Study on Properties of Photosensitive Polysiloxane Urethane Acrylate for Solder Mask

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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 RTIR, DMTA and TGA. It is noted that the PSUA system showed a notable photosensitivity and a good compatibility with the acrylic monomers and resins. PSUA cured film exhibited excellent tensile strength, thermal property, water resistance, chemical resistance and toughness. PSUA resin can be used as solder mask materials for printed circuit.

Keywords: polysiloxane, UV curing, urethane acrylate, solder mask

1 Introduction

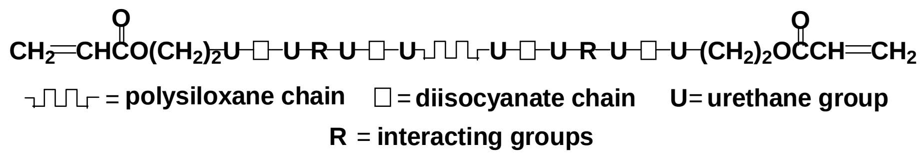
At present, lead-free bonding technology substitutes for leaded bonding technology in printing circuit board manufacturing process for environmental protection. Solder mask matching for lead-free bonding technology should possess higher performances as follows[1-5]: (1) Chemical plating resistance, namely, resistance to NiAu、Sn、Ag and OSP.. Moreover, solder mask should resist higher temperature of solution in chemical plating process (2) Thermal shock resistance. The temperature resisted by solder mask increases from 230-240 ^{o}C to 240-260 ^{o}C. (3) Excellent flexibility. Liquid imaging solder mask for high density flexible printing circuit should possess good bend resistance. The temperature resisted by photosensitive imaging, UV curing and heat curing solder masks needs to increase about 30 ^{o}C.

In this paper, photosensitive imaging flexible solder mask containing photosensitive polysiloxane oligomer was studied and prepared. Polylsiloxane resin endowed solder mask with higher bend resistance, heat resistance and electric reliability because of their unique properties, such as good resistance to high temperature, good antiweatherability, electric insulation and flexibility [6-12]. We have designed molecular structure of photosensitive polysiloxane oligomer (PSUA). Polysiloxane resin was endowed with photosensitivity and enhanced intensity, chemical resistance and compatibility with other resins and acrylate monomers by introduction of urethane acrylate, epoxy and vinyl etc. into the structure of polysiloxane resin molecule. Addition of as-synthesized PSUA into the formulation of solder mask can enhance the resistance to high temperature, bend resistance and electric reliability of the solder mask.

2 Experimental

2.1 Materials

Urethane acrylate resin and epoxy acrylate resin were provided by Eternal Chemical Co., Ltd. Taiwan.1,6-hexanediol diacrylate (HDDA), 2-hydroxyethyl acrylate (HEA), triethylene glycol diacrylate (TEGDA) and trimethylol propan triacrylate (TMPTA) were purchased from Beijing Dongfang Chemical Co. Polysioxane urethane acrylate resin (PSUA) was synthesized by us and the molecular structure of PSUA was shown in **Scheme**1. Photoinitiators, 2-hydroxyl-2-methyl-1-phenyl propane-1-one (Darocur 1173) was obtained from Ciba Geigy Co.. Commercial resin (AR-12) was supplied by Beijing Lituoda Sci-Tech. Co., Ltd.



Scheme 1 The molecular structure of PSUA

2.2 Analyses and characterization

Preparation of UV-curable film: PSUA and HDDA were mixed with a weight ratio of 70/30 and subsequently the photoinitiator was added into the mixture to form a stock sample. The polymerization was monitored in situ by FT-NIR (Nicolet5700, Thermo Electron, USA, 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 10mW / cm^2 (Honle UV meter, Germany).The conversion of the acrylate double bond was followed by the change of absorption area from 6103 cm^{-1} 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 ^oC with a heating rate of 10 ^oC/min. Dynamical thermal mechanical analyses (DMTA) were performed on DMTA-IV (Rheometric Scientific Co., USA). The tensile properties of PSUA film were measured with a material testing instrument (Instron-1211, USA) at 25 ^oC. The rate of extension was 10mm/min. Pencil hardness apparatus AR015 (Tianjing Instrument Co., China) was employed to measure the hardness of PSUA film.

3. Results and discussion

3.1 Photosensitive and physical and mechanical properties of polysioxane urethane acrylate resin (PSUA) oligomer

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

3.1.1 Photosensitive property of PSUA

Photosensitive property of PSUA was studied by real-time FTIR and the result shows that the double bond conversion of PSUA reached 90％ after irradiated by UV light for 1 min(**Figure 1**). It is indicated PUSA possesses good photosensitive properties.

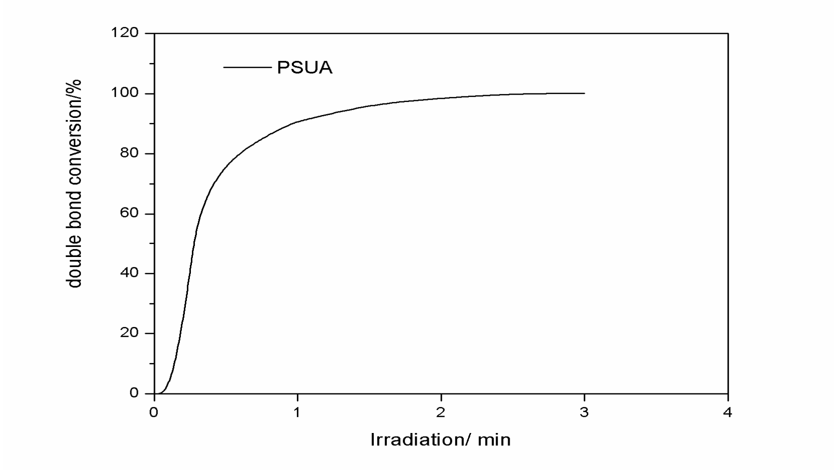


Figure 1 The relation of conversion of PSUA and irradiation time

3.1.2 Compatibility of PSUA with monomers and resins

PSUA was mixed with monomers HEA, TEGDA, 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 prior to 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.

3.1.3 Thermal stability of PSUA cured film

Thermal behaviors of PSUA were analyzed by TGA as shown in **Figure** 2 and **Table** 1. The TGA curves indicate that PUSA is very stable to heating, and decomposition temperature of PSUA is 402.2 ^{o}C. **Table** 1 shows that thermal losses are only 5% of pure PSUA cured film, but thermal 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.

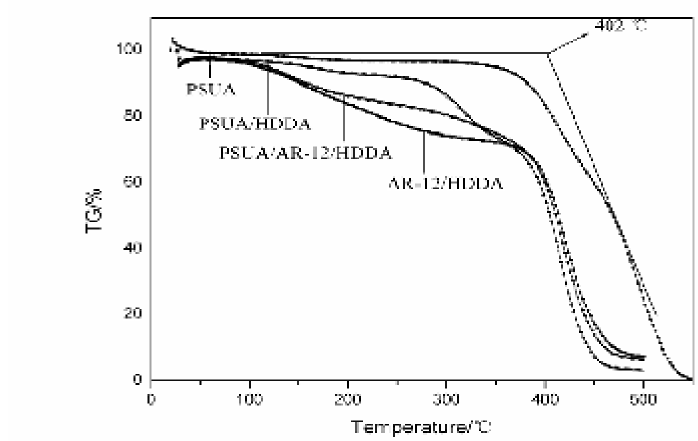


Figure 2 TGA of cured film

Table 1 Thermal losses of the cured films

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

3.1.4 Tensile properties of PSUA cured film

The test results of tensile properties of PSUA cured films show that PSUA cured film has higher elongation percentage, which was up to 59%. However, elongation percentage of commercial resin (AR-12) is only 20% and tensile strength and tensile modulus of PSUA cured film are higher than that of commercial resin (AR-12) cured film. It is indicated that PSUA cured film has more excellent flexility and satisfies property requirements of flexible printed circuit board.

Table 2 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

3.1.5 Glass translation temperature (Tg) of PSUA

Figure 3 and **Figure 4** show that PSUA and AR-12 have lower Tg and they are 39.9 ^{o}C and 40.9 ^{o}C, respectively.

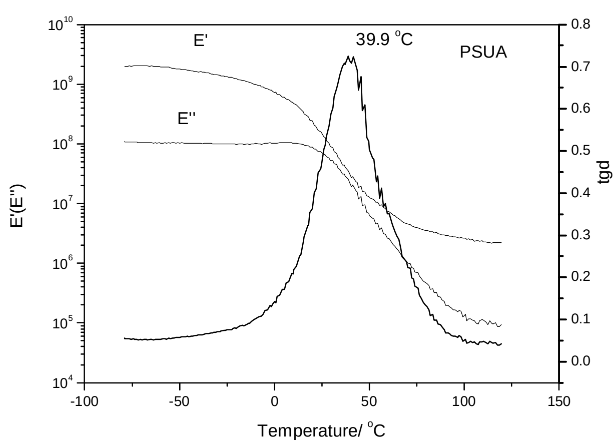


Figure3 DMTA of PSUA resin

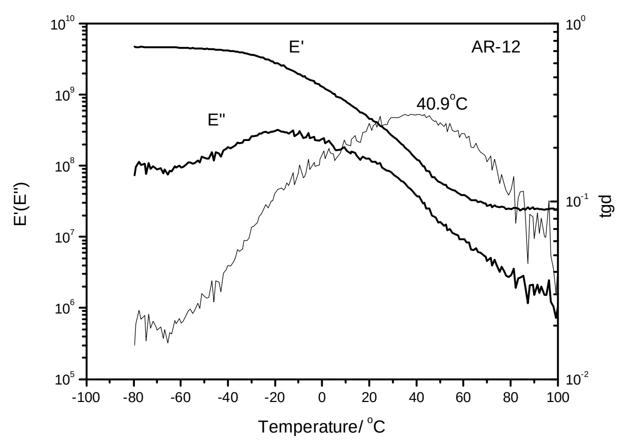


Figure 4 DMTA of AR-12 resin

In addition, to test the chemical resistance, PSUA UV cured films were immerged in10% H_2SO_4, 10% HCl, 10% NaOH, 10% isopropanol, respectively, for 30 min at room temperature and experimental results indicated that PSUA film has excellent solvent resistance performance.

The above study results indicate that as-synthesized PSUA resin possesses higher photosensitive property and excellent compatibility and PSUA cured film has good solvent resistance performance, flexility and thermal stability. The decomposition temperature of PSUA is 402 ^{o}C.

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

Table 3 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	$\geqslant 1\times 10^{10}\,\Omega$	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 1hr 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 for25 periods	The tested cured film did not crack and separate after bended for25 periods	OK
Flame retardancy	SJ/T10309-92 -4.10	Combustion time≤ 1.5s,125℃, Combustion time≤1.4s after 24h	＜FV-0 grade	OK
Thermal shock resistance	according to technology requirements of the client	265±5℃，5s，3 times	The tested cured film did not gum, change color and fall out	OK

Test report was certified by Ministry of Information Industry PCB Quality Supervising Test Center.

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, aqueous solubility, chemical plating resistance and hardness, and so on, epoxy acrylate resin, polyester acrylate resin, and modified epoxy acrylate resin 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. 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 **Table 3** and **Table 4**.

Table 4 Fundamental technology conditions of flexible imaging solder mask L-S8600

Items	Testing method	Test results	Evaluation
Pencil hardness	Pencil angle: 45^{o}, Load: 1kg	4H	OK
Flexibility	Semidiameter of curvature: R=0.2mm Load: 500g	≮80 times	OK
Flame retardancy		UL94V-0 grade	OK
Thermal shock resistance	285℃ 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

For the solder masker of printing circuit board, it itself must be lead-free and halogen-free, and therefore the SGS (SOCIETE GENERALE DE SURVEILLANCE S.A) test of material itself is primary for circuit board materials. SGS testing results of printing ink L-S8600 were listed in the **Table 5**. It is observed from **Table 5** that technology performance of flexible imaging solder mask L-S8600 answered operating requirements of the solder masker for printing circuit board.

Table 5 The test results of SGS of flexible imaging solder mask L-S8600

Number	items	unit	Limiting value of testing (wt%)	Test results
1	cadmium（Cd）	ppm	2	N.D
2	plumbum（Pb）	ppm	2	N.D
3	mercury（Hg）	ppm	2	N.D
4	hexad chromium（Cr VI）	ppm	2	N.D

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

4 Conclusions

This paper 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, flexility and thermal stability. The decomposition temperature of PSUA is 402 ^{o}C. 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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