Build. Mater.*, 2009, **23**, 2016–2026.
4 C.-C. Cheng, T.-M. Cheng and C.-H. Chiang, *Automation in Construction*, 2008, **18**, 87–92.
5 A. L. Gama and S. R. K. Morikawa, *Exp. Mech.*, 2008, **48**, 247–252.
6 R. Ali, D. R. Mahapatra and S. Gopalakrishnan, *Smart Mater. Struct.*, 2005, **14**, 376–386.
7 S. Rattanachan, Y. Miyashita and Y. Mutoh, *Sci. Technol. Adv. Mater.*, 2005, **6**, 704–711.
8 S.-G. Shin, H.-J. Lim and J.-H. Lee, *Han'guk Chaelyo Hakhoechi*, 2003, **13**, 732–736.
9 B. Zhang, B. Benmokrane, J.-F. Nicole and R. Masmoudi, *Mater. Struct.*, 2002, **35**, 357–364.
10 Y. Zhao and F. Ansari, *Sens. Actuators, A*, 2002, **100**, 247–251.
11 A. Singhvi and A. Mirmiran, *Journal of Reinforced Plastics and Composites*, 2002, **21**, 351–373.
12 I. B. Kwon, C. G. Kim and C. S. Hong, *Compos. Sci. Technol.*, 1997, **57**, 1639–1651.
13 R. Montanini and L. Dacquisto, *Smart Mater. Struct.*, 2007, **16**, 1727–1735.
14 K. T. Wan and C. K. Y. Leung, *Sens. Actuators, A*, 2007, **135**, 458–464.
15 S.-Y. Cho, J.-G. Kim and C.-M. Chung, *Sens. Actuators, B*, 2008, **134**, 822–825.

16 S.-Y. Cho, J.-E. Kim, J.-G. Kim and C.-M. Chung, *Polymer (Korea)*, 2008, **32**, 189–192.
17 N. Bruns, K. Pustelny, L. M. Bergeron, T. A. Whitehead and D. S. Clark, *Angew. Chem., Int. Ed.*, 2009, **48**, 5666–5669.
18 E. R. Generazio, *Adv. Ceram. Matrix Compos.*, 1996, 169–201.
19 V. Zilberstein, D. Grundy, V. Weiss, N. Goldfine, E. Abramovici, J. Newman and T. Yentzer, *Int. J. Fatigue*, 2005, **27**, 1644–1652.
20 C. M. Kingsbury, P. A. May, D. A. Davis, S. R. White, J. S. Moore and N. R. Sotts, *J. Mater. Chem.*, 2011, **21**, 8381–8388.
21 S. Karthikeyan and R. P. Sijbesma, *Macromolecules*, 2009, **42**, 5175–5178.
22 K. Hesse and S. Hunig, *Liebigs Ann. Chem.*, 1985, 715–739.
23 S.-Y. Cho, J.-G. Kim and C.-M. Chung, *J. Nanosci. Nanotechnol.*, 2010, **10**, 6972–6976.
24 R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3936–3953.
25 L. Shen, X. Lu, H. Tian and W. Zhu, *Macromolecules*, 2011, **44**, 5612–5618.
26 H.-D. Becker, *Chem. Rev.*, 1993, **93**, 145–172.
27 H. Bouas-Laurent, A. Castellan, J.-P. Desvergne and R. Lapouyade, *Chem. Soc. Rev.*, 2000, **29**, 43–55.
28 A. L. Black, J. M. Lenhardt and S. L. Craig, *J. Mater. Chem.*, 2011, **21**, 1655–1663.
29 M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White and J. S. Moore, *Chem. Rev.*, 2009, **109**, 5755–5798.
30 T. Wolff and N. Muller, *J. Photochem.*, 1983, **23**, 131–140.
31 Y. Ito and H. Fujita, *J. Org. Chem.*, 1996, **61**, 5677–5680.
32 H. Minato, C. Kato and I. Mori, *Polym. J.*, 1976, **8**, 167–173.
33 C.-M. Chung, Y.-S. Roh, S.-Y. Cho and J.-G. Kim, *Chem. Mater.*, 2004, **16**, 3982–3984.
34 X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698–1702.
35 S. D. Bergman and F. Wudl, *J. Mater. Chem.*, 2008, **18**, 41–62.
36 K. M. Wiggins, J. A. Syrett, D. M. Haddleton and C. W. Bielawski, *J. Am. Chem. Soc.*, 2011, **133**, 7180–7189.
37 J. N. Brantley, K. M. Wiggins and C. W. Bielawski, *Science*, 2011, **333**, 1606–1609.
38 M. J. Kryger, M. T. Ong, S. A. Odom, N. R. Sottos, S. R. White, T. J. Martinez and J. S. Moore, *J. Am. Chem. Soc.*, 2010, **132**, 4558–4559.