Study on Properties of a Novel Photosensitive Polysiloxane Urethane Acrylate for Solder Mask

Fang Sun,[1,2] **Shengling Jiang**[3]

[1]*State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[2]*College of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[3]*College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*

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ABSTRACT: The photosensitive and physical and mechanical properties of a novel polysiloxane urethane acrylate (PSUA) for solder mask were investigated using real-time FTIR, DMTA and TGA. It is noted that PSUA showed a notable photosensitivity and a good compatibility with the acrylic monomers and resins. PSUA cured film exhibited excellent thermal property, tensile strength and toughness, and chemical resistance. The decomposition temperature of PSUA was 402 °C. Thermal weight losses of pure PSUA cured film at 300 °C were only 5%. Elongation percentage of PSUA cured film was up to 59%. PSUA resin can be used for solder mask materials for printed circuit. Technology performances of photosensitive imaging flexible solder mask containing PSUA answers operating requirements of the solder masker for printing circuit board. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3035–3039, 2010

Key words: polysiloxane; UV curing; urethane acrylate; solder mask

INTRODUCTION

At present, lead-bearing bonding technology is replaced with lead-free bonding technology in printing circuit board manufacturing process for environmental protection. Solder mask matching for lead-free bonding technology should possess higher performances as follows[1–5]: (1) Chemical plating resistance, namely, resistance to NiAu, Sn, Ag and organic solderability preservatives (OSP). Moreover, solder mask should resist higher temperature of solution in chemical plating process (2) Thermal shock resistance. The temperature resisted increases from 230–240°C to 240–260°C. (3) Excellent flexibility. Liquid imaging solder mask for high density flexible printing circuit should possess good bending resistance.

Silicone resin possesses good resistance to high temperature, flexibility and electric reliability etc. because of character of Si—O bond.[6–12] Introduction of silicone resin as a primary resin into the formulation of solder mask could improve heat resistance, flexibility and electric reliability of solder mask. Therefore, we have designed and synthesized a novel photosensitive polysiloxane oligomer polysioxane urethane acrylate (PSUA) to gain photosensitive imaging flexible solder mask with excellent property. PSUA was endowed with photosensitivity and enhanced intensity, chemical resistance and compatibility with other resins and acrylate monomers by introduction of acrylate groups, urethane chain, polyether chain into the structure of polysiloxane resin molecule. In this article, photosensitive and physical and mechanical properties of PSUA were investigated using real-time FTIR, DMTA, and TGA. Photosensitive imaging flexible solder mask containing PSUA was studied and prepared. Its fundamental technology performances were tested and reached the national standard of SJ/T10309-92 (solder mask for circuit board), moreover, some technology performances were better than national standard.

Correspondence to: F. Sun (sunfang60@yeah.net).
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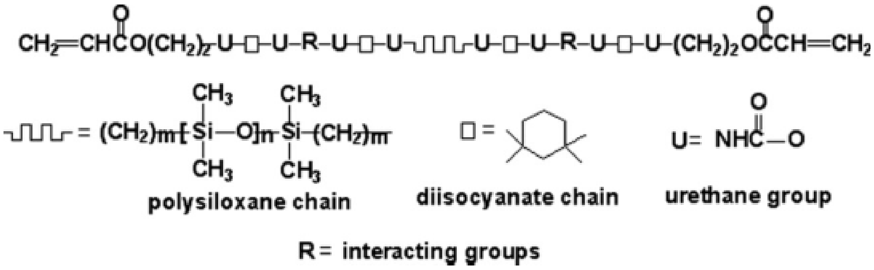
EXPERIMENTAL

Materials

Urethane acrylate resin and epoxy acrylate resin were provided by Eternal Chemical. Taiwan.1, 6-hexanediol diacrylate (HDDA), 2-hydroxyethyl acrylate (HEA), isobornyl acrylate (IBOA), tripropylene glycol diacrylate (TPGDA), and trimethylol propane triacrylate (TMPTA) were purchased from Beijing Dongfang Chemical. Hydroxyalkyl polydimethylsiloxane (H-PDMS, hydroxy group content: 1.06 mol/



Scheme 1 The molecular structure of PSUA.

g) was supplied by Dow Corning. Isophorone Diisocyanate (IPDI) and dihydroxy alcohol were purchased from Qingdao Xinyutian Chemical. Photoinitiators, 2-hydroxyl-2-methyl-1-phenyl propane-1-one (Darocur 1173) was obtained from Ciba Geigy. Commercial polyether urethane acrylate resin (AR-12) was supplied by Beijing Lituoda Sci-Tech.

Synthesis of PSUA resin

Firstly, IPDI (5.33 g, 0.024 mol) was added into a four-necked flask (250 mL) with dropping funnel, reflux condenser, thermometer and a mechanical stirrer. The mixture of H-PDMS (22.44 g, 0.012 mol) and DBTDL (0.083 g) was dropwise added into the flask by the charge pipe for 10 min at 30°C and the reaction was carried out for 3 h at this temperature. Then interacting agent (2.16 g, 0.024 mol) was added into the flask and heated up to 40°C. After the reaction was carried out for 3.5 h, the product (I) was obtained. Then, IPDI (5.32 g, 0.024 mol), HEA (2.78 g, 0.024 mol), DBTDL (0.0243 g) and 4-Methoxyphenol (0.09 g) were added into a four-necked flask (250 mL) with dropping funnel, reflux condenser, thermometer and a mechanical stirrer. After the reaction mixture was stirred at 2°C for 4 h, the product (II) was obtained. Finally, the product (I) reacted with product (II) at 60°C for 3 h in the presence of DBTDL as catalyst to obtain final product PSUA (M_n = 7408). The molecular structure of PSUA was shown in Scheme 1.

IR (KBr, cm^{-1}): 3332 cm^{-1}, 1536 cm^{-1} (—NH—), 2904–2952 cm^{-1} (—CH_3, —CH_2—), 1035 cm^{-1} (—C—O), 1172 cm^{-1}, 1102 cm^{-1} (>C=O), 1259 cm^{-1}, 803 cm^{-1}, 1099 cm^{-1} (Si—O), 1630 cm^{-1}, 810 cm^{-1} (C=C).

Analyzes and characterization

Preparation of UV-curable film: PSUA and different reactive monomers were mixed with a certain weight ratio and subsequently the photoinitiator Darocur 1173 (2 wt %) was added into the mixture to form a homogeneous sample. The sample was then coated on a glass plate and exposed to a UV lamp (1 kW) in air to obtain a cured film (100 μm thickness).

The polymerization was monitored *in situ* by FT-NIR (Nicolet 5700, Thermo Electron, equipped with an extended range KBr beam-splitter and an MCT/A detector). A horizontal transmission accessory (HTA) was designed to enable mounting of samples in a horizontal orientation for FTIR measurements. A UV spot light source (EFOS Lite, Canada) was directed to the sample with light intensity of 10 mW/cm^2 (Honle UV meter, Germany). The conversion of the acrylate double bond was followed by the change of absorption area from 6103 to 6229 cm^{-1} in the near-IR range. Furthermore, the series FTIR runs were repeated several times and the error on the reported double bond conversion as a function of polymerization time was less than 2%. And in most case, it was less than 1%.

Thermal stability was determined with STA-449C simultaneous thermal analyzer (Netzsch, Germany). Samples were run from 30 to 500°C with a heating rate of 10°C/min. Dynamical thermal mechanical analyzes (DMTA) were performed on DMTA-IV (Rheometric Scientific). The tensile properties of PSUA film were measured with a material testing instrument (Instron-1211) at 25°C. The rate of extension was 10mm/min. Pencil hardness apparatus AR015 (Tianjing Instrument, China) was employed to measure the hardness of PSUA film.

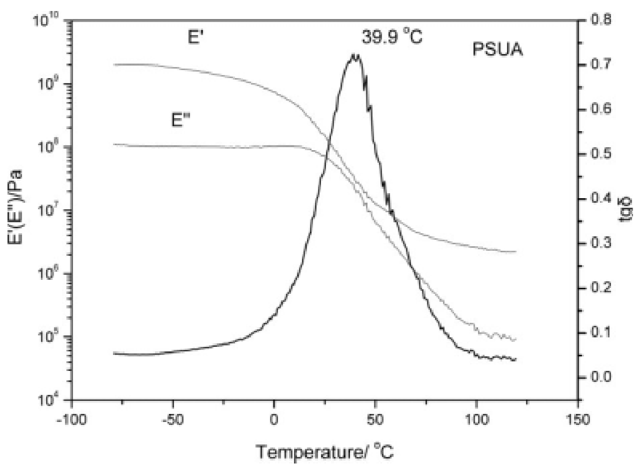


Figure 1 DMTA of PSUA resin.

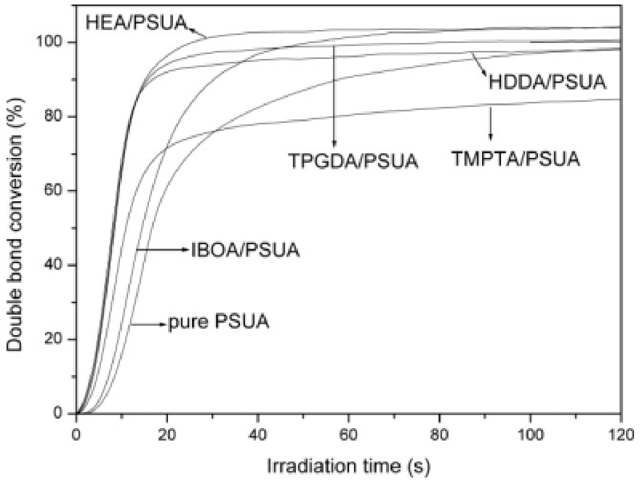


Figure 2 The relation of double bond conversion of PSUA system and irradiation time. Composition of pure PSUA system: PSUA: 1173 = 100 : 2 (wt). Composition of PSUA system with monomer: PSUA: monomer = 70 : 30 (wt), (PSUA + monomer): Darocur 1173 = 100 : 0.5 (wt).

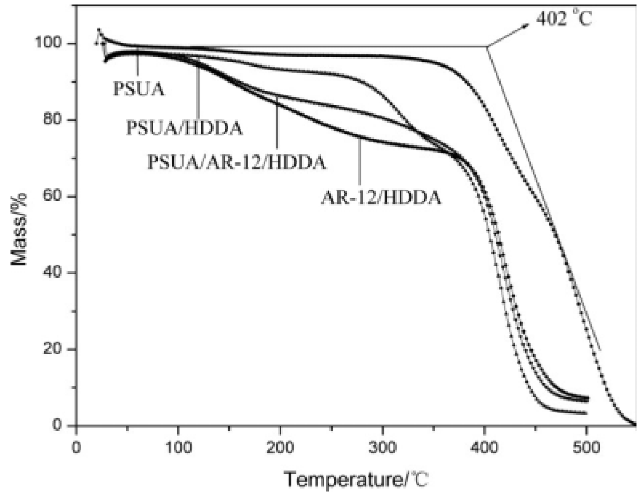


Figure 3 TGA of cured films.

RESULTS AND DISCUSSION

In this work, photosensitive property, the thermal stability, tensile strength, elongation, hardness, glass translation temperature (T_g), solvent resistance and compatibility of PSUA oligomer were tested and compared with commercial resin (AR-12).

Compatibility of PSUA with monomers and resins

PSUA was mixed with monomers HEA, TPGDA, TMPTA, urethane acrylate resin and epoxy acrylate resin respectively with the weight ratio of 1/1, 1/2, 1/3, and 1/4. The mixtures were stirred for 10 min and stored for 24 h at room temperature before a visual observation of the clarity degree of the mixture. It was found that PSUA has a good compatibility with all the acrylic monomers and resins at the weight ratio investigated, which could enhance the miscibility of the constituents in coatings.

In addition, Figure 1 shows that PSUA has lower glass translation temperature (39.9 °C), indicating PSUA has good flexibility.

Photosensitive property of PSUA

Photosensitive property of PSUA was studied by real-time FTIR and the result was showed in Figure 2. The double bond conversion of pure PSUA reaches 90% after irradiated by UV light for 1 min. It is indicated PSUA possesses photosensitive properties. The addition of acrylate diluents could speed up photopolymerization process of the PSUA system and double bond conversion of PSUA system with HEA reaches 90% after irradiated by UV light for 20 s. The final double bond conversion of the systems composed PSUA with different monomers is different and final conversion of the systems increase in the following order TMPTA < HDDA < TPGDA < IBOA < HEA. Double bond conversion of PSUA systems decreases with increase of monomer functionality. The result could be ascribed to viscosity and functionality of monomer. Three-dimensional gel structure more easily forms in the systems with multifunctional monomers compared with monofunctional monomers, leading to that uncured double bonds trapped in the polymeric networks can not polymerize further. In addition, double bond conversion of PSUA system with TMPTA is the lowest owing to high viscosity and functionality of TMPTA.

Thermal stability of PSUA cured film

Thermal behaviors of PSUA were analyzed by TGA as shown in Figure 3 and Table I. The TGA curves indicate that PSUA is very stable to heating, and decomposition temperature of PSUA is 402°C. Table I shows that thermal weight losses of pure PSUA

TABLE I
Thermal Losses of the Cured Films

Composition of the systems (wt %)	PSUA	PSUA/HDDA = 3 : 2	PSUA/AR-12/HDDA = 1.5 : 1.5 : 2	AR-12/HDDA = 3 : 2
Thermal losses at 300°C (%)	5%	15%	19%	27%

TABLE II
Tensile Properties of the Cured Films

Composition of the systems (wt %)	Tensile force (N)	Tensile strength (MPa)	Elongation percentage (%)	Tensile modulus (MPa)
PSUA/HDDA = 3 : 2	2.17	6.34	59	41.3
AR-12/HDDA = 3 : 2	2.38	6.21	20	39.3

cured film at 300°C are only 5%, but thermal weight losses of the cured films of PSUA/HDDA and PSUA/AR-12/HDDA and AR-12/HDDA were 15, 19, and 27%, respectively. It is demonstrated that addition of PSUA can markedly improve the thermal stability of cured film.

Tensile properties of PSUA cured film

The tensile properties of cured films are listed in Table II. The cured PSUA film shows higher elongation percentage (59%) than that of commercial resin AR-12 (20%). And tensile strength and tensile modulus of PSUA cured film are also higher than that of AR-12 cured film. It is indicated that PSUA cured film has more excellent flexibility and satisfies property requirements of flexible printed circuit board.

In addition, to test the chemical resistance, PSUA cured films were immerged in10% H_2SO_4, 10% HCl, 10% NaOH, 10% isopropanol, respectively, for 24 h at room temperature and experimental results show that PSUA film has excellent solvent resistance performance.

The performance of flexible solder mask containing photosensitive polysiloxane urethane acrylate (PSUA)

Although PSUA possesses advantages for lead-free bonding technology, it needs cooperation with acrylic monomer and other resins to obtain solder mask with excellent properties. To improve photosensitive property, chemical plating resistance and hardness, and so on, epoxy acrylate resin, polyester acrylate resin, and modified epoxy acrylate resin

TABLE III
Fundamental Technology Performance of Flexible Imaging Solder Mask L-S8600

Item	Testing standard	Technology requirements	Testing results	Evaluation
Appearance of cured film	According to 4.3 section in SJ/T10309-92	Appearance of cured film should be homogeneous without pastiness, bubbling, changing color and cracking	Lustre of tested cured film was homogeneous without pastiness, bubbling, changing color, cracking.	OK
Insulation resistance	SJ/T10309-92-4.8.1	$\geq 1 \times 10^{10}\ \Omega$	(1) 2.5×10^{-13} 2.6×10^{13} 1.2×10^{13} 2.8×10^{13} (2) 3.2×10^{11} 2.0×10^{11} 2.8×10^{11} 1.7×10^{12}	OK
Chemical resistance	SJ/T10309-92-4.9	The cured film does not gum, change color and fall out after marinated in 10% HCl, 5% NaOH, C_2H_5OH and $C_2H_3Cl_3$, respectively, for 1hr at room temperature	The tested cured film did not gum, change color and fall out after marinated in 10% HCl, 5% NaOH, C_2H_5OH, $C_2H_3Cl_3$, respectively, for 1 hr at room temperature	OK
Pencil hardness	SJ/T10309-92-4.4.4	≥2H	≥4H	OK
Adhesion	SJ/T10309-92-4.5	The cured film does not crack and separate after bended for 25 periods	The tested cured film did not crack and separate after bended for 25 periods	OK
Flame retardancy	SJ/T10309-92-4.10	Combustion time ≤1.5s, 125°C, Combustion time ≤1.4s after 24 h	<FV-0 grade	OK
Thermal shock resistance	According to technology requirements of the client	265 ± 5°C, 5s, 3 times 285 ± 5°C, 5s, 3 times	The tested cured film did not gum, change color and fall out	OK

TABLE IV
Fundamental Technology Conditions of Flexible Imaging Solder Mask L-S8600

Items	Testing method	Test results	Evaluation
Pencil hardness	Pencil angle: 45°, Load: 1 kg	4H	OK
Flexibility	Semidiameter of curvature: $R = 0.2$ mm Load: 500 g	$\nless$80 times	OK
Flame retardancy		UL94V-0 grade	OK
Thermal shock resistance	285°C 5s, 3 times hot air leveling 5s, 3 times	No change	Suited for lead-free solder
Chemical plating resistance			Resistance to NiAu, Sn, Ag chemical plating

TABLE V
The Test Results of Pony of Flexible Imaging Solder Mask L-S8600

Number	Items	Limiting value of testing ($\times10^{-6}$ wt %)	Test results
1	Cadmium (Cd)	2	N.D
2	Plumbum (Pb)	2	N.D
3	Mercury (Hg)	2	N.D
4	Hexad chromium (Cr VI)	2	N.D

Limiting value of testing was weight percent of the sample.
Description of sample:
L-S8600 was green printing ink.
Remarks: N.D means no detection.

were added to the composition of solder mask containing PSUA. We have designed about hundred formulations and tested their application performances to gain the formulation of flexible imaging solder mask L-S8600 with excellent properties. Fundamental technology performances of flexible imaging solder mask L-S8600 were tested by Ministry of Information Industry PCB Quality Supervising Test Center and reached the national standard of SJ/T10309-92 (solder mask for circuit board), moreover, some technology performances were better than national standard. The testing results were listed in Tables III and IV.

For the solder masker of printing circuit board, it must be lead-free and halogen-free, and therefore the PONY test of material itself is necessary for circuit board materials. PONY testing results of flexible imaging solder mask L-S8600 were listed in the Table V. It is observed from Table V that technology performance of flexible imaging solder mask L-S8600 answers operating requirements of the solder masker for printing circuit board.

CONCLUSIONS

This article studied the photosensitive and physical and mechanical properties of as-synthesized photosensitive polysiloxane urethane acrylate oligomer (PSUA) by real-time FTIR, TGA and DTMA. PSUA resin possesses higher photosensitive property and excellent compatibility and PSUA cured film has good solvent resistance performance, flexibility and thermal stability. The decomposition temperature of PSUA is 402°C. Thermal weight losses of pure PSUA cured film at 300°C were only 5%. Elongation percentage of PSUA cured film was up to 59%. The composition of flexible solder mask containing PSUA was investigated and optimum formulation of flexible solder mask, namely, L-S8600 was gained. Fundamental technology performances of flexible imaging solder mask L-S8600 were tested and reached the national standard of SJ/T10309-92 (solder mask for circuit board), moreover, some technology performances were better than national standard. L-S8600 answered operating requirements of the solder masker for circuit board.

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