

Note

SYNTHESIS AND PROPERTIES OF UV-CURABLE POLYSILOXANE METHACRYLATE OBTAINED BY ONE-STEP METHOD

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Abstract In this study, a UV-curable polysiloxane methacrylate (PSMA) was synthesized by a one-step method. The reaction was catalyzed by chloroplatinic acid between polymethylhydrosiloxane (PMHS) and hydroxyethyl methacrylate (HEMA), as proved by FTIR and ¹H-NMR. The preliminary results indicate that the obtained UV-cured PSMA film has very good thermal stability, excellent transparency and satisfactory tensile strength. Our work provides a simple but efficient way to prepare UV-curable PSMA, which may find potential applications in UV-curing optical fiber, metal and glass coating and other fields.

Keywords: Polysiloxane methacrylate; UV-curing; Synthesis.

INTRODUCTION

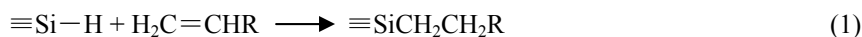
Polysiloxanes (PSA) are gaining increasingly attention in the field of electronics, printing, coating and adhesion due to their unique properties, for instance, good resistance to high temperature, excellent antiweatherability, impressive resistance to ozone and so forth^[1–7]. In general, polysiloxanes are crosslinked thermally, and this process usually takes much time and energy^[8]. On the contrary, ultraviolet (UV) curing techniques are getting wide applications because of the advantages of high efficiency, low-energy consumption and reduced pollution^[6–12]. Regrettably, most UV-curable PSA are synthesized in two steps^[7, 13–18]. For example, a typical route of synthesizing UV-curable polydimethylsiloxane epoxy acrylate (PES) is first to obtain epoxy polysiloxane then react with acrylic acid for the preparation of PES^[16]. The two-step method is complex and requires multiple procedures, so its application in the UV-curing field is restricted.

In this paper, we synthesized PSMA *via* one step, utilizing the hydrosilylation between polymethylhydrosiloxane (PMHS) and hydroxyethyl methacrylate (HEMA). PMHS is a silicon industry by-product, which is cheap, nontoxic and stable to air and moisture. It can transfer its hydrides to a variety of metal catalysts (including Sn, Ti, Zn, Cu and Pd) that can then participate in a wide range of reduction^[19]. Usually hydrosilylation includes two kinds of reaction, the one is called hydrosilylation addition reaction (HAR) and the another is hydrosilylation dehydrogenation reaction (HDR). The former one refers to the addition of silicon hydrides (PMHS-SiH) across unsaturated bonds (*e.g.* C=C)^[20, 21], whereas HDR takes place between PMHS-SiH and —OH groups^[22]. The two reactions are illustrated in (Eq. (1)) and (Eq. (2)), respectively.

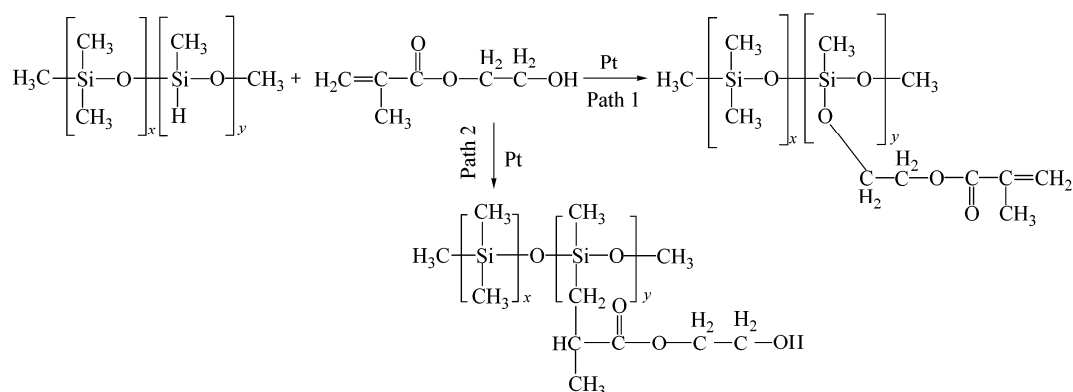
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Coincidentally, Pt catalysts (*e.g.* chloroplatinic acid) can simultaneously catalyze HAR and HDR^[23, 24]. Barnes reported that in the presence of chloroplatinic acid, there existed competition between dehydrogenation process and addition process. In the patent, the author also pointed out that the former reaction was predominant even when unsaturated bonds were present^[25]. Thus by controlling the competition between dehydrogenation and addition process, the UV-curable acrylate groups and polar hydroxyl groups could be grafted onto the polysiloxane backbones, according to the reaction illustrated in Scheme 1.



Scheme 1 Reaction path between PMHS and HEMA

In this way the UV-curable polysiloxane methacrylate could be easily synthesized by one step reaction and the hydroxyl groups guarantee its miscibility with other monomers such as HEMA. This work reports the preliminary result on the synthesis and properties of the UV cured PSMA films

EXPERIMENTAL

Materials

PMHS (1.6 mol reactive hydrogen per 100 g PMHS) and chloroplatinic acid were supplied by Chengdu Taly Industrial Chemical Co., Ltd of China. Photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (HMPP) was purchased from Aldrich Chemical Co. HEMA, Hydroquinone (HQ), toluene and other reagents and solvents were all obtained from Kelong Co. (Chengdu, China) in AR grade and were used as received.

Synthesis of PSMA

A 250 mL three-necked round bottom flask was dried and equipped with a reflux condenser with a dropping funnel and nitrogen inlet. An excess of HEMA (2 equivalents of Si-H), 50 mL toluene were first taken into the flask. 0.2 g HQ was added to inhibit the self polymerization of the monomer. Then 0.05 g chloroplatinic acid was charged into the flask under stirring. After the temperature was reached to 95°C, 5 g PMHS was added drop-wise under nitrogen atmosphere. The reaction was maintained at 95°C and a small amount of sample was taken out for FT-IR investigation every hour at intervals. The reaction was stopped after 5 h, then the solution was washed 3 times by deionized water to thoroughly remove the unreacted HEMA and other impurities. Finally, toluene was afterwards discarded by reduced pressure distillation. The remainder was PSMA, a transparent viscous liquid.

Preparation of UV-cured Films

PSMA and HEMA were mixed with a weight ratio of 1:1. HEMA was used as reactive diluents to decrease the viscosity as well as enhance the crosslinking density of the cured film. 3 wt% photoinitiator (HMPP) was added

to the mixture for the initiation of curing reaction. The obtained mixture was stirred for 10 min and then coated on hydrophobic glass substrate by means of a wire-wound applicator. In this way, uniform thick films with a thickness of 200 μm could be well prepared. The coated films were irradiated by a UV-curing machine equipped with a high-pressure mercury lamp (500 W) for 30 s with a distance of 15 cm from lamp to the surface of samples in nitrogen atmosphere. The cured film was carefully peeled off from the substrate and then stored in vacuum oven at 6°C for 24 h before characterization.

Instruments and Testing Methods

Fourier transform infrared (FTIR) spectroscopy analysis was performed on a Nicolet-6700 spectrophotometer and scanned between 500 cm^{-1} and 4000 cm^{-1} . The samples were dissolved in chloroform and coated on KBr tablets before collection.

^1H -NMR was recorded on a Varian Unity INOVA (400 MHz) spectrometer, using tetramethylsilane (TMS) as an internal standard, CDCl_3 or DMSO-d_6 as solvent.

Thermal properties of PMHS, cured HEMA and cured PSMA films were measured on a thermogravimetric analysis (TGA) Q500 (TA Instruments) with a heating rate of 10 K/min in N_2 . The average weight of the samples was 5–10 mg.

Water absorption measurements of UV-cured films were carried out in distilled water at 25°C^[26]. Weighed sample was kept in water for at least 48 h until equilibrium was attained. From the weight difference of the film before and after soaking in water, the water absorption value was calculated.

Mechanical testing was carried out with an Instron 5567 model universal testing machine. Tensile measurements were made on rectangular specimens 10 mm wide, 0.2–0.3 mm thick and with a gauge length of 60 mm^[1]. A crosshead speed of 5.0 mm/min was applied to determine the tensile strength and elongation at break. Five replicate samples were measured in a given experiment.

RESULTS AND DISCUSSION

In this experiment, two reactions take place between PMHS and HEMA according to totally different mechanisms. The methacrylic functionalized polysiloxanes couple the properties of siloxanes with the free radical UV-curing of a methacrylic system. Methacrylate polysiloxanes were synthesized by dehydrogenation process between Si-H and $-\text{OH}$ as illustrated in path 1 of Scheme 1. Whereas in path 2, the addition reaction of PMHS and HEMA gives the polar hydroxyl groups grafted part, which enables the PSMA to be miscible with other polar UV-curable monomers or photoinitiators. Hydroxyethyl methacrylate (HEMA) was used as a reactive diluent at 50 wt% for UV-curing the methacrylated siloxanes. Without HEMA, not all the polysiloxanes formed continuous films, and the samples did not have the adequate flexibility and strength necessary for removal from the substrate^[2].

Structure Characterization of PSMA

In Fig. 1(a), the FTIR spectra of samples collected at a certain time interval monitored the reaction process of PMHS and HEMA. The three peaks at 1639, 1736 and 2160 cm^{-1} are attributed to the stretching vibration of $\text{C}=\text{C}$, $\text{C}=\text{O}$ and Si-H respectively. It is clear that the Si-H peak area decreases as time goes on and the absorption band of Si-H peak shifts to the lower wave numbers (from 2167 cm^{-1} to 2161 cm^{-1}). Blue shift is emerged because of the formation of hydrogen bonding between the hydrogen atoms and the oxygen atoms of HEMA that grafted on the polysiloxane backbones.

Figure 1(b) shows the changing trend of the Si-H peak as time goes on. The peak of Si-CH_3 at 1261 cm^{-1} is chosen as an inner standard peak since the Si-CH_3 stretching is unchanged during the reaction^[27]. Y_t is defined as follows: $Y_t = \text{Height}_t(\text{Si-H})/\text{Height}_t(\text{Si-CH}_3)$, which means the height ratio of the peak of Si-H and that of Si-CH_3 at different reaction time ($t = 0.5, 1, 2, 4$ and 5 h. When $t = 0.5$ h, HEMA was dripped off.). Y_t can reflect the reaction conversion of Si-H ^[27, 28]. It can be seen that the Y_t decreases dramatically after HEMA was added. However, after 2 h, it nearly not changes. It may be caused by the steric hindrance formed by the grafted HEMA on the polysiloxane backbones no matter *via* dehydrogenation or

addition process. Besides the changing trend of Si—H peaks, it is also interesting to find that, the C=C peak appeared at 0.5 h and didn't change much since then, whereas the absorption peak of C=O gradually increased and reached to the highest point when the reaction ended. Accordingly, it could be inferred that the hydrogen dehydrogenation (path 1, Scheme 1) which brings the UV-curable double bond mainly took place at the beginning of the reaction. On the other hand, the addition process (path 2, Scheme 1) was across the whole reaction. By comparing the two different reactions, it is concluded that the dehydrogenation process favors the early stage when the PMHS was added by drops and its molar ratio is less than HEMA. However, after PMHS dripped out, the dehydrogenation process could be almost terminated and the addition process predominated the later reaction. This could be understood as due to the fact that the former reaction only takes place in a specific circumstance where PMHS molecules are surrounded by excessive HEMA molecules. Whereas the addition process may run throughout the reaction and it would not be affected much by the molar ratio of HEMA to PMHS. Our result is in accordance with Barnes' findings^[25]. Even though we can't prove whether the dehydrogenation process is predominant in the early state, it really happens when the content of HEMA is far excessive than PMHS.

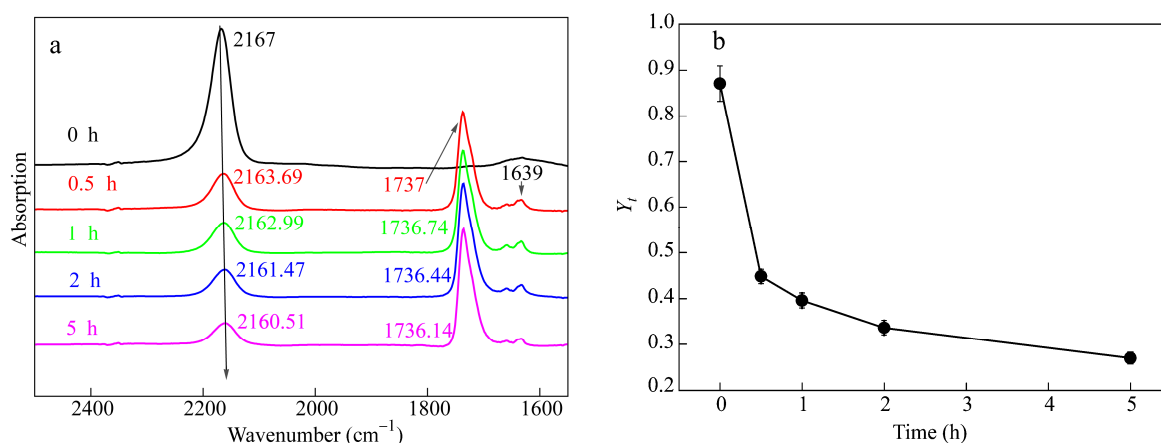


Fig. 1 (a) FTIR spectra of PMHS at different reaction time; (b) Height ratio of Si—H and Si—CH₃ at different reaction time

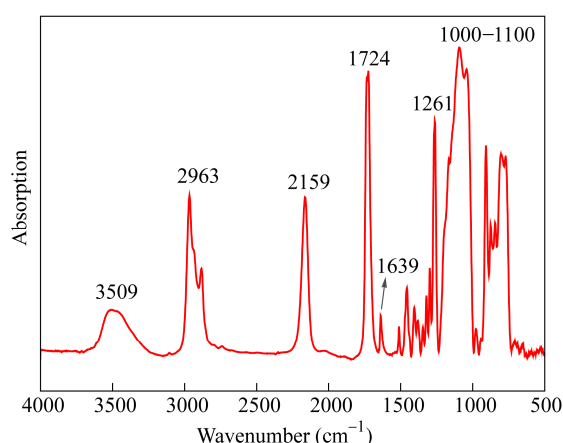


Fig. 2 FTIR spectrum of final product (PSMA) after 5 h reaction

Since the reaction mechanism is well explained above, the structure of the final product could be easily characterized by FTIR and ¹H-NMR. Figure 2 shows the typical FTIR spectrum of the final product of PSMA. It

can be seen that there are strong absorption peaks at 3509 and 2963 cm^{-1} which are ascribed to the vibration of $-\text{OH}$ and $-\text{CH}_2$, respectively. The absorption peak at 1724 and 1639 cm^{-1} were attributed to $\text{C}=\text{O}$ bond and $\text{C}=\text{C}$ vibration. Also the absorption peaks at 2160 , 1261 , 1096 and 889 cm^{-1} are ascribed to the vibration of $\text{Si}-\text{H}$, $\text{Si}-\text{CH}_3$, and $\text{Si}-\text{O}-\text{R}$, respectively. $-\text{OH}$ and part of the $\text{C}=\text{O}$ groups are formed due to the addition process, as illustrated in path 2. $\text{C}=\text{C}$ and other part of $\text{C}=\text{O}$ groups are ascribed to the dehydrogenation process, giving PSMA UV-curable properties.

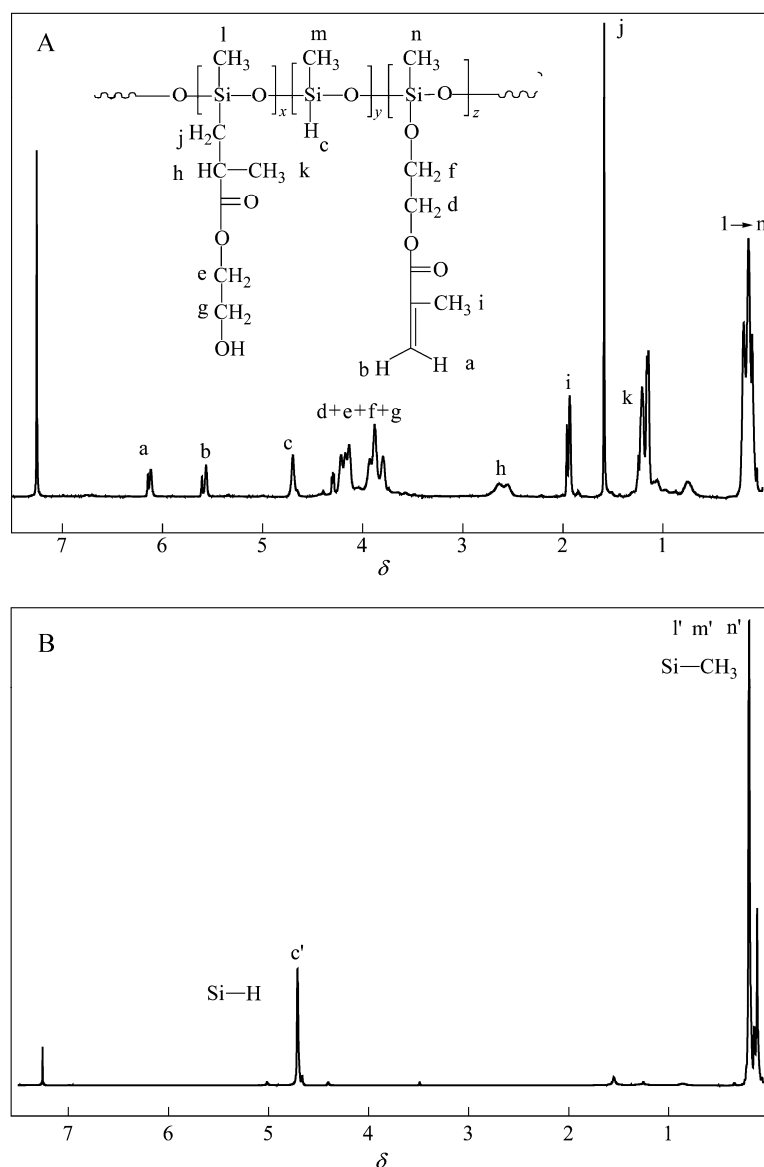


Fig. 3 (A) ^1H -NMR spectrum of final product (PSMA) after 5 h reaction;
(B) ^1H -NMR spectrum of PMHS before reaction

The ^1H -NMR spectra of PSMA and PMHS are shown in Fig. 3. ^1H -NMR is the most useful approach for measuring the hydrogen chemical environment because of its high sensitivity to hydrogen bond strength, while the area of peaks evidently reflects the abundance of hydrogen at different chemical shifts^[21]. In Fig. 3(A), all the relevant peaks of oligomer could be found. The peak at $\delta = 0-0.4$ results from the group of $-\text{CH}_3$ in the

chain of Si—O—Si in the molecule of PSMA. Compared with the spectrum of PMHS as illustrated in Fig. 3(B), it can be seen that the peak at $\delta = 4.7$ belongs to Si—H. The peaks at $\delta = 2.6$, 1.6 and 1.2 are ascribed to —CH, —CH₂ and CH₃, which have been labeled as h, j, and k in Fig. 3(A) respectively. The three new groups were yielded by the addition process between Si—H and C=C of HEMA. Two small peaks (a, b) that have been observed at $\delta = 5.5$ –6.2 belong to C=CH₂ and the peaks of —CH₃ (i) attached to the vinyl group appear at $\delta = 1.9$, which proves the happening of hydrosilylation dehydrogenation reaction. Either through the addition or the dehydrogenation process, the signals of —CH₂—CH₂ (e, d, f, g) have been obtained at $\delta = 3.7$ –4.3. These results prove that both reactions (hydrosilylation addition reaction and hydrosilylation dehydrogenation reaction) exist in the synthesis process.

To quantitatively discuss the grafting ratio of PMHS, the peaks at $\delta = 1.6$ (Si—CH₂) and 5.6 (C=CH) are selected. The two peaks can represent the addition and dehydrogenation processes respectively. The relative areas of Si—CH₂, C=CH, and Si—H peaks are 1, 4.48 and 1.52. After calculation, the Si—H conversion is 68.1% and the ratio of addition and dehydrogenation reactions is 2.24. Combined with the M_n and hydrogen containing of PMHS ($M_n = 1.73 \times 10^4$, 1.6% Si—H), one PSMA chain has about 130 —OH groups and 58 C=C groups on an average.

Properties of the UV-cured film

We have also tested the properties of UV-cured PSEM films. The prepared film containing 50 wt% of HEMA is found to have a perfect optical transparency as is seen in Fig. 4(a), which indicates a good distribution of HEMA and interaction between PSMA and HEMA. The good interaction guarantees the mechanical properties of the final cured films. For example, a good flexibility is observed, which is completely different from the rigid cured HEMA films even though the content of HEMA in the cured polysiloxane films accounts a relatively large part.

The water absorption value q is 6.94%, according to the formula:

$$q = (Q_s - Q_d)/Q_d \times 100\%$$

where Q_s and Q_d are the weights of a swollen and dry sample, respectively. The introduction of polar components leads to the high water absorption value.

Thermal and mechanical properties were also tested, and the results are as followed. The cured films' thermolysis is shown in Fig. 4(b). A thermogravimetric analyzer is often used for studying the thermal stability of polymeric materials. The thermal properties of the three samples were investigated in nitrogen atmosphere by TGA. UV-cured HEMA and raw PMHS were also tested for comparison with the cured PSMA film. From Fig. 4(b), the PSMA film shows 10% weight loss at 250°C, which is similar to that of PMHS. The thermogram of PMHS proves that the raw material has a wide molecular weight distribution. Therefore it can be inferred that the weight loss of cured PSMA film is caused by the low molecular weight polysiloxane in material. The film start to fast decompose at 370°C, which is 30 K higher than the cured HEMA and has a similar thermal stability to that of silicone rubber^[15]. Despite the fact that 50 wt% of HEMA is added, the thermal property of PSMA film isn't affected much. This is the result of the somewhat unusual molecular structure of the polysiloxane chains. The Si—O bond is one of the most thermally stable bonds formed by silicon and has a bond dissociation energy of 462 kJ/mol compared with 359 kJ/mol for C—O, 347 kJ/mol for C—C and 319 kJ/mol for Si—C bond. The thermal stability of polysiloxanes is thus partly a consequence of the high bond energy. Besides, the PSMA film shows higher decomposition temperature than PMHS and have 20% residual weight at 600°C.

The result of tensile property is illustrated in Fig. 4(c). From the typical stress-stain curve, it can be seen that the cured film obtains a good flexibility with elongation at break of 22.1%, and the tensile strength is 7.24 MPa. Although 50 wt% of HEMA is added into the oligomer, the cured film still shows good flexibility, which makes the property of the film be close to that of silicone rubber. The strength of the film synthesized by one-step method gives an edge over that reported in other studies^[16, 29]. For instance, Wang has reported that the strength and elongation at break of the cured film was 6.9 MPa and 20% respectively. We have to admit that the

properties of the UV-cured film fail in comparison with those of the silicon rubber, but it does gain its edge in the UV-curing field.

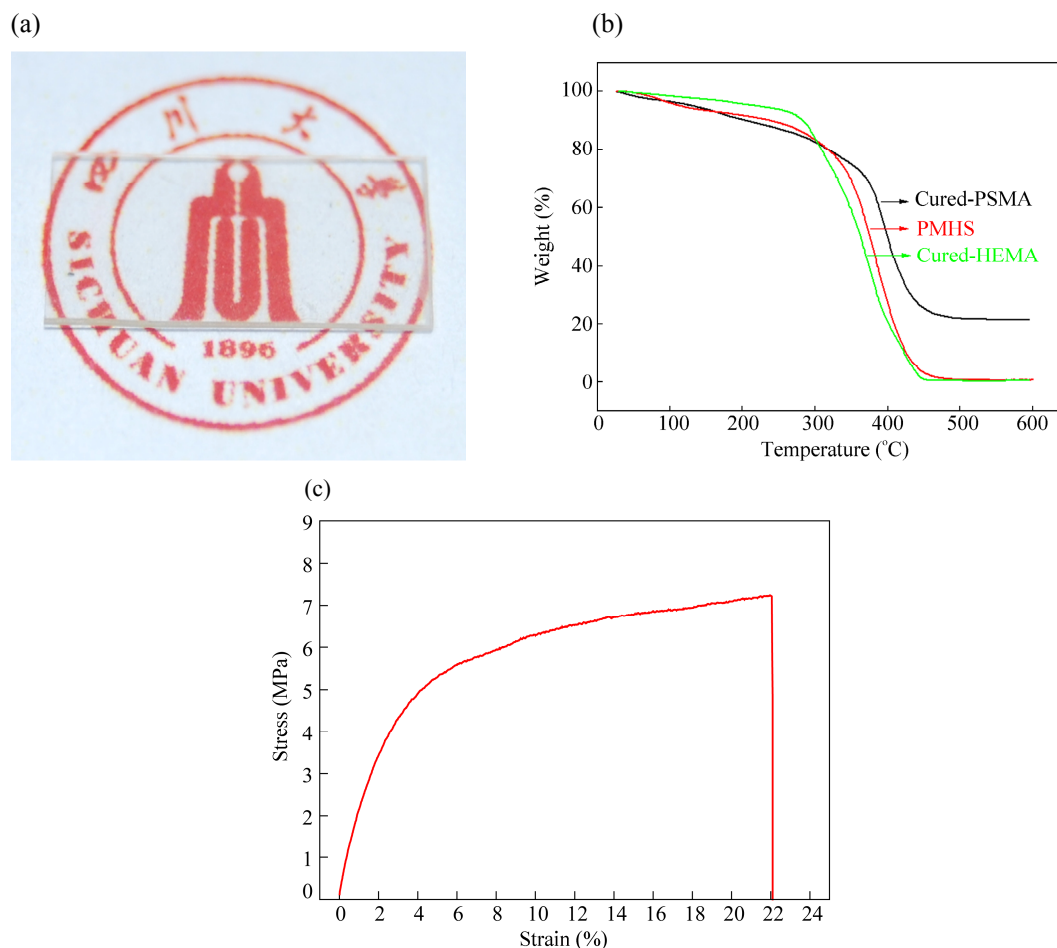


Fig. 4 (a) Picture of a UV-cured film; (b) TGA curve of PMHS, cured PSMA and HEMA; (c) Stress-strain curve of UV-cured PSMA film

CONCLUSIONS

In this study, photosensitive polysiloxane methacrylate (PSMA) was successfully synthesized by a one-step method. The FTIR and $^1\text{H-NMR}$ results prove that both the dehydrogenation and addition processes take place and the former one prefers the early stage of the process when the mole of PMHS is less than that of HEMA. The UV-cured film has a high decomposition temperature and good flexibility with satisfactory tensile strength and transparency. Nevertheless, this is only a preliminary result, other properties of the cured film need to be further explored in the later study.

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