

Novel Reactive Diluents for UV/Moisture Dual-Curable Coatings

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Received 14 January 2005; accepted 22 March 2005

DOI 10.1002/app.21967

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The novel silicone-modified polyacrylate reactive diluents for UV/moisture dual-curable coatings were synthesized from *N,N*-bis[3-(trimethoxysilyl)propyl]amine and multifunctional acrylates such as ethoxylated trimethylolpropane triacrylate and polyethyleneglycol diacrylate through Michael addition reaction. Their structures were characterized by NMR and FTIR and their average molecular weights were determined by vapor pressure osmometry. With FTIR, it was found that the obtained diluents could be cured both by UV radiation and moisture mode. The ²⁹Si-NMR showed that dimer was the main condensation prod-

uct at the initial stage of moisture curing. The rheological behavior of the diluents investigated by rotary viscometer indicated they were very close to Newtonian fluid, and the viscosity of coatings decreased evenly with increasing concentration of reactive diluents in the coatings. In particular, they were found to be highly efficient in diluency and reactivity for UV polymerization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1500–1504, 2005

Key words: curing of polymers; UV/moisture dual-curing; Michael addition; coatings; rheology

INTRODUCTION

Radiation curing, which effectively and instantaneously converts a usually liquid, low-viscosity formulation of ingredients into a polymerized and crosslinked solid polymer network, has become a well-accepted technology in polymer science.^{1,2} Beneficial properties such as rapid curing, reduced solvent emission, moderate curing condition, and the ability to coat heat-sensitive devices and circuits make photocurable compositions attractive for many electronic applications.^{3,4} Conformal coatings such as polyurethane, acrylics, epoxies, and silicones have been used to protect printed wiring assemblies from moisture, ionic contaminants, and particulates.⁵

A major limitation in using photocured coatings on printed wiring assemblies is the inaccessibility of light to cure portions of the coating that are shadowed by odd-configuration modules. To obviate this, a secondary curing mechanism, such as moisture curing, is necessary.⁶ Some oligomers or monomers contain functional groups that are unreactive until exposed to

atmospheric moisture. Moisture reacts with the functional groups, thus allowing them to polymerize. Most room-temperature vulcanizing (RTV) silicones and some polyurethanes cure in this manner. To obtain UV/moisture dual-curable compositions, some new polymer resins have been synthesized that combine in one molecule both the photosensitive group and the moisture cure group. Bennington⁷ invented an acrylate-terminated polydimethylsiloxane, which was prepared by reaction of hydroxyl-terminated polydimethylsiloxane with dimethylchloromethacryloxypropylsilane. We synthesized a UV/moisture dual-curable prepolymer by reacting polyols with excess diisocyanates and end-capping with hydroxyalkyl methacrylate and silane-coupling compound containing amine group,⁸ the synthetic process of which is displayed in Figure 1.

The high viscosity of most radiation-curable oligomers or prepolymers precludes their direct use in the majority of coatings. Thus, it is necessary to reduce their viscosity to facilitate the application of the formulation to the substrate.^{9,10} There are various methods of reducing the viscosity. One is the addition of normal organic solvents, although it is less frequently used in applications because of the increasingly restrictive regulation of volatile organic compound emission. The major limitation of viscosity reduction by the use of water is poor physical compatibility with most existing oligomer systems. The third method of reducing the overall viscosity of the oligomer system is to use reactive diluents containing carbon-carbon

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Contract grant sponsor: Guangdong Science and Technology Commission; contract grant number: 2001-367.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 60378029.

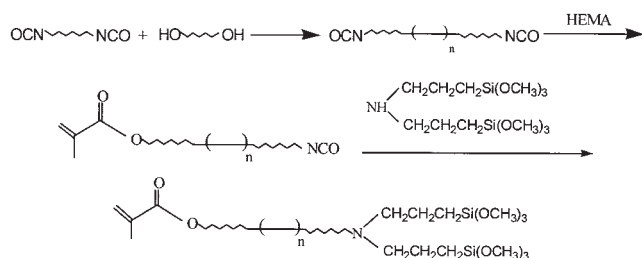


Figure 1 Synthetic process of UV/moisture dual-curable prepolymers (SPUA).

unsaturated groups, which have the advantages of being incorporated into the final film and adjusting the properties of the cured materials. Reactive diluents are typically acrylates, methacrylates, and vinyl monomers. However, common reactive diluents do not possess moisture-curing ability.

In this work we synthesize novel UV/moisture dual-curable reactive diluents (SPAs) from *N,N*-bis[3-(trimethoxysilyl)propyl]amine (BTMSPA) and multifunctional acrylate through Michael addition. UV and moisture-curing behaviors of SPAs have been studied by photo-DSC (DPC), infrared spectroscopy (IR), and ^{29}Si -NMR. Their rheological behavior, diluency, and reactivity were also investigated.

EXPERIMENTAL

Materials

Prepolymer (SPUA) was prepared by reacting polyols with excess diisocyanates and end-capped with hydroxyalkyl methacrylate and silane-coupling compound containing amine group, as described previously.⁸ Polyethylene glycol diacrylate (PEGDA) based on PEG 400 was supplied by Sartomer Co. (Exton, PA) and ethoxylated trimethylolpropane triacrylate (EOT-MPTA) by UCB Chemicals Co. (Brussels, Belgium). *N,N*-Bis[3-(trimethoxysilyl)propyl]amine (A-1170, BTMSPA) was a product of GE Silicones Co. (Wilton, CT). 2-Hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) was obtained from Ciba Geigy (Basel, Switzerland). Dibutyltin dilaurate (DBTDL) was purchased from Acros Organics (Morris Plains, NJ). Methanol were purchased from Guangzhou Chemical Products (China) and purified by distillation before use.

Synthesis of silicone-modified polyacrylate (SPA)

A-1170 and multifunctional acrylate (PEGDA or EOT-MPTA) in equal molar ratios, together with 10 mL of methanol, which was used as a phase-transfer agent, were charged to a 250-mL three-neck flask equipped with a stirrer, thermometer, and reflux condenser. The

reaction was performed under N_2 protection. The mixture was heated to 50°C with mechanical stirring. The tertiary amine value of the obtained SPA was determined by titration with HClO_4 /diethylene glycol monomethyl ether solution, which was used to monitor the degree of Michael addition.¹¹ Subsequently, methanol was evaporated when the tertiary amine value was almost unchanged. Although the products are mixtures having several different structures, the main chemical structures are displayed in Figure 2 according to the IR and NMR spectra.

Measurements

^1H -NMR and ^{13}C -NMR spectra of the oligomers were recorded in CDCl_3 and *d*-acetone on a Varian Unity 300 NMR spectrometer (Varian Associates, Palo Alto, CA), operating at 300 and 75.5 MHz, respectively. The ^{29}Si -NMR spectrum was recorded in *d*-acetone on a Varian INOVA 500 MB spectrometer, operating at 99.3 MHz. Chemical shifts are given in ppm.

Infrared spectroscopy was performed on a Nexus 670 FTIR instrument (Nicolet Instrument Technologies, Madison, WI) at 4-cm^{-1} resolutions with 32 scans per spectrum. The infrared spectra were obtained for the prepolymers on monocystal silica substrate.

The average molecular weights were determined by vapor pressure osmometry (VPO), which was carried out on a vapor pressure osmometer (Knauer GmbH, Berlin, Germany) at 45°C with 2-butanone as solvent.

Photo-DSC (DPC) was performed on a modified CDR-1 DSC (Shanghai Balance Instrument Plant, China), which was used to measure the exothermal rate of irradiated samples. The light intensity was 2.45 mW/cm^2 (the detector was sensitive in the wavelength range of 320–400 nm). The exothermal rate, as a function of time, was recorded under isothermal condition at room temperature for continuous-illumination reactions.¹²

Viscosity and rheological properties of the materials were investigated by using a steady-stress rheometer (TA-ARES; TA Instruments, New Castle, DE). This rheometer was equipped with parallel plates (diameter

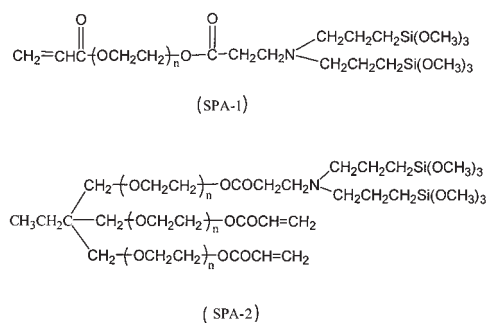


Figure 2 Chemical structures of reactive diluents (SPAs).

TABLE I
Properties of Siloxane-Modified Polyacrylate (SPA)

Sample	Acrylate	M_n (VPO)	M_w/M_n (GPC)	Viscosity, η^a (Pa · s)
SPA-1	PEGDA	868	1.08	0.041
SPA-2	EOTMPTA	930	1.09	0.270

^a The apparent viscosity at 1 s^{-1} shear rate.

ter 50 mm), and the test temperature was controlled by water circulation.

RESULTS AND DISCUSSION

Characterization of SPAs

The novel UV/moisture dual-curable reactive diluents (SPAs) were obtained through Michael addition. The obtained SPAs were clear liquids, and their number-average molecular weight M_n ranged between 800 and 1000 (VPO) (see Table I). The IR spectrum of SPA is shown in Figure 3. The disappearance of the N—H stretching band (3407 cm^{-1}) and the lessening of $\text{CH}=\text{CH}_2$ characteristic absorption peaks¹³ (1638 , 1406 , 986 cm^{-1}) in the products confirm that BTMSPA had reacted with EOTMPTA. The presence of absorption peaks at 1088 and 817 cm^{-1} is attributed to Si—O—C stretching of the siloxane group. The change of peak at 810 cm^{-1} is inconspicuous for the interference of the peak at 817 cm^{-1} .

The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of SPA-1 and their assignment are shown in Figure 4.^{14,15} The addition reaction was proceeding, as evidenced by the diminishing of the $^1\text{H-NMR}$ signals of the acrylate group at 6.42, 6.11, and 5.83 ppm as well as the $^{13}\text{C-NMR}$ signals at 131.4 and 128.0 ppm. The C=C conversion calculated by $^1\text{H-NMR}$ was 41.2% for SPA-1 and 42.5% for SPA-2. The participation of double bonds in the formation of Michael addition product

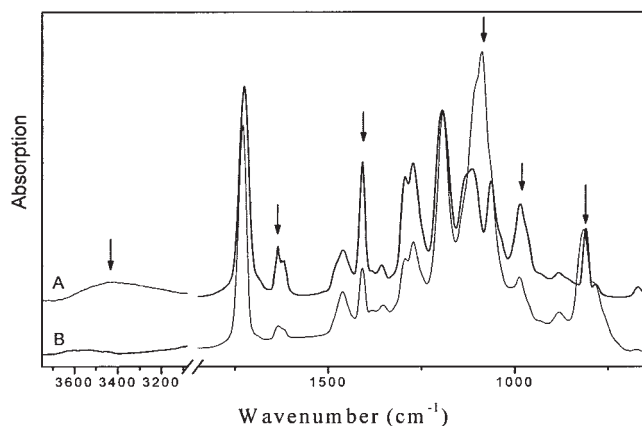


Figure 3 FTIR spectra before (A) and after (B) Michael addition between EOTMPTA and BTMSPA.

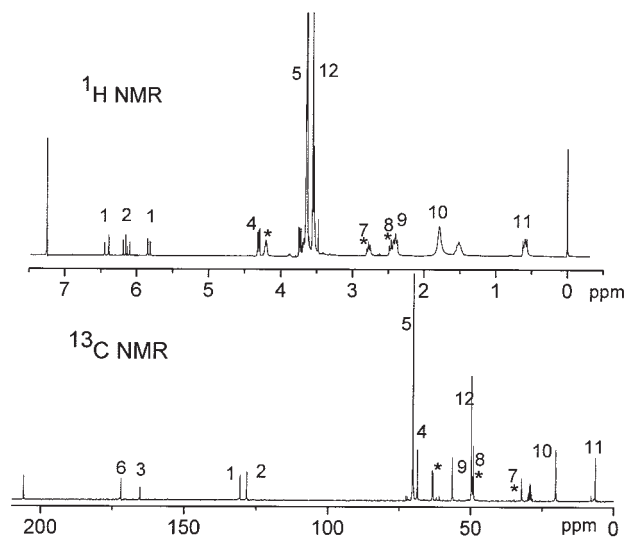
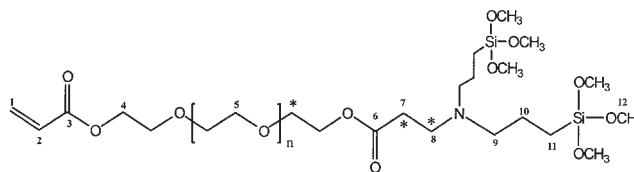


Figure 4 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of SPA-1.

was further evidenced by the emergence of the chemical shifts observed at 2.22, 2.70, and 2.40 ppm in the $^1\text{H-NMR}$ spectrum and 63.2, 49.1, and 32.4 ppm in the $^{13}\text{C-NMR}$ spectrum, respectively. These typical chemical shifts were attributed to the protons and carbon atoms marked with a star in the structure shown in Figure 4.

Spectral identification for dual-curing processing

The obtained SPAs can undergo UV and moisture curing because both a photosensitive group and a moisture-sensitive group are present in the molecules. Figure 5(a) shows the IR spectra of cured films. After UV curing, the absorption bands at 1638 , 1406 , and 810 cm^{-1} attributed to the acryloyl group disappeared, and C—O stretching of esters (1190 cm^{-1}) shifts to a lower wavenumber (1168 cm^{-1}) with the decreasing content of conjugated C=C. The trimethoxysilyl group is hydrolysis sensitive and the condensation reaction will occur in neutral media.¹⁶ The films with 2 wt % DBTDL will become tack-free within several hours at 80% relative humidity. The peaks at 1088 and 817 cm^{-1} decrease and the shoulder peak at 1055 cm^{-1} in Figure 5(a) increases, which means the Si—O—CH₃ groups have hydrolyzed and condensed to form the Si—O—Si bridge or network. The initial process of the hydrolysis and condensation of alkylsilane groups were revealed by the $^{29}\text{Si-NMR}$ spectrum, as shown in

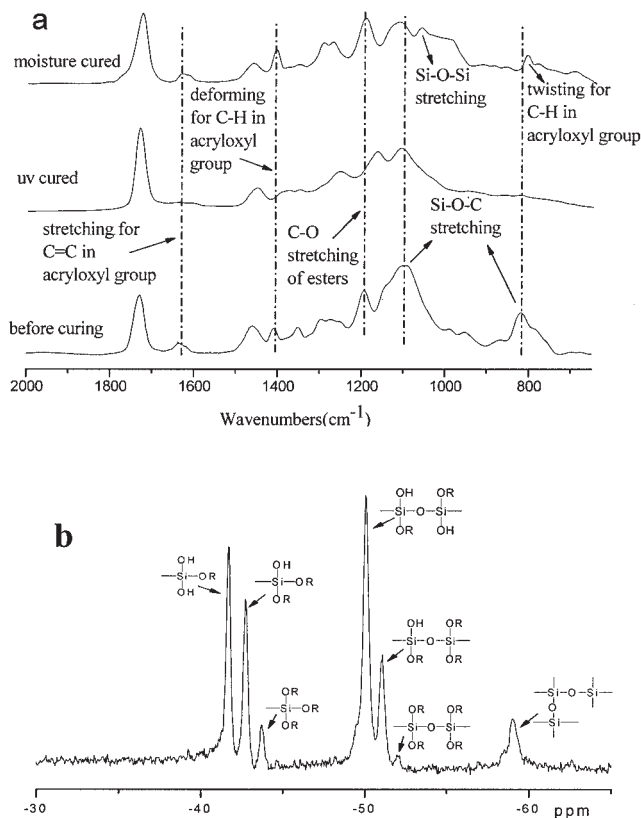


Figure 5 (a) FTIR spectra of SPA-1 through different curing methods (3 wt % Darocur 1173 and 2 wt % DBTDL; thickness of films: $\sim 20 \mu\text{m}$; UV light intensity: $37.5 \text{ mW}/\text{cm}^2$; curing time: $\sim 20 \text{ s}$; moisture curing at 80% relative humidity for 24 h). (b) ^{29}Si -NMR spectrum of SPA-1 at the initial stage of moisture curing (2 wt % DBTDL).

Figure 5(b). The moisture-cured film exhibited typical chemical shifts assigned to M (-41 to about -44 ppm), D (-49 to about -52 ppm), and T (-59 ppm) silicate units corresponding to silanol or trialkoxysilane monomer, dimer of silanol, and trimer of silanol, respectively. It appears that the extent of condensation is low at the initial stage; therefore, the hydrolysis products and dimeric species are the major products.

Dilucency power of SPAs

Dilucency power is the most important property of a diluent when selecting components for a formulation. The apparent viscosity and shear stress against shear rate of SPA are shown in Figure 6. It was found that the apparent viscosity of SPA appreciably decreased with increasing shear rate at low shear rate. Asymmetric molecules would be entangled and randomly oriented at rest. When the shear rate increased, the molecules became oriented and points of entanglement were reduced, so the materials became less viscous. At very high shear rates, the process of molecular disentanglement and orientation may be complete. The ap-

parent viscosity no longer changed with increasing shear rate, and in this range near-Newtonian behavior may be observed.

Both SPA-1 and SPA-2 have short molecular chains, which easily induces disentanglement. The relationship between shear stress and shear rate is linear (correlation coefficients > 0.99). The flow index of SPA systems calculated from the $\log \tau$ versus $\log D$ plot was close to one (both 0.97). The above indices indicate that the SPA systems are very close to Newtonian fluids. Some work¹⁷ indicates that the flow index is somewhat dependent on molecular weight. The narrower the polydispersity, the more Newtonian the polymer and the nearer the index is to unity, conclusions that were also validated in this work. In addition, SPA-2 has more points of entanglement in molecules and more interaction between molecular chains than SPA-1, so it shows more exceptional "shear thinning" behavior.

The viscosities of the obtained SPA are relatively low (Fig. 6), which renders these compounds interesting as reactive diluents in formal coating formulations. Figure 7 shows the dependency of the viscosity of the oligomer (SPUA) on the amount of SPA and some other common reactive diluents. The viscosity of the system decreased with the percentage of reactive diluents. SPAs have good dilucency to a SPUA system like that of other common reactive diluents. Furthermore, the dilucency of SPA-1 is more effective than that of SPA-2 because of its lower degree of entanglement. With increasing content of SPA, the interchain associations arising from hydrogen bonding between urethane groups decreased and thus the viscosity decreased. Because $1 \text{ Pa}\cdot\text{s}$ is considered the appropriate viscosity for most final application formulations, the weight percentage of reactive diluents necessary is about 40% for SPA-1 and 50% for SPA-2.

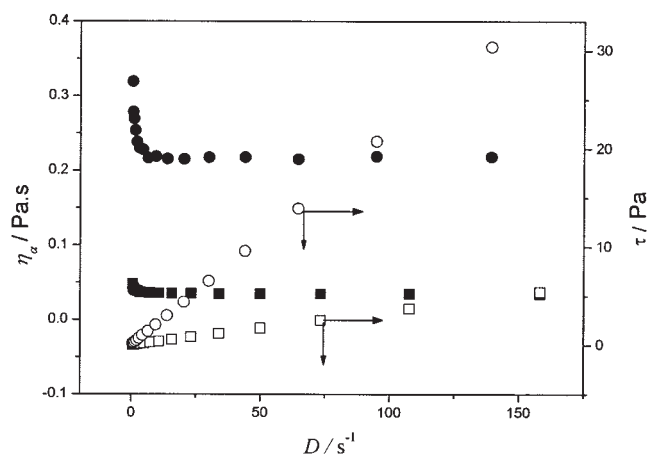


Figure 6 Plots of η_a versus D and τ versus D for SPA-1 (cube) and SPA-2 (circle).

Photopolymerization of formulation containing SPAs

Reactivity is also necessarily considered when selecting components for a formulation. Figure 8 illustrates the effect of different diluents on curing kinetics of SPUA oligomers. It was found that the addition of SPAs could significantly increase the UV curing speed and final conversion. This may be ascribed to the reduced viscosity of the formulation and the increase of the acryloxyl group concentration in the total system to be cured. The rate of polymerization increases rapidly up to a maximum value $(R_p)_{\max}$ in the early stage of the reaction, typically below 20% conversion. When the initiation rate becomes very large, the diffusion of the reactive species will become the limiting factor. The addition of SPAs can particularly reduce the viscosity of the systems, which will enhance the chain mobility and be favorable for diffusion. In addition, the higher the initial concentration of acryloxyl groups in formulation, the faster the propagation resulting from the increase of potential encounters between acryloxyl groups.

CONCLUSIONS

The novel diluents (SPA) obtained through Michael addition possess both UV and moisture-curing ability. Although the extent of curing is low under moisture condition, the moisture-curing films could become tack-free within a short time. In particular, they were found very efficient in diluency and reactivity for UV polymerization.

The authors gratefully acknowledge the financial support by the Guangdong Science and Technology Commission (Grant

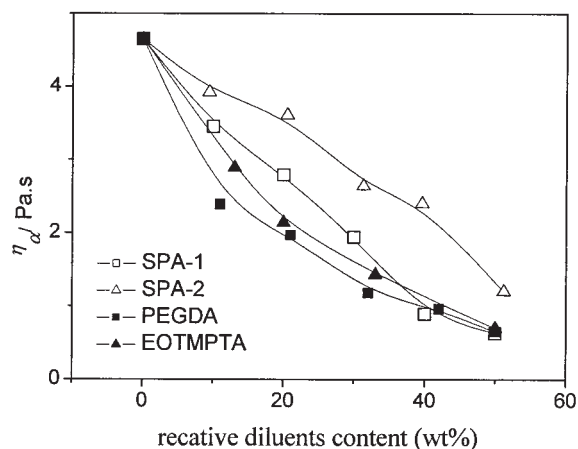


Figure 7 Relation between apparent viscosity and the diluent contents (SPUA as the oligomer).

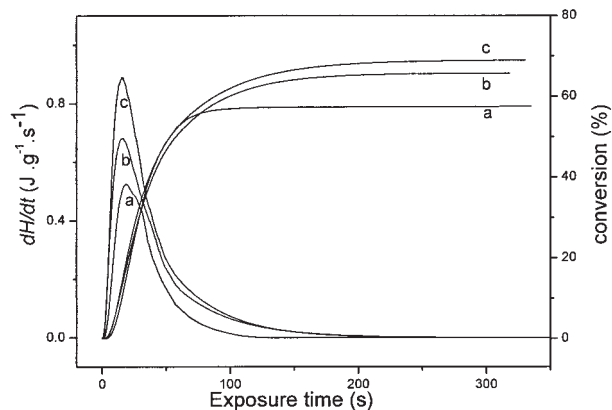


Figure 8 Effect of different reactive diluents on UV curing in air. Curve a: no reactive diluent. Curve b: SPA-1 as reactive diluent. Curve c: SPA-2 as reactive diluent (60 wt % SPUA; 35 wt % reactive diluent; 3.0% Darocur 1173; 2.0 wt % DBTDL; incident light intensity: 2.45 mW/cm²).

2001-367) and the National Natural Science Foundation of China (Grant 60378029).

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