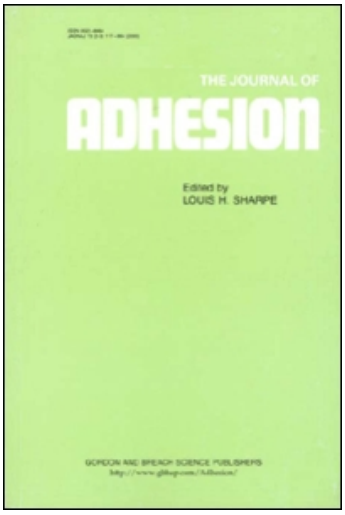

The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Development of a Light-Deactivatable PSA *Via* Photodimerization

Scott R. Trenor[a]; Timothy E. Long[b]; Brian J. Love[c]
[a] Macromolecular Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA [b] Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA [c] Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

To cite this Article Trenor, Scott R. , Long, Timothy E. and Love, Brian J.(2005) 'Development of a Light-Deactivatable PSA *Via* Photodimerization', The Journal of Adhesion, 81: 2, 213 — 229
To link to this Article: DOI: 10.1080/00218460590922011
URL: http://dx.doi.org/10.1080/00218460590922011

The Journal of Adhesion, 81:213–229, 2005

ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460590922011

Taylor & Francis
Taylor & Francis Group

Development of a Light-Deactivatable PSA *Via* Photodimerization

Scott R. Trenor
Macromolecular Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

Timothy E. Long
Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

Brian J. Love
Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA

Photoreactive pressure-sensitive adhesives (PSAs) were developed to create photodeactivatable resins. Coumarin-functionalized poly(2-ethylhexyl acrylate-co-hydroxyethyl acrylate) was prepared via *traditional free-radical polymerization followed by quantitative hydroxyl group esterification and studied as model photoactive PSAs. The polymers were solution-cast into films and photocrosslinked* via *dimerization of the coumarin derivatives with ultraviolet-A (UVA) light irradiation (>300 nm). Ultraviolet-Visible (UV-Vis) spectroscopy indicated that approximately 60% of the coumarin groups photodimerized when exposed to 22 J cm^{-2} of UVA irradiation. The formation of reversible coumarin crosslinks gelled the model PSA and reduced peel strength from 1.62 to 0.05 N/mm. UVC irradiation photocleaved the coumarin dimers, reducing the crosslink density and raising the peel strength to 0.10 N/mm. This reversibility of the coumarin photodimerization and consequent peel-strength modulation may provide a mechanism for the repeated use of these model adhesives.*

Keywords: Coumarin; Photodimerization; PSA; UV crosslinking

Received 12 August 2004; in final form 6 December 2004.

The authors acknowledge financial support from the Virginia Tech Center for Adhesive and Sealant Science (CASS) and the Adhesive and Sealant Council Education Foundation. They also acknowledge support by the U.S. Army Research Laboratory and the U.S. Army Research Office under Grant Number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI.

Address correspondence to Brian J. Love, Department of Materials Science and Engineering (0237), Virginia Tech, Blacksburg, VA 24061, USA. E-mail: blove@vt.edu

INTRODUCTION

Conventional methods for crosslinking often employ chain-like reactions using reactive species such as unstable radicals or cations [1–5]. Whereas these reactions often require the use of an initiator and the addition of thermal energy to initiate crosslinking, alternative crosslinking methods, most notably photoactive crosslinking developed by Plambeck in the 1950s [6], have sought to eliminate the need for special initiators and the use of the heat.

Webster and coworkers recently crosslinked acrylic-based adhesive systems to create releasable PSA bandages [7–9]. The methacrylic functional sites were photocrosslinked using halogen lamps and sunlight as irradiation sources with Irgacure 784® (Ciba Specialty Chemicals, Basel, Switzerland) as the photoinitiator. Peel strengths were reduced as much as 79% with 2 min of irradiation, and higher light intensities and doses achieved a greater reduction in peel strength [7–12]. Although this system was considered a breakthrough in medical grade PSAs, it does exhibit several drawbacks: diffusion of the photoinitiator may potentially lead to nonhomogenous crosslinking and premature photocrosslinking may occur because of ambient exposure, causing the PSA to lose tack and fail prematurely.

Ebe and coworkers developed a releasable pressure-sensitive tape based on a precursor adhesive synthesized from *n*-butyl acrylate and acrylic acid [13]. Their adhesive mixtures experienced a 97% reduction in the peel strength upon UV exposure. The lower peel strength was attributed to a 2% volume contraction and an increase in the storage modulus at room temperature, which also led to a 60°C shift in the tan δ peak.

Novel functional groups such as coumarin, cinnamate, and maleimides are also used as photocrosslinkers [14–24]. These small molecules undergo a $2\pi + 2\pi$ cycloaddition when exposed to UV irradiation and form crosslink points *via* nonradical radiative pathways, negating the need for photoinitiators. Derivatives of 7-hydroxycoumarin (Figure 1) photodimerize when irradiated in the ultraviolet-A (UVA) region of the electromagnetic spectrum (>300 nm) [17, 25–28]. The dimer, which is composed of a cyclobutane ring, is subsequently cleaved when irradiated at wavelengths shorter than 290 nm. One distinct advantage of photocrosslinking *via* $2\pi + 2\pi$ cycloaddition is that this reaction does not suffer from oxygen inhibition, as do many photoinitated polymerizations [17, 29].

Here, we describe the synthesis of functional acrylic copolymers and the incorporation of photocrosslinking coumarin functionalities *via* a side group esterification reaction. The performance of these

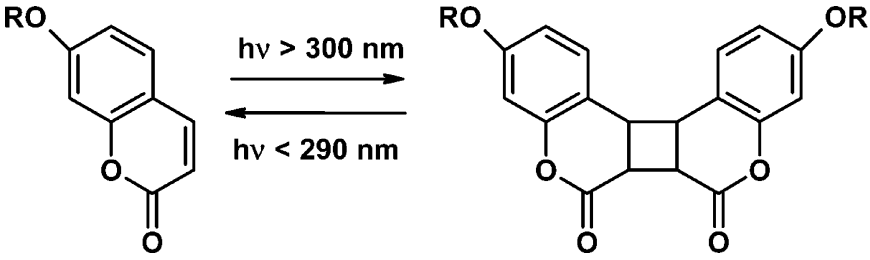

FIGURE 1 Photoreversible dimerization of 7-hydroxycoumarin.

photocrosslinkable polymers as PSAs was evaluated before and after irradiation.

EXPERIMENTAL

Materials

7-Hydroxycoumarin, ethyl bromoacetate, 2,2′-azobisisobutyronitrile (AIBN), and thionyl chloride were purchased from Sigma Aldrich Chemical Company (Milwaukee, WI, USA) and used as received. 2-Hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and 2-ethylhexyl acrylate (EHA) were purchased from Aldrich and passed through a neutral Al_2O_3 column to remove radical inhibitors. All other solvents and reagents were purchased commercially and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under an N_2 atmosphere prior to polymer esterification.

Instrumentation

^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded using either a Varian Unity 400 MHz or a Varian Inova 400 MHz spectrometer (Varian, Palo Alto, CA, USA) at 25°C in $CDCl_3$. UV-Vis spectroscopy was performed using an Analytical Instrument Systems Inc. spectrometer (Flemington, NJ, USA) equipped with fiber-optic light guides, a DT1000CE light source, and an Ocean Optics USB2000 UV-Vis detector (Ocean Optics, Drenedin, FL, USA). Molecular weights were determined *via* Gel Permeation Chromatography (GPC) at 40°C in $CHCl_3$ High Performance Liquid Chromatography (HPLC grade) at 1 mL min^{-1} through 3 inline PLgel 5 μm MIXED-C columns (Polymer Laboratories, Amberst, MA, USA) and an inline Wyatt Technology Corp. miniDAWN® multiple-angle laser light scattering (MALLS) detector (Wyatt Technology, Santa Barbara, CA, USA).

Differential scanning calorimetry (DSC) was performed with a Perkin Elmer Pyris 1 at a heating rate of 10°C min^{-1} under nitrogen (Perkin Elmer, Boston, MA, USA). The glass transition temperature (T_g) was measured during the second heat using the midpoint of the transition. Irradiation temperature was measured with a Raytek Thermalert TX optical pyrometer (Raytek, Santa Cruz, CA, USA). Film thickness was measured using microcalipers or estimated from film-coating weight. Two sets of peel samples were prepared. The first set was measured with a TA.XT2i Texture Analyzer (Texture Technologies Corp., Scarsdale, NY, USA/Stable Micro Systems, Godalming, Surrey, UK) utilizing a 90-deg peel wheel (aluminum) and poly(ethyleneteraphthalate) (PET) backing materials. The second set was tested on an Instron using a 180-deg peel rig (Instron, Canton, MA, USA).

UV Irradiation

UVA irradiation was accomplished using a F300s series microwave-powered electrodeless lamp source coupled with an LC-6B bench top conveyer manufactured by Fusion UV Systems, Inc. (Gaithersburg, MD, USA) or an Hg arc lamp manufactured by ThermoOriel (Mountain View, CA, USA). In the Fusion system, a "D" bulb (linear power output of 80 W cm^{-1}) was utilized in conjunction with a glass filter, blocking wavelengths below 300 nm. The belt speed was set at 6.1 m min^{-1}, providing a dose of approximately 1.1 J cm^{-2}. UVA irradiance and effective energy density were measured before and after each sample set with an EIT UV Power Puck radiometer (EIT UV Power Puck, Sterling, VA, USA). The UVA intensity of the Oriel system was 35 mW cm^{-2}. Exposure time controlled the sample dose. Extent of photoreaction was monitored using UV-Vis spectroscopy. The average of four samples was used to develop the conversion profiles. The temperature in the Fusion system during irradiation ranged from 30 to 40°C.

Synthesis of Coumarin Poly(EHA-*co*-HEA) Precursors

The related synthetic methodology of the 7-hydroxycoumarin derivatives is published elsewhere [30, 31]. Briefly, 7-hydroxycoumarin (10.0 g, 61.6 mmol) was combined with ethyl bromoacetate (12.4 g, 73.9 mmol), potassium carbonate (12.5 g, 90 mmol), and acetone (450 mL) and refluxed for 3 h. After salt filtration, the product was recrystallized from ethanol with an isolated yield of 90%. The product (7-ethoxycarbonylmethoxycoumarin) (7.05 g, 28.2 mmol) was subsequently hydrolyzed for 18 h in a mixture of 1,4-dioxane (280 mL),

water (400 mL), and sodium hydroxide (15.8 g, 395 mmol). The resulting product (7-carboxymethoxycoumarin) was extracted with a 3:1 chloroform–methanol mixture and recrystallized from ethanol with an isolated yield of 85%. The 7-carboxymethoxycoumarin (2.44 g, 11 mmol) was refluxed for 3 h in thionyl chloride (20.0 mL, 277 mmol) providing 7-chlorocarbonylmethoxycoumarin at a yield greater than 98%. Unreacted thionyl chloride was quantitatively removed under reduced pressure. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.65 (d, 1H, CH), 7.43 (d, 1H, Ar H), 6.86 (d, 1H, Ar H), 6.80 (s, 1H, Ar H), 6.31 (d, 1H, CH), 5.02 (s, 2H, CH_2).

Synthesis of Precursor Copolymer

The EHA (20.0 g, 104 mmol) and 2-HEA (3.54 g, 30.4 mmol) monomers were combined and diluted with ethyl acetate (95 mL, 75 vol%) and mixed under constant stirring in a 250-mL round-bottomed flask. Finally, the initiator, AIBN (47.2 mg, 0.2 wt%), was added to the reaction vessel. The reaction mixture was sparged with nitrogen for 10 min, then placed in a 65°C oil bath and allowed to polymerize for 24 h. The polymer was precipitated into approximately 600 mL of a 4:1 methanol–water solution. The isolated polymer product was dried under vacuum at 65°C for 24 h.

Copolymer Modification with 7-Chlorocarbonylmethoxycoumarin

A typical coumarin modification of acrylic copolymers is described (Figure 1). Poly(EHA-*co*-HEA) (5.00 g) was dissolved in 50 mL distilled THF, then combined with triethylamine (0.913 g, 9.0 mmol) and stirred under nitrogen in a 100-mL round-bottomed flask. Triethylamine was added at a 20 mol% excess compared with the coumarin moiety. 7-Chlorocarbonylmethoxycoumarin (1.79 g, 7.52 mmol) was dissolved in 20 mL distilled THF and added dropwise *via* an addition funnel to the poly(EHA-*co*-HEA) and triethylamine mixture. The addition funnel was then rinsed with an additional 5 mL distilled THF. The reaction mixture was stirred at 0°C overnight under an N_2 blanket with a foil-covered reaction vessel. After salt filtration, the resulting polymer was precipitated into approximately 300 mL of a 3:1 methanol–water solution, stored in an aluminum foil–covered 60-mL bottle, and dried *in vacuo* at 65°C for 24 h. The purified yield was 74%.

UV-Vis Spectroscopy, Gel Fraction, and Peel Strength Sample Preparation

Homogenous films (1 to 2 μm thick) were solvent-cast from chloroform onto quartz microscope slides and drawn using a doctor blade for the UV-Vis studies. Homogenous films (~18 μm thick) were also cast from chloroform onto Mylar™ backing material (25 μm thick) and drawn using a doctor blade for the peel tests. The solvent was removed under vacuum at 75°C, and then a silicone release liner was applied to the adhesive layer, forming a sandwich structure. The adhesive was exposed to UV light through the Mylar™ film. Strips $\sim 2.5 \times 15$ cm in size were cut and the adhesive tape was applied to the Texture Analyzer peel-wheel attachment following removal of the release liner. After a 2-min dwell, the 90-deg peel of the substrate was performed at $2\,\text{mm}\,\text{s}^{-1}$. The second set of peel samples were applied to borosilicate glass microscope slides and irradiated through the glass, then peeled (180-deg peel test) at a rate of $5\,\text{mm}\,\text{s}^{-1}$ after a 10-min dwell time. The average force (3 samples) was recorded as the peel strength for both sample sets. The gel fraction samples were solvent-cast directly on silicone release liners and drawn using a doctor blade.

RESULTS AND DISCUSSION

Synthesis and Modification of Poly(EHA-*co*-HEA) Random Copolymer

The precursor poly(EHA-*co*-HEA) copolymer was synthesized *via* conventional free-radical solution polymerization in ethyl acetate. AIBN initiated the polymerization and was added at 0.2 wt% compared with the total monomer weight. The resulting macromolecule exhibited an M_n of 75,300 g mol^{-1} with a molecular weight distribution of 3.74. The composition of the copolymer was examined using ^{1}H NMR spectroscopy and corresponded well with the feed ratios of 75 mol% EHA and 25 mol% HEA.

Modification of these EHA-*co*-HEA copolymers proceeded *via* an esterification reaction between the hydroxyl group of the HEA and the coumarin acid chloride derivative (Figure 2). Manipulation of the molar ratio of hydroxyl functionality and coumarin derivative controlled the level of functionalization. Triethylamine was employed as an acid trap and was added in a 20% molar excess compared with the acid chloride to promote full conversion. Two coumarin-functionalized EHA-*co*-HEA copolymers were synthesized with coumarin

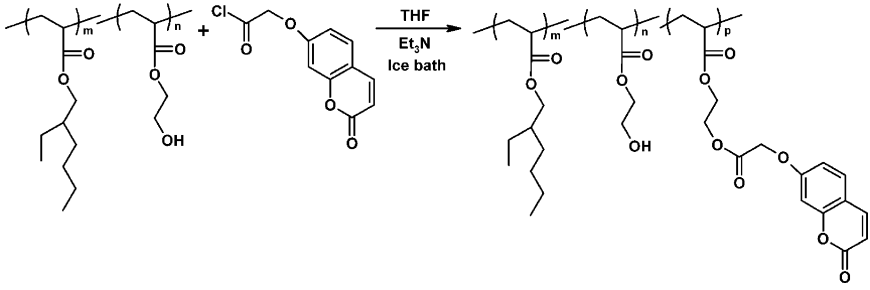

FIGURE 2 Coumarin functionalization of EHA-*co*-HEA base polymer, affording the photoactive model PSA.

concentrations of 6 and 10 mol% (Table 1). ^{1}H NMR of the modified EHA-*co*-HEA copolymers confirmed the synthesis of the two different levels of the coumarin functionality. The coumarin resonances were observed at 7.64, 7.44, 6.93, 6.30, and 4.84 ppm (Figure 3). A lower peak area of the methylene adjacent to the hydroxyl at 3.75 ppm was observed along with the presence of the methylene resonance adjacent to an ester linkage at $\sim$4.42 ppm. Moreover, a new signal was observed in the UV-Vis spectrum of the polymer, characteristic of the double-bond absorbance associated with the coumarin functionality at 319 nm (Figure 4) [17, 30, 32].

Irradiation and Evaluation of the Photocrosslinking Process

UVA light photocrosslinked the coumarin-functionalized model PSAs in the bulk. The λ_{Max} absorbance at 319 nm in the UV-Vis absorbance spectrum is typical of 7-hydroxycoumarin containing polymers (Figures 4 and 5). The intensity drop of the coumarin absorbance at 319 nm tracked the extent of dimerization. As the unsaturated methylene in the coumarin was dimerized into a cyclobutane ring, the extent of conjugation of the coumarin moiety was decreased, reducing the absorbance at 319 nm and increasing the absorbance at 239 nm

TABLE 1 Composition and Glass Transition Temperature of the Coumarin-Functionalized Model PSAs

EHA (mol%)	HEA (mol%)	Coumarin-functionalized HEA (mol%)	T_g (°C)
75	19	6	−36
75	15	10	−26

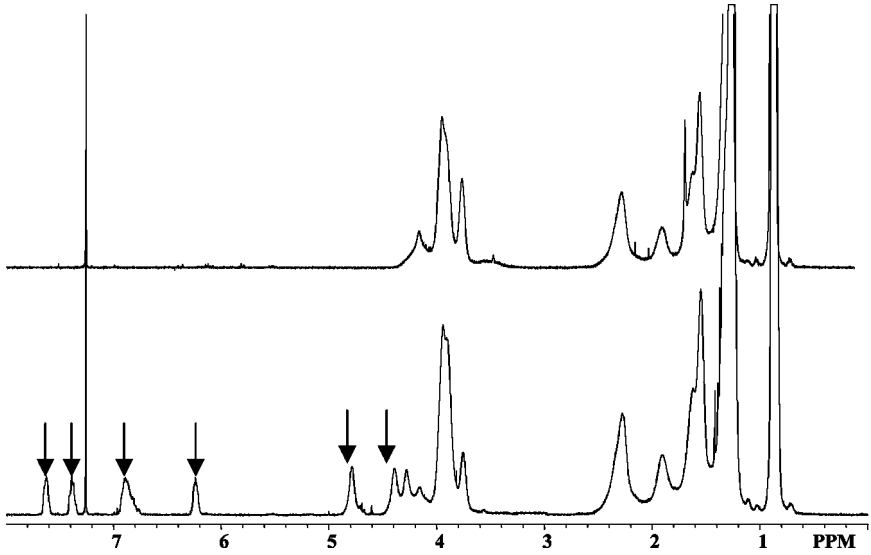

FIGURE 3 ^{1}H NMR spectra of the precursor poly(EHA-*co*-HEA) (upper) and a coumarin-functionalized poly(EHA-*co*-HEA) (lower). Resonances resulting from the coumarin group are indicated with arrows.

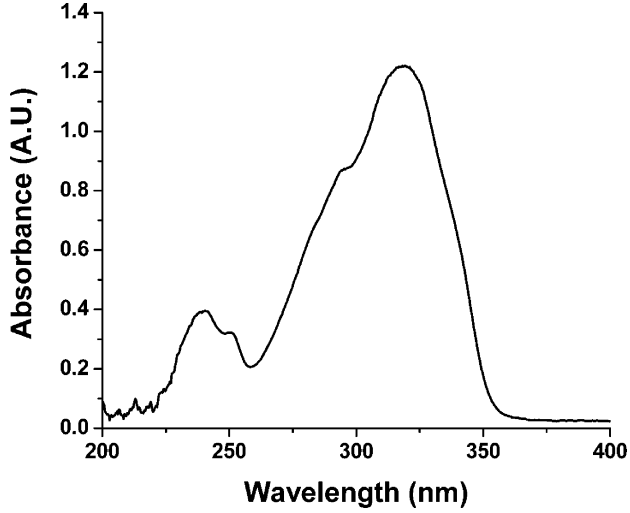

FIGURE 4 UV-Vis absorbance of 10 mol% coumarin-functionalized poly (EHA-*co*-HEA) model PSA.

[14, 17, 27, 33, 34]. The intensity decrease was proportional to the consumption of the 3,4-olefin in the coumarin derivative, whereas a higher absorbance is indicative of cyclobutane cleavage and reversion to the original lactone structure [14, 17]. Figure 5 shows the typical decrease in absorbance (photocrosslinking of 10 mol% coumarin-functionalized PSA) upon irradiation above 300 nm (UVA intensity $\sim 1.1\,J\,cm^{-2}$ pass^{-1}).

Figure 6 shows the normalized UV-Vis absorbance profiles at 319 nm for both coumarin-functionalized PSAs as a function of dose. As samples were irradiated, the absorbance at λ_{Max} initially decreased and then reached a plateau as the maximum coumarin consumption was approached. This maximum was controlled by a combination of factors including chain mobility and coumarin concentration. The 10 mol% coumarin containing PSA had faster coumarin conversion than the 6 mol% coumarin PSA. This was expected, as the probability of the photodimerization reaction depends on coumarin group proximity, and the 10 mol% sample had 65% more coumarin than the 6 mol% sample. The increased density of coumarin groups in the 10 mol% sample led to a higher coumarin consumption rate. Likewise, the 10 mol% sample displayed a higher extent of reaction, as there were more coumarin groups to react before the crosslinking reaction

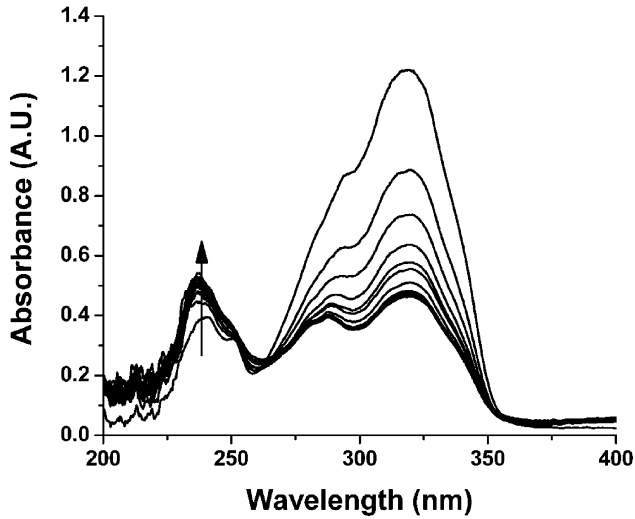

FIGURE 5 Decrease in the absorbance at 319 nm and increase in the absorbance at 239 nm as a function of increasing UVA radiation dose (approximately 2.2 J cm^{-2} between individual spectra).

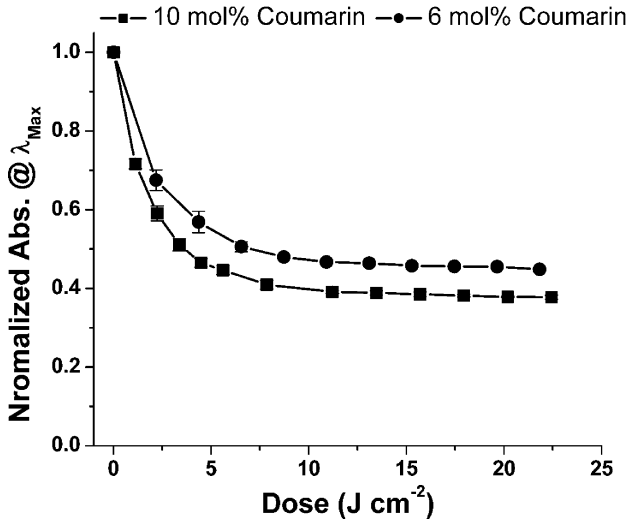

FIGURE 6 Comparison of coumarin consumption as a function of dose for the 6 and 10 mol% coumarin-functionalized model PSAs.

hindered the chain mobility to the extent that unreacted coumarin groups could not "find" other coumarin moieties with which to react. Previous studies indicated that the T_g of these polymers was insensitive to photocrosslinking [35].

A distinct advantage to this coumarin-functionalized acrylate system is its stability in ambient light. The methacrylate-functionalized PSAs developed by Webster and coworkers crosslinked on exposure to low doses of ambient light [7–9]. Figure 7 shows the effect of ambient light exposure on the 6 mol% coumarin-functionalized model PSA. The laboratory is illuminated with fluorescent lighting at a UVA intensity of 0.15 μW cm^{-2}, which corresponds to a dose of 540 mJ cm^{-2} h^{-1}. Over 7 days, less than 2 mol% of the coumarin was consumed, which is within the day-to-day precision of the spectrometer. This ambient light stability allows for everyday use of the adhesive without a light shield or special lighting.

The evolution of gelled polymer was measured *via* Soxhlet extraction in THF. A photocrosslinked polymer precipitates in THF after irradiation, forming a mixture of an insoluble gel and any remaining uncrosslinked product. Because only a few photoreactions per chain are necessary to form a crosslinked product, high gel fractions were expected [21, 36]. Figure 8 shows the generation of gel as a function of UVA dose. Gel development was inversely proportional to the

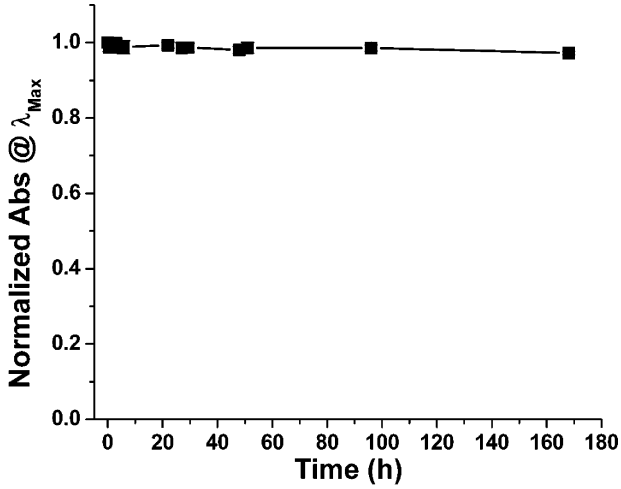

FIGURE 7 Coumarin consumption as a function of irradiation time on exposure to ambient light (6 mol% coumarin-functionalized model PSA).

consumption of coumarin groups. The gel fraction quickly increased, then plateaued after exposure to approximately 11 J cm^{-2} of UVA light (10 passes under the UV lamp). Polymer gel fraction increased to a maximum of 86 and 89% for the 5 and 10 mol% polymers, respectively.

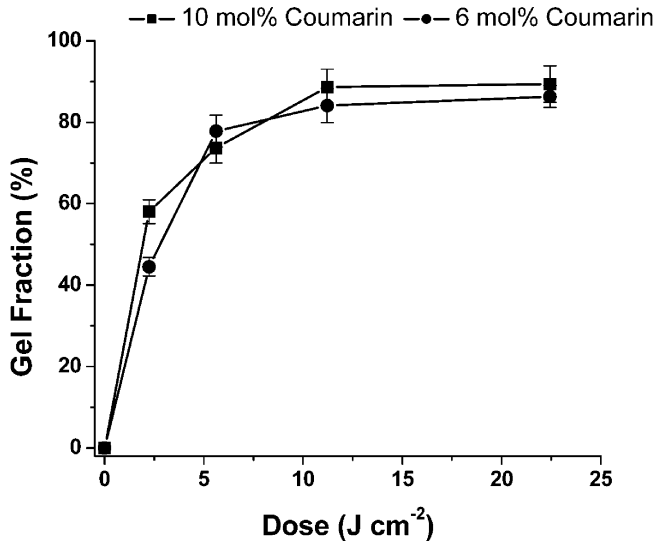

FIGURE 8 Evolution of gel fraction of the 6 and 10 mol% coumarin-functionalized model PSAs as a function of UVA irradiation.

Effect of Irradiation on Peel Strength

Irradiated then Bonded

In this first set of peel-strength data, the adhesive was irradiated before forming the bond with the substrate. As the PSAs were cross-linked with UVA irradiation, the peel strengths decreased from their initial values of 2.58 and 1.61 N per cm-width for the 10 and 6 mol% PSAs, respectively. The dose-dependent peel strength data were normalized in Figure 9 to the nonirradiated peel strength to ease comparison of the two sets of data, because initial peel strengths differed between the two PSAs. All samples failed *via* an apparent adhesive mechanism with the exception of the nonirradiated 6 mol% sample, which failed cohesively. With less than 2 J cm^{-2} of UVA irradiation, the peel strengths of the 10 and 6 mol% samples decreased 90 and 70%, respectively. As in the case of the UV-Vis data and the gel fraction measurements, subsequent irradiation offered little change in the peel strengths. After approximately 22 J cm^{-2} of UVA light, the peel strengths decreased by more than 97% compared with the initial values. Figure 10 summarizes the effect of UVA irradiation on the 10 mol% coumarin-functionalized model PSA. As the PSA was irradiated, the coumarin groups photodimerized. Because the irradiation was performed before the model adhesives were applied to the test

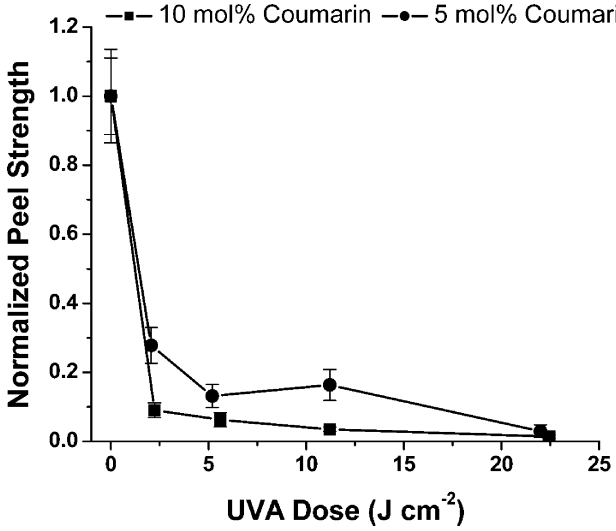

FIGURE 9 Decrease in the normalized average peel strength of the 5 and 10 mol% coumarin-functionalized model PSAs as a function of UVA dose.

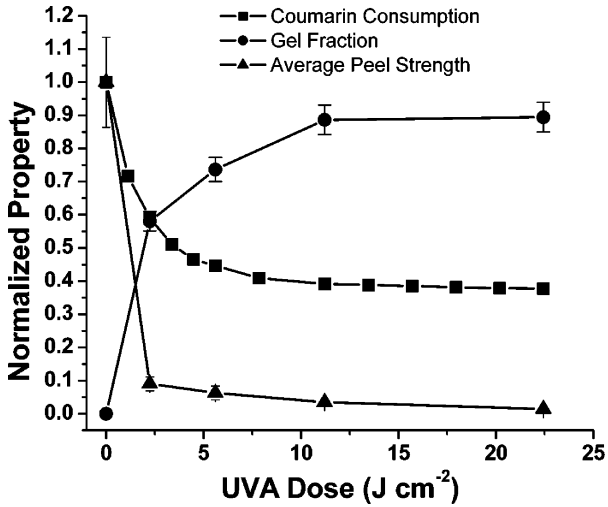

FIGURE 10 Effects of UVA irradiation on coumarin consumption, gel fraction, and 90-deg peel strength for the 10 mol% coumarin-functionalized model PSA.

substrate, the reduced peel strength was attributed to reduced viscous flow of the already crosslinked adhesives and, thus, an inability to wet the substrate properly and form an adhesive bond [37].

Bonded then Irradiated

A second set of peel samples was irradiated following the formation of the adhesive bond with glass microscope slides. The composition of this set of model PSAs varied slightly from the adhesives used throughout this rest of this report (Table 2). Irradiation of the adhesive through the bond substrate was performed with the Thermo-Oriel irradiation system. The UVA intensity was 35 mJ cm^{-2}. The effect of irradiation time on the gel fraction and peel strength is shown in Figure 11. As the adhesive was irradiated through the glass slide, the gel fraction of the adhesive increased to a maximum of 64%, while the adhesive peel strength decreased from 2.5 to 0.70 N per cm-width. The failure mechanism also changed with dose. The nonirradiated peel samples failed cohesively, whereas the irradiated samples failed (apparently) adhesively. In addition, fibrillation was observed in the nonirradiated sample, whereas no fibrillation was observed following irradiation. Although the reduced peel strength of the irradiated-then-bonded samples was attributed to a lack of

TABLE 2 Composition of the Model PSA Used for the Glass Substrate 180-deg Peel Tests

M_n	M_w/M_n	EHA (mol%)	HEMA (mol%)	Coumarin-functionalized HEMA (mol%)
53,000	3.30	80	10	10

wetting, this adhesive had wetted the substrate before UV exposure. Thus, the lower peel strength in the bonded-then-irradiated sample was attributed to a decrease in the chain mobility, resulting in a decrease in the ability of the adhesive to dissipate energy during peel testing [37].

One additional advantage of coumarin photodimerization crosslinking of PSAs is the ability to reverse the cyclobutane ring that forms the polymer crosslink point with UVC irradiation (<290 nm). This feature may lead to the ability to reuse the PSA. Initial data (Figure 12) from the 5 mol% functionalized PSA shows a 100% increase in the peel strength of the UVA-irradiated adhesive following subsequent UVC irradiation. Further finetuning of the PSA system could afford higher initial peel strengths and optimize reversibility.

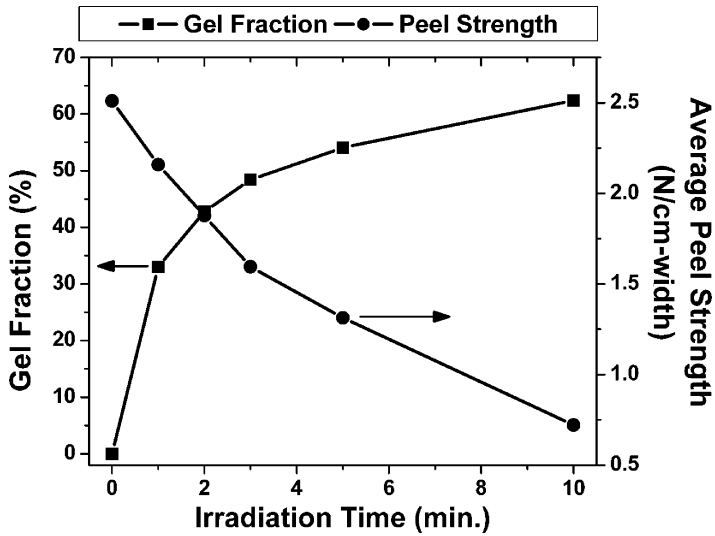

FIGURE 11 Increase in gel fraction and the decrease in peel strength for the bonded-then-irradiated samples.

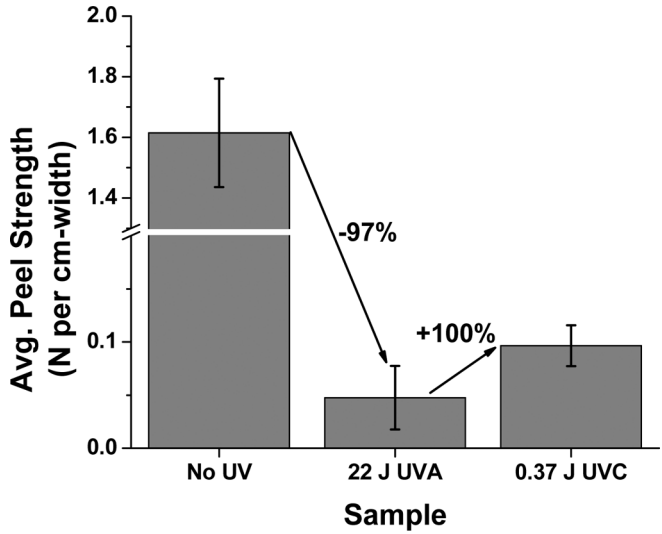

FIGURE 12 Effect of irradiation of the 6 mol% coumarin-functionalized model PSA, affording a possible route for repeated use.

CONCLUSIONS

Photocrosslinkable model PSAs were prepared from a quantitative esterification reaction of poly(2-ethylhexyl acrylate-*co*-hydroxyethyl acrylate) and an acid chloride–derivatized 7-hydroxycoumarin. The coumarin groups in the polymer dimerized in UV light and the gel fraction of the coumarin-modified PSAs increased with increasing UV irradiation. The increase in the gel fraction reduced peel strength from 1.62 to 0.05 N/mm when exposed to 22 J cm^{-2} of UVA irradiation. The lower adhesion upon irradiation for the model PSAs (irradiated-then-bonded and bonded-then-irradiated) was attributed to two different mechanisms. The decreased peel strength of the irradiated-then-bonded samples was attributed to a lack of wetting, whereas the decrease in the bonded-then-irradiated samples was attributed to a decrease in the energy dissipation of the model PSA. Photocrosslinkable polymers synthesized with coumarin functionalities are stable on exposure to ambient light, a trait not achieved in previously published studies involving other photocrosslinkable PSAs. If subsequent formulation was optimized for adhesive applications (with the addition of higher T_g monomers), this system may have increased initial peel strengths and similar decreases in peel strength with irradiation. In addition, systems utilizing coumarin photodimerization

possess a significant advantage over other photoreversible systems because of the inability to regain adhesive strength on demand by photocleaving the model coumarin dimers with UVC irradiation.

REFERENCES

[1] Nakano, S. and Endo, T., *Prog. Org. Coat.* **22**, 287–300 (1993).
[2] Keller, P., *Chem. Mater.* **2**, 3–4 (1990).
[3] Peacock, A. J., *Polym. Commun.* **28**, 259–260 (1987).
[4] Staeger, M., Finot, E., Brachais, C. H., Auguste, S., and Durand, H., *Appl. Surf. Sci.* **185**, 231–242 (2002).
[5] Keller, R. C., *Rubber Chem. Technol.* **61**, 238–254 (1988).
[6] Plambeck Jr., L., U.S. Patent # 2,760,863 (1956).
[7] Boyne, J. M., Millan, E. J., and Webster, I., *Int. J. Adhes. Adhes.* **21**, 49–53 (2001).
[8] Webster, I., *Int. J. Adhes. Adhes.* **19**, 29–34 (1999).
[9] Chivers, R. A. and Webster, I., *International Conference on Adhesion and Adhesives*, 7th Cambridge, United Kingdom, Sept. 15–17, 1999.
[10] Webster, I., World Patent #WO 96/29374 (1996).
[11] Webster, I., World Patent #WO 99/18136 (1999).
[12] Webster, I., U.S. Patent # 6,184,264 B1 (2001).
[13] Ebe, K., Seno, H., and Horigome, K., *J. Appl. Polym. Sci.* **90**, 436–441 (2003).
[14] Trenor, S. R., Long, T. E., and Love, B. J., *Macromol. Chem. Phys.* **205**, 715–723 (2004).
[15] Robertson, E., Deusen, W., and Minsk, L., *J. Appl. Polym. Sci.* **2**, 308–311 (1959).
[16] Minsk, L. M., Smith, J. G., Van Deusen, W. P., and Wright, J. F., *J. Appl. Polym. Sci.* **2**, 302–307 (1959).
[17] Trenor, S. R., Shultz, A. R., Love, B. J., and Long, T. E., *Chem. Rev.* **104**, 3059–3077 (2004).
[18] Kuckling, D., Adler, H. J. P., Arndt, K. F., Hoffmann, J., Plotner, M., and Wolff, T., *Polym. Adv. Technol.* **10**, 345–352 (1999).
[19] Kuckling, D., Ivanova, I. G., Adler, H. J. P., and Wolff, T., *Polymer* **43**, 1813–1820 (2002).
[20] Schonberg, A., Latif, N., Moubasher, R., and Awad, W. I., *J. Chem. Soc.*, Abstracts, 374–379 (1950).
[21] Decker, C. and Bianchi, C., *Polym. Int.* **52**, 722–732 (2003).
[22] Zahir, S., *J. Appl. Polym. Sci.* **23**, 1355–1372 (1979).
[23] Choi, D. H. and Cha, Y. K., *Polym. Bull.* **48**, 373–380 (2002).
[24] Trenor, S. R., Long, T. E., and Love, B. J., *Eur. Polym. J.* **41**, 219–224 (2005).
[25] Ciamician, G. and Silber, P., *Ber. Dtsch. Chem. Ges.* **35**, 4128–4131 (1902).
[26] Anet, R., *Chem. Ind.* 897–899 (1960).
[27] Hammond, G. S., Stout, C. A., and Lamola, A. A., *J. Am. Chem. Soc.* **86**, 3103–3106 (1964).
[28] Anet, R., *Can. J. Chem.* **40**, 1249–1257 (1962).
[29] Crivello, J. V. and Sangermano, M., *J. Polym. Sci., Part A: Polym. Chem.* **39**, 343–356 (2001).
[30] Matsuda, T., Mizutani, M., and Arnold, S. C., *Macromolecules* **33**, 795–800 (2000).
[31] Matsuda, T. and Mizutani, M., *Macromolecules* **33**, 791–794 (2000).
[32] Chen, Y. and Jean, C. S., *J. Appl. Polym. Sci.* **64**, 1749–1758 (1997).

[33] Chen, Y. and Geh, J. L., *Polymer* **37**, 4481–4486 (1996).
[34] Chen, Y. and Jean, C. S., *J. Appl. Polym. Sci.* **64**, 1759–1768 (1997).
[35] Trenor, S. R., Huyck, R. H., Long, T. E., and Love, B. J., (2004) in preparation.
[36] Decker, C., *Pigment Resin Technol.* **30**, 278–286 (2001).
[37] Tobing, S. D. and Klein, A., *J. Appl. Polym. Sci.* **79**, 2230–2244 (2001).