

Synthesis and Properties of Ultraviolet/Moisture Dual-Curable Polysiloxane Acrylates

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Received 19 July 2004; accepted 31 October 2004

DOI 10.1002/app.21521

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

ABSTRACT: Ultraviolet (UV)/moisture dual-curable polysiloxane acrylates (PSAs) were prepared from *N,N*-bis[3-(triethoxysilyl)propyl]amine (G402) and ethoxylated trimethylolpropane triacrylate (EB160) through Michael addition. The obtained prepolymers were characterized by ¹H-NMR and FTIR. The rheological behavior of the prepolymers exhibited the properties of a Bingham fluid and the apparent viscosity was directly correlated with molecular weight. The photocuring kinetics of PSA were studied using photo-DSC and all the polymerization conversions were high. With increasing content of tertiary amine in the prepolymer, the photocuring rate in air increased as well. The moisture-curing kinetics of the prepolymers was studied using FTIR. It was found that the curing mechanism may

be described as the transforming of Si—O—C into Si—O—Si structure, which was consistent with the theoretical expectation. DSC and TGA were used to characterize the glass-transition temperatures and the thermomechanical stability of the prepolymers. Measurements of physical properties showed excellent gloss, impact strength, and high electric resistance for both UV- and moisture-cured films, but poor adhesion for UV-cured films and lower hardness for moisture-cured films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 846–853, 2005

Key words: silicones; polysiloxanes; UV curable; films; Michael addition

INTRODUCTION

UV-radiation curing has become a well-accepted technology because of its distinct advantages: it is environmentally benign, efficient, consumes less energy, and is a mild curing condition.^{1,2} However, some odd configurations exist in shadow areas, such as in electronic printed circuit boards, to which UV radiation cannot reach. For this reason, a secondary curing mechanism, such as heat or moisture curing, was introduced to overcome these shadowed areas. The drawback of heat curing is that a high curing temperature would affect some sensitive components.³ The moisture-curing mode includes isocyanate groups reacting with active hydrogen as well as the hydrolysis and condensation of alkoxy silane groups. The primary disadvantages of the former are toxicity, instability, and high cost.

Because of their excellent thermal stability, low-temperature flexibility, and high dielectric strength, silicones have been used for coating, potting, or encapsulating electrical devices such as integrated circuits.⁴ To obtain UV/moisture dual-curable silicone

compositions, the routine practice is to attach hydrolyzable alkoxy groups to polymerizable groups. The alkoxy group can react with water in the air to form a silanol and an alcohol. The silanol group can then condense to form siloxane groups with the elimination of water or alcohol.⁵ Bennington⁶ invented an acrylate-terminated polydimethylsiloxane, which was prepared by reacting a hydroxyl-terminated polydimethylsiloxane with dimethylchloromethacryoxypropylsilane.

In this article, we report on the synthesis of polysiloxane acrylates (PSA) from *N,N*-bis[3-(triethoxysilyl)propyl]amine (G402) and ethoxylated trimethylolpropane triacrylate (EB160) through Michael addition. Because of their low viscosity, the addition of reactive diluent is not necessary for the formulation of a UV/moisture dual-curable composition. UV- and moisture-curing behaviors of PSA were studied by photo-DSC (DPC) and infrared spectroscopy (IR). The rheological behavior of PSA was investigated. The thermal and physical properties of the cured films, through different curing mechanisms, were also studied.

EXPERIMENTAL

Materials

In the synthesis of PSA and the preparation of dual-curable compositions, the following materials were used: (1) *N,N*-bis[3-(triethoxysilyl)propyl]amine (G402, chemically pure; Aokai Biologic and Chemical Products, Inc.,

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

TABLE I
Formulation of Polysiloxane Acrylate (PSA)

PSA	Component	Molar ratio	Tertiary amine value (mmol/g)
I	EB160 : G402	4.2 : 1	0.43
II	EB160 : G402	2.0 : 1	0.79
III	EB160 : G402	1.5 : 1	0.99

Dalian, China); (2) ethoxylated trimethylolpropane triacrylate (EB160; UCB, Brussels, Belgium); (3) a hydroxyphenyl ketone photoinitiator (Darocur 1173, chemically pure; Ciba-Geigy, Basel, Switzerland); (4) methanol (analytically pure; Chemical Products Inc., Guangzhou, China). The formulation of PSA is given in Table I.

Synthesis of the PSA

The component mentioned in Table I together with 10 mL of methanol, used as a phase-transfer agent, were charged into a 250-mL three-neck flask with a mechanical stirrer. The reaction (Scheme 1) was performed under N₂ protection. The mixture was heated to 50°C and maintained for 7 h with mechanical stirring. When the tertiary amine value remained almost unchanged, the reaction system was connected to a vacuum of 50 mmHg and kept at 50°C for 0.5 h to remove methanol in the system.

Preparation of UV-cured films

Formulations of dual-curable coatings from the obtained PSA and 5 wt % Darocur 1173 were applied onto various substrates (iron sheets, stainless steel plates) and placed on a UV-curing line equipped with a 2400-W medium-pressure mercury lamp. The thickness of the coating was 20 μm and the light intensity was measured to be 37.5 mW/cm² (the detector was sensitive in the wavelength range of 320–400 nm) at the sample position. The curing time was 30 s.

Preparation of moisture-cured films

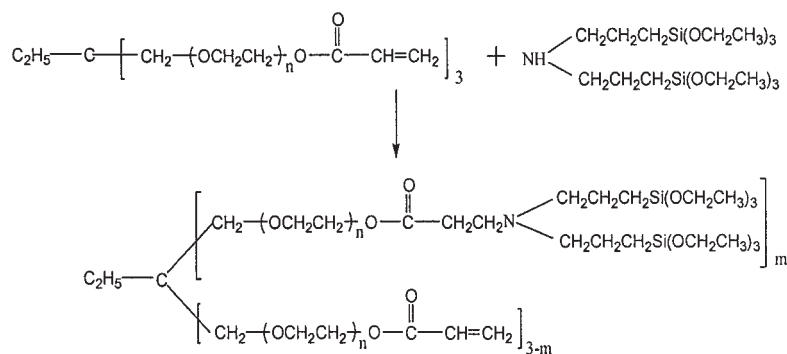
Formulations of dual-curable coatings from the obtained PSA and 5 wt % Darocur 1173 were applied onto various substrates (iron sheets, stainless steel plates) at room temperature and stored at 75% relative humidity for 48 h. The formulations were protected from UV light during the moisture-curing process.

Characterization methods

The tertiary amine value of the obtained PSA was determined by titration with 0.5 mol/L HClO₄/diethylene glycol monomethyl ether solution,⁷ which was used to monitor the degree of Michael addition. The conversion used in the present study was >95% and the number-average molecular weights were 983 for PSA I and 2253 for PSA III. Polydispersity values were 1.32 for PSA I and 2.25 for PSA III, as determined by GPC.

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 polymer films on KBr pellet before curing as well as after UV curing or moisture curing. A Varian Unity 300 NMR spectrometer (Varian Associates, Palo Alto, CA) was used to record the ¹H-NMR of the oligomers, and all NMR spectra were determined from CDCl₃ solution at ambient temperature.

Viscosity and rheology properties were measured by using a rotary viscometer (Brookfield viscometer Model DV-II+; Brookfield Engineering Laboratories, Middleboro, MA) with a No. 18 spindle at ambient condition. DSC measurements were carried out under nitrogen purging (40 mL/min) and at a heating rate of 10°C/min, from -10 to 90°C, on a TA 2910 Modulated DSC instrument (TA Instruments, New Castle, DE). The kinetics of degradation of the cured films was measured using a Shimadzu TGA-50 instrument (Shimadzu, Kyoto, Japan), from room temperature to 800°C, at a heating rate of 20°C/min and a nitrogen flow rate of 40 mL/min.



Scheme 1 Synthesis of polysiloxane acrylates (PSAs).

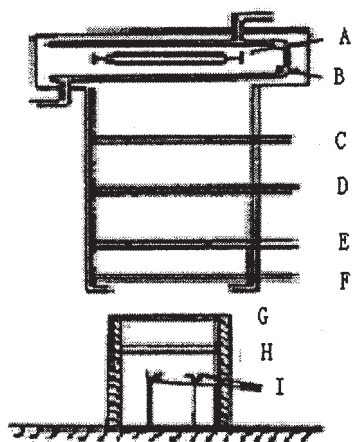


Figure 1 Schematic diagram of DPC for studying UV curing: (A) medium-pressure mercury lamp; (B) circulating water heat filter; (C, D) filters; (E) convex lens; (F) shutter; (G, H) quartz glasses; (I) sample and reference pans.

Photo-DSC (DPC) was a modified CDR-1 DSC (made by Shanghai Balance Instrument Plant, China), which was used to measure the exothermal rate of irradiated samples (shown in Fig. 1). The light intensity was measured to be 3.25 mW/cm^2 (the detector was sensitive in the wavelength range of 320–400 nm). The exothermal rate as a function of time was observed under isothermal conditions at room temperature for continuous illumination reactions.⁸

Some physical properties of the PSA were measured according to Chinese National Standard Test procedures listed in Table II.⁹ The resistance of cured films was measured using a ZC36 high-resistance instrument (Shanghai No. 6 Ammeter Factory, China) at 25°C and at a relative humidity of 66%.

TABLE II
Testing Procedures for the Dual-Cured Films

Property	Procedure
Gloss	GB 1743-79
Pencil hardness	GB/T1730-93
Adhesion	GB 1720-79
Impact strength	GB/T1732-93
Flexibility	GB/T1731-93

RESULTS AND DISCUSSION

Characterization of PSA oligomer by IR and $^1\text{H-NMR}$ spectroscopy

Figure 2 shows the FTIR spectrum of a PSA oligomer (PSAII) obtained from Michael addition. The disappearance of the N—H stretching band (3407 cm^{-1}) and the lessening of $\text{CH}=\text{CH}_2$ characteristic absorption peaks (1638 , 1406 , 986 , and 810 cm^{-1}) confirm that G402 had reacted with EB160. The presence of an absorption peak at 1080 cm^{-1} is attributed to C—O stretching of the siloxane group.

The $^1\text{H-NMR}$ spectrum of PSA oligomer (PSAII) is shown in Figure 3.

The assignment of chemical shifts is as follows: 6.43 , 5.88 ($-\text{CH}=\text{CH}_2$, m), 6.05 ($-\text{CH}=\text{CH}_2$, m), 4.10 – 4.35 ($-\text{O}-\text{CH}_2\text{CH}_2-$, m), 3.81 [$-\text{Si}(\text{OCH}_2\text{CH}_3)_3$, m], 3.65 ($-\text{O}-\text{CH}_2\text{CH}_2-$, m), 3.40 [$-\text{C}(\text{CH}_2-)_3$, m], 2.80 [$-\text{N}(\text{CH}_2-)_2$, m], 2.45 ($-\text{COCH}_2\text{CH}_2-$, m), 1.65 ($-\text{COCH}_2\text{CH}_2-$, s), 1.42 – 1.60 [$-(\text{CH}_2)_3-$], 1.22 [$-\text{Si}(\text{OCH}_2\text{CH}_3)_3$, m], 0.80 (CH_3CH_2- , m), 0.62 ($-\text{CH}_2\text{Si}-$, m).

The emergence of peaks at 2.45 ($-\text{COCH}_2\text{CH}_2-$) and 1.65 ($-\text{COCH}_2\text{CH}_2$) and the diminution of peaks at 5.88 – 6.43 ($-\text{CH}=\text{CH}_2$) further confirmed formation of the target substance.

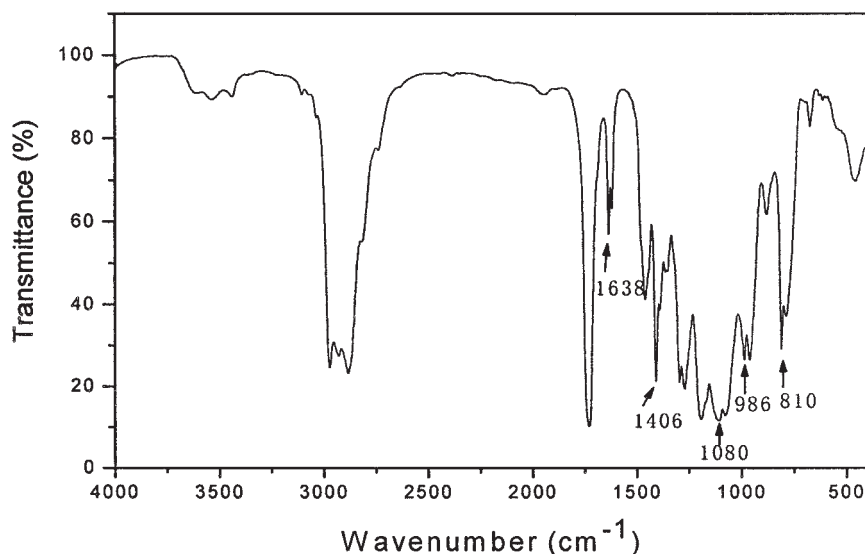


Figure 2 FTIR spectrum of PSA oligomer (PSAII).

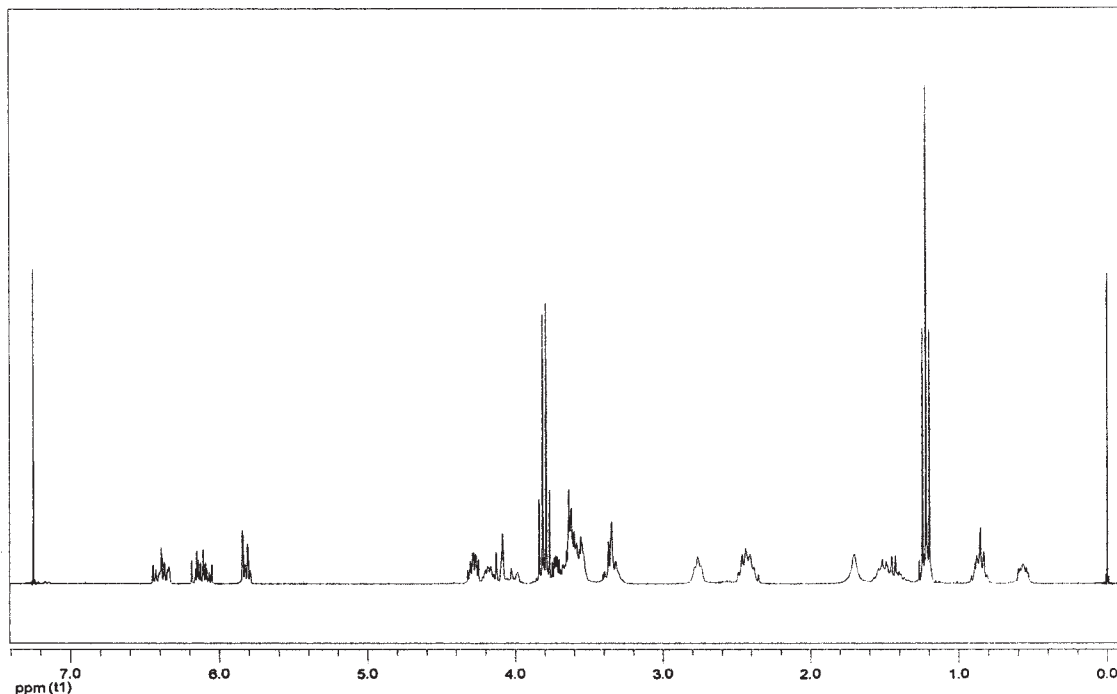


Figure 3 ¹H-NMR spectrum of PSA oligomer (PSAII).

Rheological behavior of PSA

It is well known that the rheological behavior of a fluid may be described by the following equation:

$$\tau = KD_r^n \tag{1}$$

where τ is the shear stress; D_r is the shear rate; n is the flow index, which indicates deviation from Newtonian behavior; and K is the viscosity coefficient. The greater the value of K , the higher the apparent viscosity for the fluid.

Equation (2) is obtained by transforming eq. (1) into logarithmic form:

$$\log \tau = \log K + n \log D_r \tag{2}$$

from which the values of n and K could be calculated from the slope and the intercept of the plot of $\log \tau$ versus $\log D_r$, respectively.

Flow index values of PSA systems were close to unity (0.90–0.93). The PSA systems were characteristic of a Bingham fluid because they did not flow until the shear stress was above a certain value. The following equation is applicable to a Bingham fluid¹⁰:

$$\tau - \tau_y = \eta_p D_r \tag{3}$$

where τ_y is the yield stress and η_p is the Bingham viscosity. Values of η_p and τ_y could be calculated from

the slope and the intercept of the plot of τ versus D_r , respectively (Fig. 4).

All the correlation coefficients in Table III are >0.99, which may indicate that the rheological behavior of PSA systems follows the Bingham viscosity equation. With increasing G402 content, the molecular weight of oligomer increases and the Bingham viscosity also increases, which is in accordance with the rule that viscosity directly relates to the molecular weight in similar systems.¹⁰ PSAIII has the highest yield stress because it has more hydrogen bonding and chain entanglement in the structure. It is desirable to possess

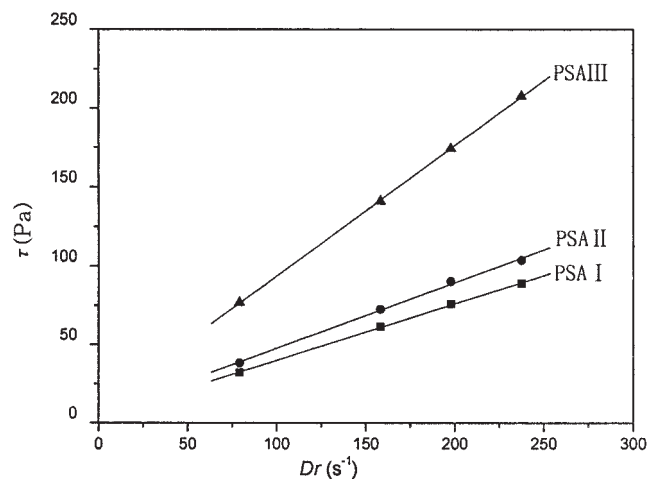


Figure 4 Plots of D_r - τ of PSA systems.

TABLE III
Effects of Different G402 Content on the Rheological Parameters of PSA

Sample	τ_y (Pa)	η_p (Pa · s)	Correlation coefficient
PSA I	3.86	0.36	0.99973
PSA II	5.81	0.42	0.99877
PSA III	10.89	0.83	0.99993

such Bingham behavior in terms of coatings application because it should promote flow during application but inhibit flow after application.

FTIR observation for the coating compositions before and after curing

FTIR spectra of the dual-curable coating and its cured films are shown in Figure 5. After UV curing, The $\text{C}=\text{H}$ out-of-plane bending at 986 and 810 cm^{-1} disappears, and $\text{C}=\text{O}$ stretching of esters (1190 cm^{-1}) moves to a lower wavenumber (1168 cm^{-1}) with decreasing $\text{C}=\text{C}$ content.

Compared with dual-curable coating before moisture curing, despite the low extent of curing, it can be seen that the characteristic absorption peak from the $\text{Si}-\text{OCH}_2\text{CH}_3$ group at 786 cm^{-1} has weakened, and the $\text{Si}-\text{O}-\text{Si}$ stretching at 1105 cm^{-1} becomes stronger and broader. Therefore, the moisture-curing mechanism is based on the transforming of $\text{Si}-\text{O}-\text{C}$ into a $\text{Si}-\text{O}-\text{Si}$ structure (Scheme 2).⁵

UV-curing behavior of the coating compositions by DPC

The DPC curves characterizing the curing behavior of the coating compositions are shown in Figures 6 and 7.

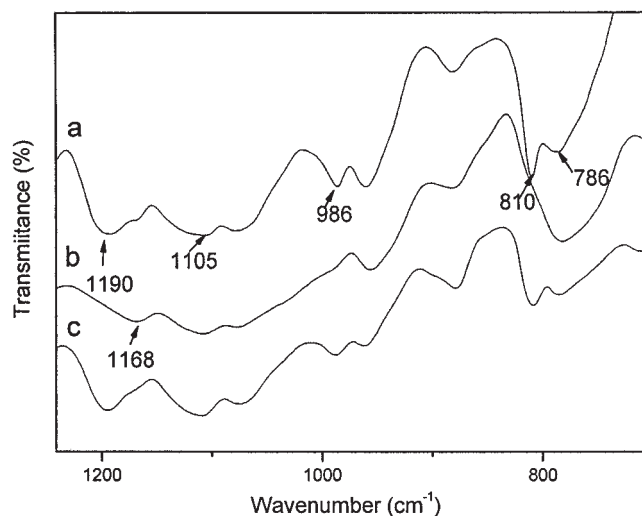


Figure 5 FTIR spectra of dual-curable coating films: (a) before curing, (b) after UV curing, and (c) after moisture curing.



Scheme 2 Hydrolysis and condensation of Si-OR.

The S-shape for the plots of conversion versus exposure time indicate the curing reactions of PSA systems are characterized by chain polymerization. Unlike typical radical polymerization, the maximum reaction rate in air is higher than that in N_2 , and the oxygen inhibition polymerization for PSA system is not obvious. It may be explained by the fact that the tertiary amine could suppress the inhibition of oxygen (Scheme 3).¹¹ In air, the tertiary amine may offer hydrogen to the peroxide free radical, produced in the process of inhibition of oxygen, the latter of which further decompose into alkyl and hydroxide radicals. The higher concentration of radicals increased the reaction rate and the early occurrence of the gel effect (the viscosity of the reacting system increases drastically with increasing conversion, which makes termination by radical combination difficult, but has little effect on the chain propagation reaction, thus giving rise to autoacceleration). However, chain transfer and radical terminations tend to occur, which quickly reduced the rate at the latter stage of curing. With increasing G402 content and decreasing $\text{C}=\text{C}$ bond density, the molecular mobility of chain radicals increases, and the glass-transition temperature (T_g) of the reacting system reduces so that vitrification suspends. Therefore, the conversion of PSAIII is the highest and that of PSAI is the lowest.

Thermal properties of the cured films

The glass-transition temperatures of PSA cured films detected by DSC are listed in Table IV. UV-cured films

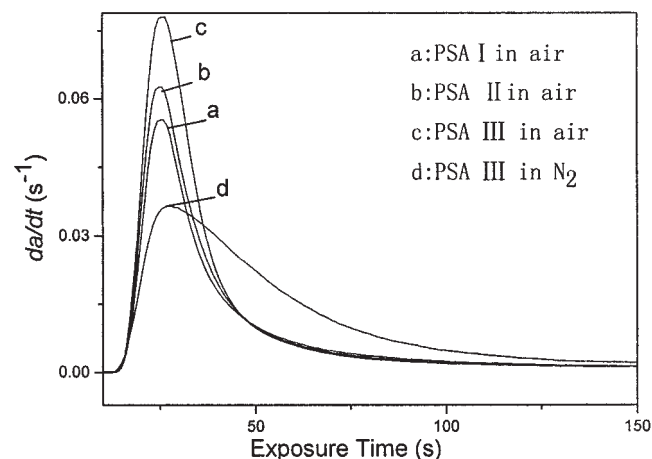


Figure 6 DPC curves for the curing rate of dual-curable coating.

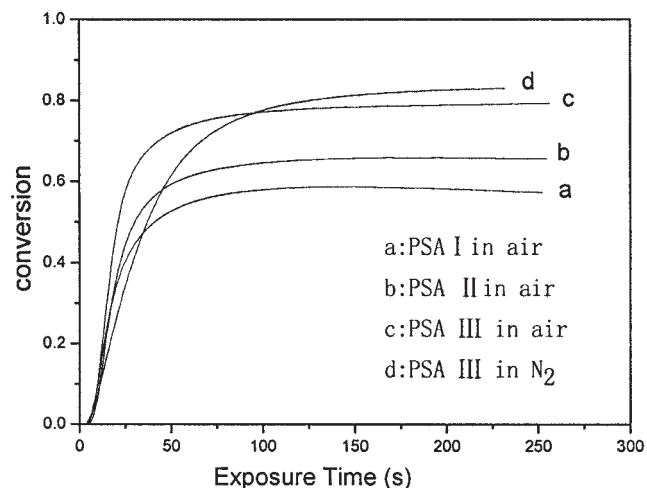
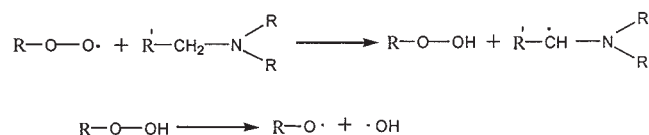


Figure 7 DPC curves for the conversion of dual-curable coating.

have higher glass-transition temperature than that of moisture-cured films. The main reasons for this phenomenon the high conversion and crosslink density in UV curing and the Si—O—Si chain is more flexible than C—O—C chain. Moreover, diminishing the C=C bond content in oligomer decreases the crosslink density of the polymer, thus reducing the free volume of the polymer and results in the lowering of the glass-



Scheme 3 Suppressing mechanism for the inhibition of oxygen by tertiary amine.

TABLE IV
Glass-Transition Temperatures of PSA Cured Films

Sample	T_g ($^{\circ}\text{C}$)	$T_{g\text{onset}}$ ($^{\circ}\text{C}$)	$T_{g\text{end}}$ ($^{\circ}\text{C}$)
PSA I UV cured	36.8	26.7	48.4
PSA II UV cured	33.5	28.6	39.3
PSA III UV cured	32.1	29.2	35.0
PSA III moisture cured	29.4	25.3	33.5

transition temperature. Therefore, it is not surprising that the glass-transition temperature of PSA UV-cured films decreases as the G402/EB160 ratio increases from PSAI, with 1 : 4.2 molar ratio, to PSAIII, with 1 : 1.5 molar ratio.

Figure 8 compares the TGA kinetic behavior of PSA cured films with different G402/EB160 ratios. The TGA parameters of these PSA cured films are summarized in Table V. The onset and maximum peak temperatures could qualitatively characterize the degradation of PSA cured films. It is seen that all the cured films have good thermal stability, but the UV-cured films are superior to the moisture-cured films. With increasing G402/EB160 ratio, the siloxane concentration increases and the conversion of the C=C group increases from PSA I to PSA III. As a result, PSAIII UV-cured films have the highest residue amount of all films investigated. Moreover, PSAIII UV-cured film has the lowest $T_{2\text{on}}$ temperature because of the lowest crosslink density.

TGA weight-loss curves for both PSA UV-cured and moisture-cured films exhibit two distinct regions of weight loss, revealed more clearly in the differential weight loss (DTGA) curve (Fig. 9). The second stage is the main degradation process and, in this course, the decomposition of different kinds of covalent linkages takes place to form char and silica as end products.

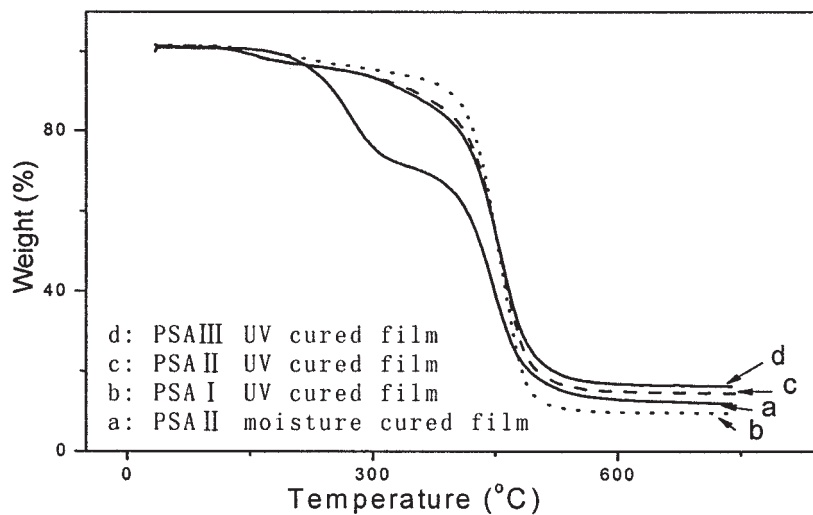


Figure 8 TGA curves of PSA-cured films.

TABLE V
TGA Parameters of PSA Cured Films

Sample	T_{1on} (°C)	T_{1max} (°C)	T_{2on} (°C)	T_{2max} (°C)	Residue (%)
PSA I UV-cured film	—	—	418.2	452.6	9.48
PSA II UV-cured film	83.0	145.4	416.2	453.2	14.37
PSA III UV-cured film	92.5	147.3	410.3	451.5	16.22
PSA II moisture-cured film	210.6	250.9	416.2	451.7	9.43

The first weight loss step of UV-cured films at about 90°C may be explained by the evaporation of water and alcohol as a result of the hydrolysis and condensation of unreacted alkoxy silane groups in UV curing. The first degradation of moisture-cured films at 210°C is considered to be related to the decomposition of unreacted acryloxy groups and evolution of CO₂.

Physical properties of the cured films

The physical properties of films cured with different curing mechanisms are listed in Table VI. It is obvious that all of these films possess excellent gloss and impact strength. The moisture-cured films show superior adhesion and flexibility to those of UV-cured films but inferior pencil hardness. The increases in flexibility from PSA I UV-cured film to PSA III UV-cured film are attributed to the decreasing crosslink density and reduced hydrogen bonding either inter- or intramolecularly. The increase of siloxane concentration caused an increase in adhesion because the Si—OH group favored anchoring the substrate.

The electric conductivity for a polymer includes ion conductance and electric conductance. The former is attributed to the releasing ion from additive and the latter to conjugated structure. Because small molecular

substances such as water and alcohol may be embedded in polymer through the hydrolysis and condensation of alkoxy silane groups, the values of volume resistivity are about one thousandth that of surface resistivity. The resistivity of moisture-cured films is much lower than that of UV-cured films, which may be attributable to the conjugated structure of unreacted acryloxy groups.

CONCLUSIONS

The polysiloxane acrylate (PSA) system can be used for UV/moisture dual-curable coating. ¹H-NMR and FTIR confirmed the obtained prepolymers. The rheological behavior of the prepolymers was characteristic of a Bingham fluid and the apparent viscosity correlated with molecular weight. Photo-DSC (DPC) results indicated that a tertiary amine could suppress the inhibition of oxygen. The moisture-curing kinetics of the prepolymers were studied using FTIR. It was found that the moisture-curing mechanism may be depicted as the transforming of Si—O—C into Si—O—Si structure. DSC analysis shows that the glass-transition temperature of PSA UV-cured films decreases with increasing G402/EB160 ratio. TGA results indicated that the UV-cured films have a better

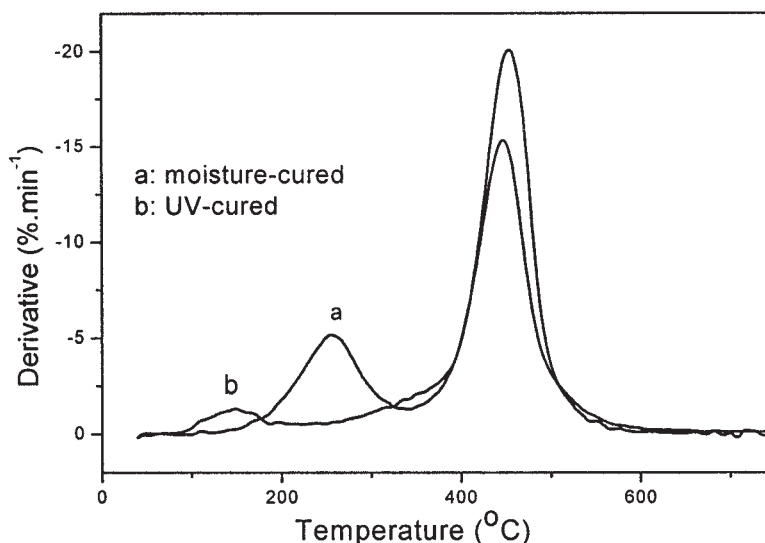


Figure 9 DTGA traces of PSAII-cured films.

TABLE VI
Physical Properties of PSA Cured Films

Property	Sample			
	PSA I UV cured film	PSA II UV cured film	PSA III UV cured film	PSA III moisture cured film
Gloss ^a	109.0	107.4	108.6	97.7
Impact strength, kg cm ⁻¹	40	46	43	50
Pencil hardness	H	2H	2H	<6B
Adhesion (grade)	7	4	4	1
Flexibility, mm	15	4	4	1
ρ_s^b ($\times 10^{14}/\Omega$)	22	15	19	0.3
ρ_v^c ($\times 10^{11}/\Omega/\text{cm}^{-1}$)	32	44	11	0.3

^a The angle of incidence is 60°.

^b Surface resistivity.

^c Volume resistivity.

thermal stability than that of moisture-cured films. Measurement of physical properties showed excellent gloss, impact strength, and high electric resistance for both UV- and moisture-cured films, but poor adhesion for UV-cured films and lower hardness for moisture-cured films.

This work was supported by the Guangdong Science and Technology Commission (Grant 2001-367), which is gratefully acknowledged.

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