

# A Novel Alkoxysilane-Modified High Solids Hydroxyl Acrylic Polyurethane: Preparation and Surface Properties

Fang Zhu, Gaoyong Zhang, Shuyi Xu, Xinlin Hong, Jinfeng Dong

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China

Received 26 August 2005; accepted 27 October 2005

DOI 10.1002/app.23609

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

**ABSTRACT:** Alkoxysilane-modified high solids hydroxyl acrylic polyurethane was prepared by solution polymerization. Its structure, surface, and thermal properties were investigated by  $^1\text{H}$  NMR, device of contact angle, thermo gravimetric analysis (TGA), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). Research showed that alkoxysilane modified high solids hydroxyl acrylic polyurethane has superior properties that can be used for automotive paints. The contents of silicone in the alkoxysilane-modified high solids hydroxyl acrylic polyurethane were 1.25, 1.5, 2, and 2.5 wt %. In this study,  $\gamma$ -methacryloxypropyltrimethoxysilane (MPTS) was chosen as the

modifier. Results showed that the contact angles of water and surface roughness on the film of MPTS modified high solids hydroxyl acrylic polyurethane increased, and thermal stability of the film at high temperatures improved with the increasing of the silicone content in the resins. MPTS modified high solids hydroxyl acrylic polyurethane with 2.5 wt % silicone content had better water resistance, better acid resistance, higher hardness, and excellent weatherability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1866–1871, 2006

**Key words:** silicones; coatings; AFM; surface property; thermal property

## INTRODUCTION

Manufacturers of coatings intend to reduce the emission of volatile organic compounds (VOC) to the atmosphere, in recent years. Powder coatings, waterborne coatings, UV-cured coatings, and high solids coatings are ideal products for reducing VOC.<sup>1</sup> Because of the equipment replacing cost, high solids coatings is a better option for reducing VOC in automotive refinishes without changing the existing equipment.<sup>2</sup>

Although studies on fluorinated acrylic copolymer has been an active field of research,<sup>3,4</sup> they are expensive, easily pollute the atmosphere, and lower hardness. Therefore, resins containing alkoxysilane are suitable for the coating industry. Alkoxysilanes have excellent flexibility and hydrophobicity, low surface free energy, low glass transition temperatures, weather resistance, and excellent thermal stability.

To investigate  $\gamma$ -methacryloxypropyltrimethoxysilane (MPTS) modified acrylic coatings, Park et al.<sup>5</sup> prepared MPTS modified acrylic resin for building materials and found that the resin has better durability, from the outdoor exposure test. Mamiya et al.<sup>6</sup> synthesized self-crosslinkable MPTS modified non-aqueous acrylic polymer dispersion. Chen et al.<sup>7</sup> investigated the film property of MPTS modified high

solids acrylic resins and MPTS modified acrylic latices and found that they have higher hardness and weatherability. Li et al.<sup>8</sup> prepared polyamide-silicone polyacrylate by reacting hexamethylene-1,6-diisocyanate trimer (HDI) with  $\gamma$ -aminopropyltriethoxysilane and modification by  $\beta$ -hydroxyethyl acrylate used as UV curing coating. All of these works are focused on MPTS modified acrylic resin without hydroxyl endgroup. Studies on MPTS modified high solids hydroxyl acrylic polyurethane (MHSA) has been scarce till now.

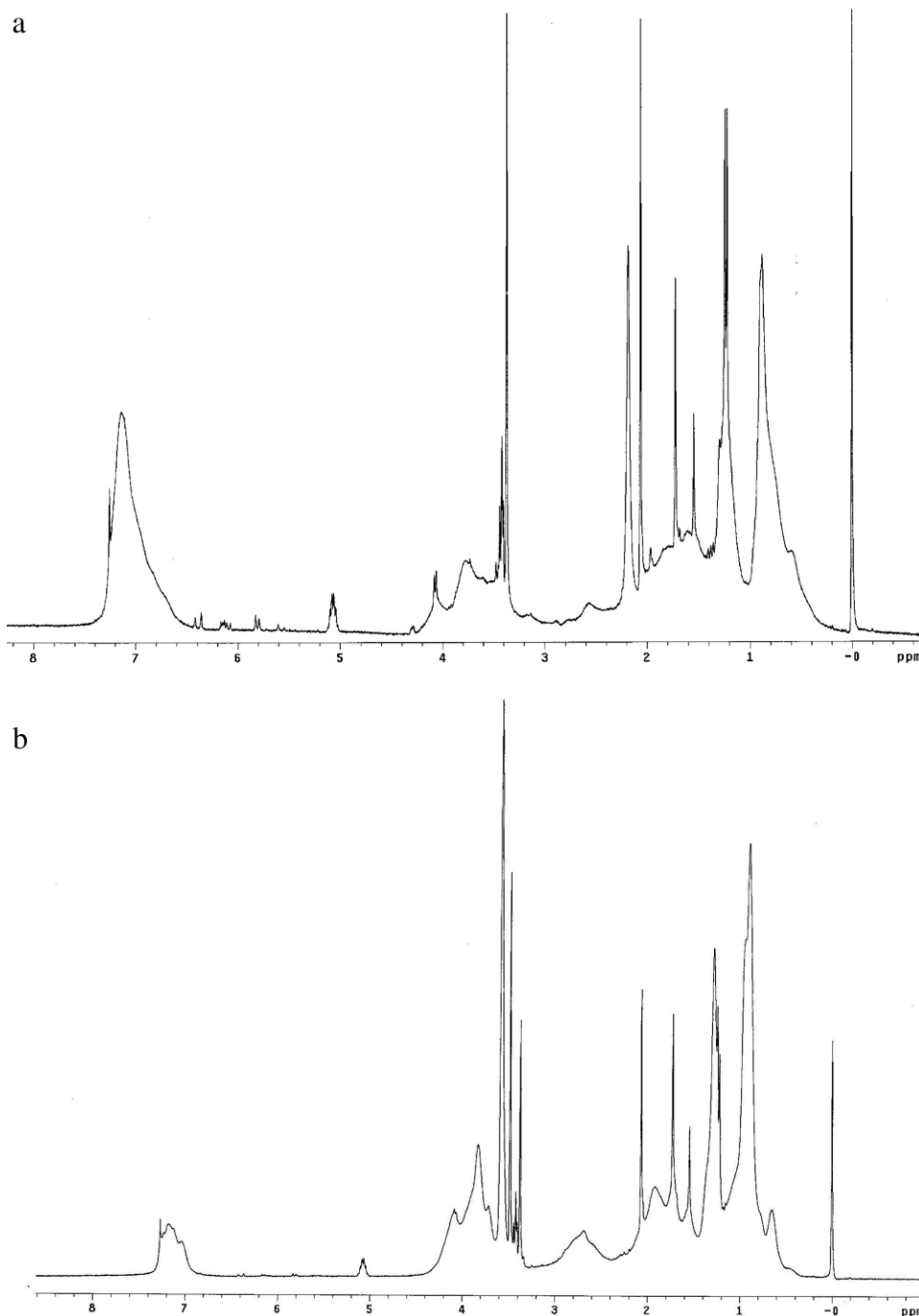
In this work, a high performance and novel high solids hydroxyl acrylic polyurethane based on MPTS was prepared by *in situ* polymerization with the incorporation of styrene (St), isobutyl methacrylate (i-BMA), 2-ethylhexyl acrylate (2-EHA) and methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA) and MPTS. The environmental friendly solvent butyl acetate was added to adjust the solid contents of high solids hydroxyl acrylic polyurethane. The thermal property, surface property, and water contact angle of the prepared films are proved to be improved. With the increase of the silicone content, viscosity decreases rapidly, while thermal stability, water contact angle, and tensile modulus increases.

## EXPERIMENTAL

### Materials

Styrene (St) and methacrylic acid (MAA) were purchased from Shanghai Chemical Reagent Company

Correspondence to: G. Zhang (colloidandpolymer@hotmail.com).



**Figure 1**  $^1\text{H}$  NMR spectra of (a) P(ST-i-BMA-2-EHA-HEMA-MAA), (b) P(ST-i-BMA-2-EHA-HEMA-MAA-MPTS).

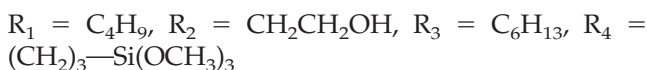
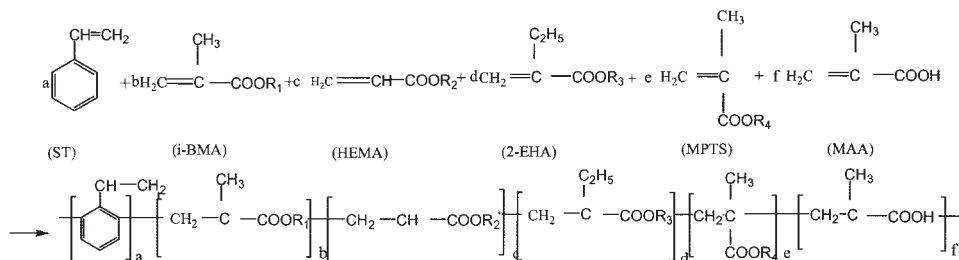
(China); isobutyl methacrylate (i-BMA), 2-ethylhexyl acrylate (2-EHA), and  $\gamma$ -methacryloxypropyltrimethoxysilane (MPTS) were purchased from Acros; 2-hydroxyethyl methacrylate (HEMA) was purchased from Tianjin Chemical Reagent Research Institute. All of these monomers were purified by vacuum distillation. 2,2'-azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Company and recrystallized before use. Hexamethylene diisocyanate (HDI) trimer (Desmodur N3390) was purchased from Bayer company (Shanghai, China).

**TABLE I**  
Physical Property of the MPTS Modified High Solids Acrylic Resin

	Silicone content (%)	$T_g$ (K)	Viscosity (mPa s)	Solid content (%)
PHSA	0	313	5500	75.04
MHSA1.25	1.25	255	3350	72.25
MHSA1.5	1.5	244	2950	71.78
MHSA2	2	233	1850	70.03
MHSA2.5	2.5	223	1800	70.15

### Synthesis of high solids poly (St-i-BMA-HEMA-EHA-MAA-MPTS)

A 500-mL round-bottom flask equipped with a mechanical stirrer, a thermometer with a temperature controller, an N<sub>2</sub> inlet, a Graham condenser and a heating mantle was used. The mixture of MPTS, ST, i-BMA, HEMA, 2-EHA, MAA, and initiator AIBN were added into the flask, using an addition funnel over a period of 6 h. After addition of all ingredients, the reaction was maintained



### Characterization

#### Structure characterization

<sup>1</sup>H NMR spectra of CDCl<sub>3</sub> solutions were recorded by a VX-300 MHz (Varian, San Francisco, CA) spectrometer operating at a proton frequency of 300 MHz. The SEC (size exclusion chromatography) characterization was carried out using a Waters 150C module equipped with a Datamodule 746 differential refractive index detector. The column set was Styragel columns (Waters) (30 cm long). The solvent was HPLC grade THF (Sigma); injection volume 100 μL; flow rate 1.0 mL/min; column temperature (35°C).

#### Surface property

A DSA 10 video contact angle measuring device from Kruss company was used for measuring contact angles of the standard liquids on the polymeric films.

at 85°C for additional 0.5 h to complete the reaction. <sup>1</sup>H NMR instrumental analysis revealed the following: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ0.898 (H—CH<sub>3</sub>—C—, s), δ1.2–1.3 (CH<sub>3</sub>—C—, m), δ1.54–1.55 (C—H, s), δ2.064 (C—CH<sub>2</sub>—CO—, s), δ3.481 (CH<sub>3</sub>—O—/Si—O—CH<sub>3</sub>, s), δ3.77–3.83 (—CH<sub>2</sub>—OH, s), δ5.099 (OH—, t), δ7.268 (C<sub>6</sub>H<sub>5</sub>—CH—CH<sub>2</sub>—, m). Viscosity (20°C) = 1800 MPa s. T<sub>g</sub> (20°C/min) = -50°C.

The reaction formula is:

The surface energy was calculated by two standard liquids. The standard liquids chosen in this study were pure water and diiodomethane.

#### Surface roughness

Surface roughness was performed at ambient conditions (25°C, relative humidity of 30–40%) using an SPM Microscope (Model: SPM-9500J3). The samples were screened at 1 × 1 μm<sup>2</sup> scan size.

#### XPS study

The X-ray photoelectron spectroscopy (XPS) measurements were performed on the air-exposed surface by a Physical Electronics XSAM800 (KRATOS), using an Mg mono Kα<sub>1,2</sub> X-ray source.

#### Thermal characterization

A Mettler DSC 822 monitored thermal transitions from -70 to 200°C. Glass transition temperatures were

TABLE II  
Physical Properties of the Polymeric Film

	Pencil hardness	Cross-hatch adhesion	Impact resistance (cm)	Acid resistance <sup>a</sup>	Water resistance
PHSA	2H	Passes	50	Damaged	Poor
MHSA1.25	2H	Passes	80	No damage	Excellent
MHSA1.5	2H	Passes	80	No damage	Excellent
MHSA2	3H	Passes	100	No damage	Excellent
MHSA2.5	3H	Passes	100	No damage	Excellent

All samples were 15–25 μm thick.

<sup>a</sup> 10% H<sub>2</sub>SO<sub>4</sub> spot test, 30 min at 80°C.

obtained from the curves recorded at 20°C/min as the midpoints of the step variation in two run.

The thermal curves of thermo gravimetric analysis (TGA) were obtained by a SETSYS 16TG/DAT/DSC, thermal analysis instrument (Setaram, France). The temperature ranged from room temperature to 700°C with a heating rate of 10°C/min, under air and nitrogen atmosphere.

## RESULTS AND DISCUSSION

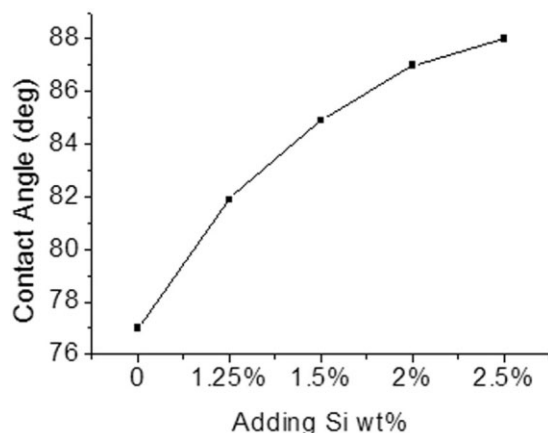
### Synthesis of silicone-modified high solids hydroxyl acrylic polyurethane and film formation

From the  $^1\text{H}$  NMR spectra (Fig. 1), it is obvious that the peak at 3.779 ppm is assigned to the  $-\text{CH}_2-$  adjacent to the hydroxyl group. In the  $^1\text{H}$  NMR spectrum of the MPTS modified high solids hydroxyl acrylic resin there are several visible peaks:  $-\text{CH}_2-\text{OH}-$  at 3.83 ppm,  $\text{CH}_3-\text{C}$  at 0.901 ppm, 0.648 ppm, 1.282 ppm,  $\text{C}-\text{H}$  at 1.546 ppm,  $\text{CH}-\text{CO}$  at 2.689 ppm,  $\text{CH}_3-\text{O}-/\text{Si}-\text{O}-\text{CH}_3$  at 3.48 ppm.

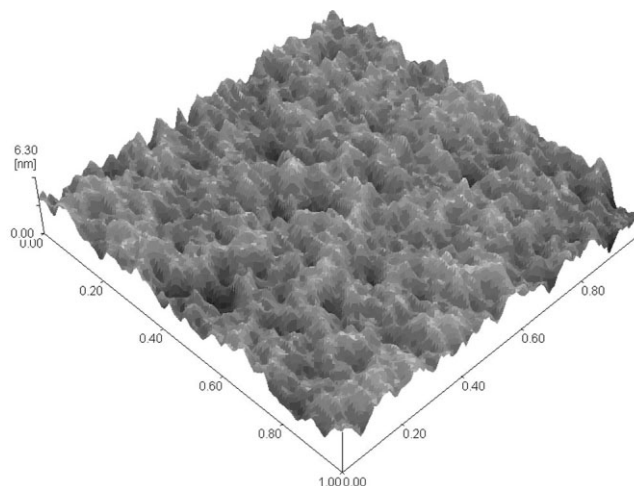
### Physical property

The physical property of the MPTS modified high solids hydroxyl acrylic resin is shown in Tables I and II. They illustrate that as the silicone content in the resin is increased, viscosity and glass temperature decreases rapidly.

The film formation of the resin was coated on mild steel panels  $20 \times 10 \text{ cm}^2$ . The panels were abraded with emery paper No. 7 for metallographic application followed by cleaning with isopropanol. The films were cured at 80–140°C for 30–40 min by adding N-3390 into resin solution. The solid content of the resin was maintained at about 70 wt %. Dry film thickness of the coatings was measured by using film thickness meter on a mild steel panel. Pencil hardness of the coatings



**Figure 2** Contact angle of water on MPTS-modified high solids hydroxyl acrylic polyurethane film.



**Figure 3** Three-dimensional topographical (height) AFM images of MPTS-modified high solids hydroxyl acrylic polyurethane (content of silicone = 2.5%).

was determined using standard pencils of hardness (6B to 5H). Impact resistance was measured by using falling weight method.

### Water contact angle

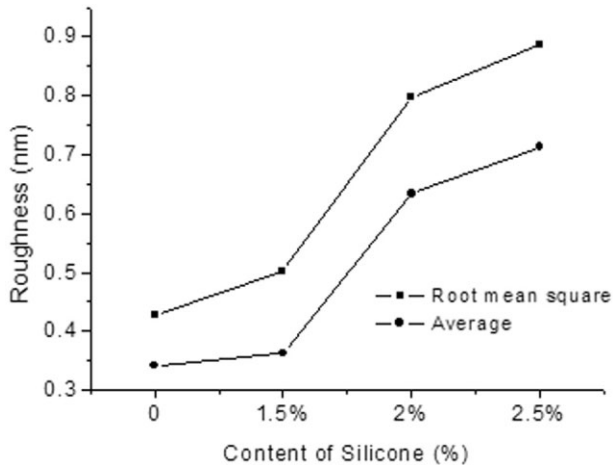
Contact angle of a liquid on a film surface is a direct reflection of the hydrophilicity or hydrophobicity of the surface. The surface properties of the film from MPTS modified high solids hydroxyl acrylic polyurethane (MHSA) were characterized by water contact angle from DSA10. For the films with silicone content from 0 to 2.5 wt %, the water contact angle kept increasing from 77° to 88°. When the silicone content in the films increased up to 2.0 wt %, the contact angle increased slowly. The contact angle of water indicates that MPTS crosslinked with acrylic monomer very well and had a good network (Figs. 2 and 3).

### Surface topology

The surface roughness was measured using atomic force microscopy (AFM). Surface roughness can cause contact angle hysteresis and affect the value of the equilibrium contact angle. The surface roughness values are summarized in Table III (Fig. 4). From Table

**TABLE III**  
Surface Roughness of MPTS Modified High Solids Hydroxyl Acrylic Polyurethane Films

Label	$R_{\text{ms}}$ (nm)	$R_a$ (nm)
PHSA	0.427	0.342
MHSA1.5	0.501	0.362
MHSA2	0.887	0.713
MHSA2.5	0.797	0.633

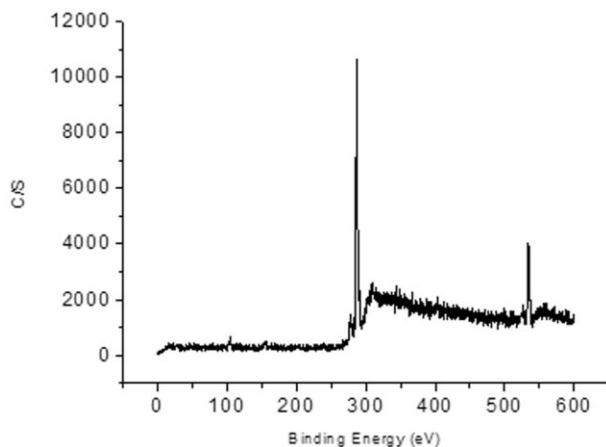


**Figure 4** Surface roughness as a function of the amount of silicone in the MPTS-modified high solids hydroxyl acrylic polyurethane.

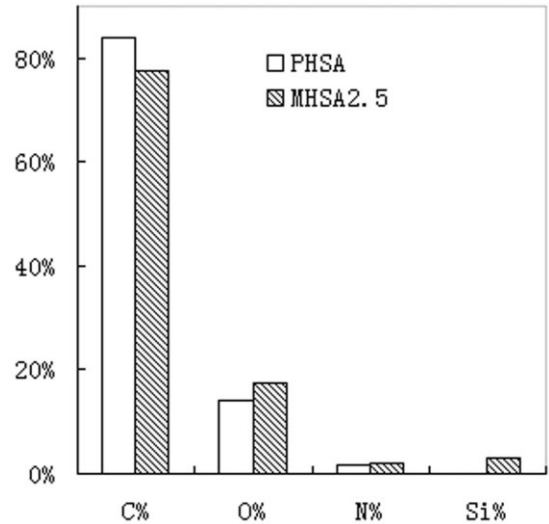
III, it can be seen that the surface roughness increased gradually with increasing MPTS content. The result implied the enrichment of MPTS increased in the film surface with the enhancement of MPTS concentration.

### XPS study

The film surface of MHSA has been investigated by X-ray photoelectron spectroscopy at  $90^\circ$  take-off angle to evaluate the surface silicone concentration (Fig. 5). The chemical composition of the surface of pure high solids hydroxyl acrylic polyurethane (PHSA) and MPTS modified high solids hydroxyl acrylic polyurethane (MHSA2.5) with 2.5 wt % silicone content are displayed in Figure 6, where the surface of MHSA exhibits values of 3% Si, 77.7% C, 17.3% O, and 2% N. The result of XPS analysis showed that Si atom of MPTS high solids hydroxyl acrylic polyurethane tends



**Figure 5** XPS spectra of MPTS modified high solids hydroxyl acrylic polyurethane (MHSA2.5-N3390).



**Figure 6** XPS surface composition of PHSA and MHSA2.5.

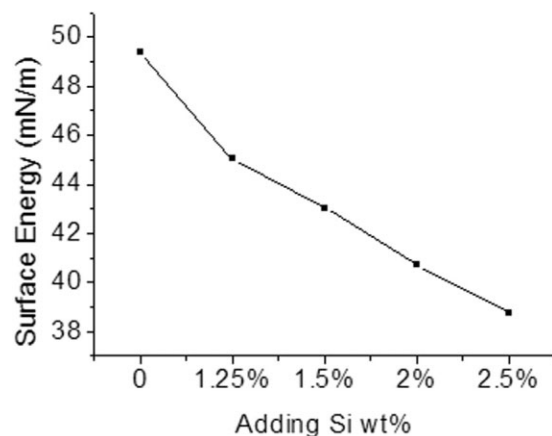
to concentrate at the film surface, resulting in excellent adhesion, weatherability, acid resistance, and water resistance.

### Surface energy

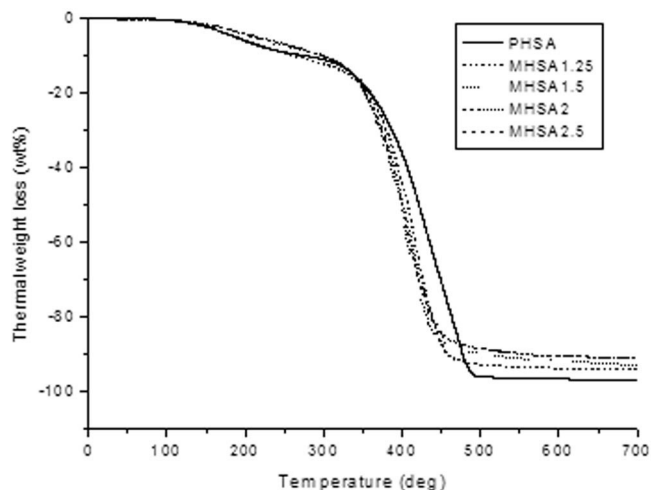
For the films with silicone content from 0 to 2.5 wt %, the surface energy decreased from 49.50 to 38.77 mN/m. The surface energy of the films in the current study is low. High solids hydroxyl acrylic polyurethane modified by a greater amount of MPTS might increase hydrophobicity of the film. This is partly due to the structure of MPTS (Fig.7).

### Thermal stability

TGA curves of PHSA and MPTS-modified high solids hydroxyl acrylic polyurethane with silicone content of



**Figure 7** Surface free energy of the film in different silicone content.



**Figure 8** Thermogravimetric analysis of polymers by different silicone contents analysis.

1.25–2.5 wt % prepared by *in situ* polymerization is presented in Figure 8. The final thermal weight loss for PHSA, MHSA1.25, MHSA1.5, MHSA2, and MHSA2.5 is 97.2088, 93.9961, 93.0107, 91.1408 and 91.0144 wt %, respectively. For the MHSA, the final thermal weight losses are 90.3395 wt % at 457.96°C for MHSA22, 88.71 wt % at 471.22°C for MHSA23, and 85.872 wt % at 458.86°C for MHSA24. There are three steps for the thermal weight loss. The first two steps are TGA curves for PHSA. The third weight loss at 450–600°C might be caused by the decomposition of groups such as —OH and —SiO(CH<sub>3</sub>)<sub>2</sub> group.

## CONCLUSIONS

High performance MHSA was successfully prepared by *in situ* solution polymerization. The water contact angles, surface roughness, and thermal stability of MHSA films were enhanced with the increasing of the silicone content in the resin. As the silicone content increased, the molecular weight, viscosity, glass transition temperature ( $T_g$ ), and surface free energy of the films were decreased because of the structure of MPTS. The result showed that MHSA with 2.5% silicone content has optimum water repellency, acid resistance, hardness, and excellent weatherability.

We are pleased to thank the Department of Chemistry at Wuhan University for their kind support in the analysis.

## References

1. Papasawa, S.; Claya, J.; Gunther, R. *J Appl Polym Sci* 2001, 43, 193.
2. Petit, H.; Krebs, A.; Uytterhoven, G.; Jong, F. D. *Prog Org Coat* 2001, 43, 41.
3. Anton, D. *Adv Mater (Weinheim, Ger)* 1998, 10, 1197.
4. Ming, W. H.; Tian, M.; van de Grampel, R. D.; Melis, F.; Jia, X.; Loos, J.; van de Linde, R. *Macromolecules* 2002, 35, 6920.
5. Park, H. S.; Wu, J. P.; Kim, M. S.; Hahm, H. S.; Kim, S. K.; Rhee, H. W. *J Appl Polym Sci* 2001, 81, 1614.
6. Mamiya, T.; Katsurahara, T.; Oshikubo, H. *Prog Org Coat* 2002, 45, 219.
7. Chen, M. J.; Pohl, E. R.; Ramdatt, P. E. *J Coat Technol* 1997, 69, 43.
8. Li, L. H.; Xu, W. J.; Wu, Y. M.; Xiong, Y. Q.; Lu, W. H.; Tang, Q. J.; *Prog Org Coat* 2005, 53, 77.