HONGBO LIU[1)2)3)], MINGCAI CHEN[2)*)], KAI XU[2)], ZHIXIA WANG[2)3)]

Preparation of new polyorganosiloxane acrylate and the properties of UV-cured acrylate compositions containing it

Summary — A new polyorganosiloxane acrylate (POSA) has been obtained as a result of Michael addition reaction of polyorganosiloxane modified with cyclohexylamine with methyl end groups (MCAPS) and hexanediol diacrylate (HDDA). ^{1}H NMR and FT-IR methods confirmed the course of a reaction of N-H groups of MCAMPS with acrylic groups of HDDA. POSA has been used to modification of UV-cured epoxy-acrylic system (HDDA + butyl acrylate + epoxy-diacrylate resin). It has been stated that even small POSA content (1—1.5 wt. %) causes significant changes of surface properties of cured coatings. Namely, contact angle and its hysteresis increase, gloss decreases while final hardness does not change. Using XDS method it was showed that POSA selectively concentrated on the surface of cured coatings.
Key words: polyorganosiloxane acrylate, epoxy-acrylic systems, modification, UV-curing, surface properties, wettability.

The UV-curable systems find important applications in many industrial fields for the production of different items in form of films, such as inks, coatings, pigments, adhesives or printed circuits, and in the electronic industry. Their use results from their unique advantages as follows: high cure speed, energy conservation, solvent-free formulation and excellent physical properties [1—7].

The UV-curable systems generally, consist of three major components: reactive polymerizable oligomers, reactive diluents and photoinitiators [8, 9]. To obtain the surface coatings showing particular properties, the use of monomers and oligomers containing silicones or siloxanes is very attractive, owing to the peculiar characteristics given by the presence of silicon atom [10, 11]. Its special characteristic was given by us in our earlier paper published in "Polimery" [12]. As it was already mentioned in that paper, an usual method of acryl functional silicone compounds preparation is the reaction of hydroxyalkylacrylate with a chlorosilane to produce the acrylic functional silicone compound, with HCl as a by-product [10, 11]. Another process of photopolymerizable polyorganosiloxanes preparation by reaction of hy-

drosiloxanes with acrylates in the presence of a platinum catalyst has been also described [13].

In our present work a new polyorganosiloxane acrylate was synthesized by Michael addition reaction and introduced into epoxy-diacrylate (BEDA) systems at various concentrations. Because no catalyst was used and no by-products were formed, the synthesis and purification were simple. Unusual surface properties of the polymeric films obtained via UV-curing technique were investigated.

EXPERIMENTAL

Materials

The basic components of formulations investigated were epoxy-diacrylate resins obtained by the reaction of Shell epoxy resins E-827 with acrylic acid. The product obtained from E-827 was denoted BEDA, and its average molecular weight was assumed to be equal to 506.

Hexanediol diacrylate (HDDA) and butyl acrylate (BA) as active diluents were purchased from Tianjiao Paint Ltd.

Methyl ended cyclohexylamine modified polyorganosiloxane (MCAPS, M_n = 3102, M_w = 3794) was supplied by Hengzhou Dalu Industry Ltd.

2-hydroxy-2,2-dimethyl-1-phenhylethan-1-one (Darocur 1173, Ciba-Geigy, Switzerland) was used as photoinitiator for UV-curing.

All the materials in this study are used as received without further purification.

[1)] Chinese Academy of Sciences, Institute of Chemistry, Beijing 100080, People's Republic of China.
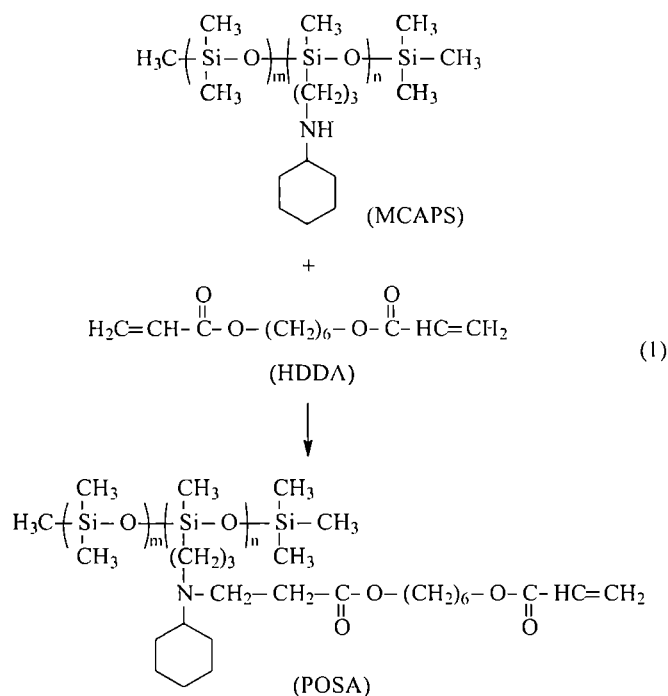[2)] Chinese Academy of Sciences, Guangzhou Institute of Chemistry, Guangzhou 510650, People's Republic of China.
[3)] Chinese Academy of Sciences, Graduate School, Beijing 100039, People's Republic of China.
[*)] To whom all correspondence should be addressed, e-mail: mcchen@mail.gic.ac.cn

Synthesis

The polyorganosiloxane acrylate (POSA) was prepared by mixing HDDA with MCAPS in proportion 2:1 vol/vol [see Equation (1)]. The mixture was heated to

$$H_3C\!\!-\!\!\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\!\!\Big]_m\!\!\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ (CH_2)_3 \end{array}\!\!\Big]_n\!\!\begin{array}{c} CH_3 \\ | \\ Si-CH_3 \\ | \\ CH_3 \end{array}$$

NH (MCAPS)

+

$$H_2C\!\!=\!\!CH\!\!-\!\!\overset{O}{\overset{\|}{C}}\!\!-\!O\!\!-\!(CH_2)_6\!\!-\!O\!\!-\!\overset{O}{\overset{\|}{C}}\!\!-\!HC\!\!=\!\!CH_2$$

(HDDA)   (1)

$$H_3C\!\!-\!\!\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array}\!\!\Big]_m\!\!\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ (CH_2)_3 \end{array}\!\!\Big]_n\!\!\begin{array}{c} CH_3 \\ | \\ Si-CH_3 \\ | \\ CH_3 \end{array}$$

$$N\!\!-\!CH_2\!\!-\!CH_2\!\!-\!\overset{}{\underset{\|}{C}}\!\!-\!O\!\!-\!(CH_2)_6\!\!-\!O\!\!-\!\overset{}{\underset{\|}{C}}\!\!-\!HC\!\!=\!\!CH_2$$
$$\quad O \quad\quad\quad\quad\quad\quad O$$

(POSA)

$m > n > 0$

70 °C for 24 h, with mechanical stirring. The liquid product was washed with ethanol at least 5 times, and dried at 50 °C in vacuum for 12 h.

Film preparation

BEDA (65 wt. %), HDDA (20 wt. %) and BA (15 wt. %), POSA (various concentrations) and photoinitiator (3 wt. %) in the liquid formulations used in the reported investigations were mixed. The liquid formulations were coated onto a glass plate with a special frame as a support. Then the samples were cured using the Ultraviolet High Pressure Mercury Lamp (1 kW, 80 W/cm, Huiyixin Electrical Light Source Technology Development Ltd, Beijing). Basic curing time of the samples investigated was 12 s. Free films were obtained by peeling them from the glass plate.

Methods of testing

^{1}H NMR analysis was performed at a Bruker 400 MHz instrument using $CDCl_3$ as solvent.

FT-IR analysis was performed using RFX-65A FT-IR Spectrophotometer (Analect, USA).

Molecular weight distribution (*MWD*) of POSA was measured by gel permeation chromatography (GPC) using Waters Model 5. GPC measurements were per-

formed in tetrahydrofuran solution by means of Ultrastyragel 10^3 Å column under the speed 1.0 mL/min at 40 °C.

The contact angle measurements were performed using Erma instrument. The measurements were made in air at room temperature. For each sample at least six measurements were performed, placing the drops of redistilled water in different parts of the sample surface.

The differences in average values were no more than 2° for the advancing angle and the receding angle.

The content of Si element on the surface of UV-cured film was analyzed using X-ray energy dispersive spectroscopy (XDS, Oxford ISIS-300). The size of a sample was 8x5 mm.

Hardness of UV-cured film was evaluated using QBY pendulum apparatus made by the Tianjin Instrument Company. The films were applied on glass plates (95×88×5 mm) by a coater with a 100 μm gap.

Surface resistance of UV-cured film was measured at 25 °C using a surface resistance tester of type ZC36 from Shanghai Instrument Co. The test voltage was 1000 V.

The specular gloss of the free dry film of size 8×1.5 cm measurements were carried out using Sheen 60 apparatus from Sheen Instruments LTD. The specular gloss of the glass (refractive index $n_D = 1.567$) was defined as 100.

RESULTS AND DISCUSSION

^{1}H NMR spectrum of POSA is shown in Fig. 1. There are the signals related to acrylic groups (5.78—6.40 ppm) shown in the spectrum of the product. This fact indicates that N-H groups of MCAPS have been reacted with acrylic groups of HDDA. The characteristic absorption peaks of acrylic groups in the product can also be proved by FT-IR spectrum (1640 cm^{-1}). The number average molecular weight (M_n) and weight average molecular weight (M_w) of POSA measured by GPC were 3387 and 4426, respectively, so the *MWD* value was 1.31.
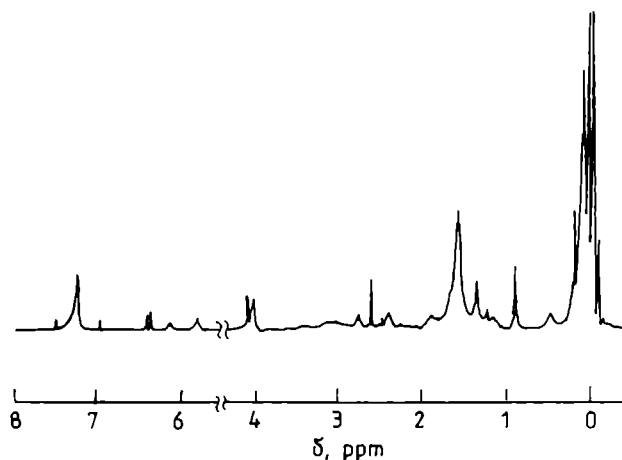

Fig. 1. ^{1}H NMR spectrum of POSA

The measurements of contact angle values of water were performed on the cured films peeled off from glass substrate. The side in contact with air was labelled the air side, and the other side — the substrate (glass) side. The contact angle of a mixture composed of pure epoxy-acrylic resin (BEDA), HDDA and BA with water was about 40° on the glass side and 42° on the air side. When POSA was added to this curable formulation, and the mixture was placed on the same substrate (*i.e.* glass) the wettability changed, as evidenced in Fig. 2 by the contact angle results, obtained with water. The data clearly
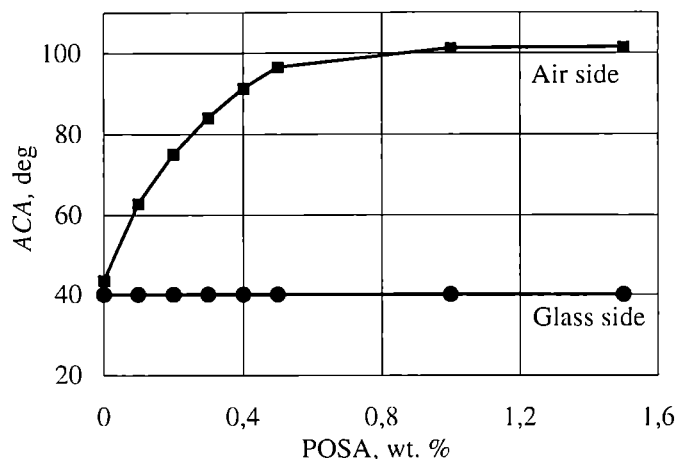

Fig. 2. *Effect of POSA concentration on the advancing contact angle (ACA) of UV-cured films*

showed that POSA was effective only on the air side of UV-cured films, while the glass side keeps the same properties as of the pure resin. It means that the less polar air side is enriched with POSA.

The advancing contact angles of UV-cured films increased with increasing of POSA content. The behavior of POSA shows a "plateau value" (101°) that was reached at a concentration called critical value — here 1.0 wt. %. This phenomenon is typical for a hydrophobic surface.

The selective modification of film surface was confirmed by XDS results. They allowed the estimation of the concentration of Si element in the outermost layer of UV-cured film. As shown in Fig. 3, a clear difference in surface composition between the air side and the glass side was noted. Namely, the absorption peak of Si element on the glass side was very low, on the contrary, an evident absorption peak of Si element on the air side of the cured film existed. Of course, with the increase in POSA concentration in UV-curable system, the content of Si element on the air side increased. So wettability is clearly correlated to Si (*i.e.* POSA) concentration at the surface. For various concentrations of POSA in a solid, also the various surface concentrations were observed, due to the selective migration of the additive.
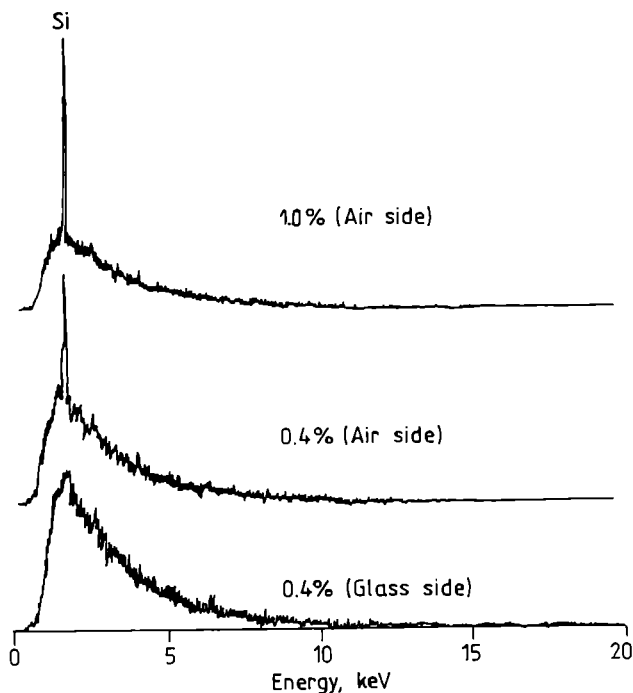

Fig. 3. *XDS results of the air and glass sides of UV-cured films differing in POSA content*

Except for the direct measurements of contact angle, further information concerning the film surface were obtained by contact angle hysteresis, *i.e.* the difference between advancing and receding angle. Hysteresis was expected for majority of the materials, particularly those containing both hydrophobic and hydrophilic groups at the surface. For the pure resin its value was 25° and 30° for the air side and the glass side, respectively. On the glass side, in the presence of polyorganosiloxane acrylate, the contact angle hysteresis did not change. However, on the air side, as Fig. 4 show, there was an increase in hysteresis. It was also dependent on POSA concentration. These results can be explained by the fact that hydrophobic monomer forms a heterogenous surface. The surface
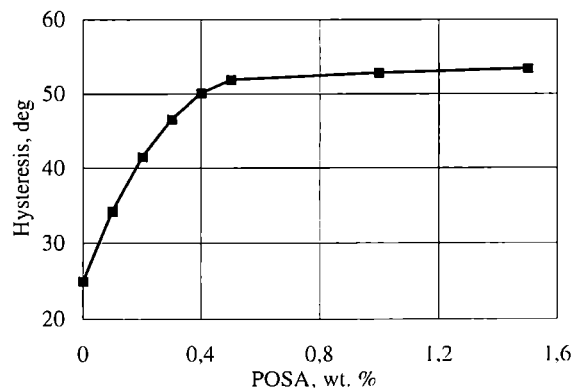

Fig. 4. *Effect of POSA concentration on the contact angle hysteresis of the air side of UV-cured films*

heterogeneity increased at first, then, as previously, kept a constant value (1 wt. % of POSA) indicating the formation of an equilibrium surface layer at these conditions.

Hardness was one of the important properties of UV-cured films for many applications, and it was related to the crosslinking network density and the conversion of acrylic groups in the molecular chain. Hardness of the UV-cured films with various POSA concentrations *versus*
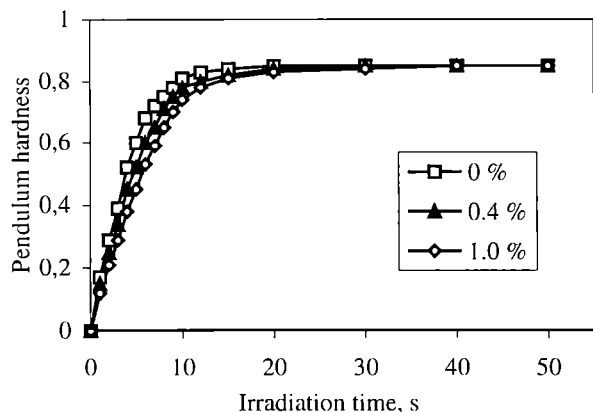

Fig. 5. Effects of POSA concentration and irradiation time on the hardness of UV-cured films

irradiation time was shown in Fig. 5. It can be seen that prolongation of the irradiation time leads to the increase in hardness to some limit because more light energy causes higher conversion of acrylic groups. Unfortunately, hardness of UV-cured film with POSA was lower than that of pure resin film at the initial stages of irradiation. With prolongation of irradiation time, hardness of all UV-cured films tended to unification.

In the presence of an effective photoinitiator the acrylate resins were rapidly crosslinked according to free-radical polymerization mechanism. Our results of measurements of hardness can be explained by solubility of POSA in pure resin. That is, the transparency of UV-curable liquid formulation decreased, which leads to the lower efficiency of UV irradiation. At the same time, only a little amount of POSA may be introduced into cured films, so the change of the crosslinking density of the films was little, which led to the almost same final hardness.

T a b l e 1. Effect of POSA concentration on the surface resistance and specular gloss of UV-cured films

POSA concentration wt. %	Surface resistance $\times 10^{14}\ \Omega$	Specular gloss
0	9.8	117.6
0.1	10.7	114.5
0.2	11.3	110.6
0.3	13.2	107.7
0.4	15.6	104.4
0.5	17.1	100.8
1.0	18.3	95.5
1.5	18.9	92.6

Table 1 shows the surface resistance of UV-cured films. Because the air side of the UV-cured film is enriched with POSA and POSA is better electrical insulator than the other acrylic components, the values of surface resistance of compositions containing POSA were higher than that one of pure acrylic film.

The surface specular gloss values of all dry films are also compared in Table 1. This property of pure acrylic film was about 117.6, while POSA introduction significantly decreases this value.

CONCLUSION

A new POSA, which can be a good additive for UV-curable systems, was synthesized by reaction of MCAPS with HDDA at Michael addition reaction. The spectroscopic analysis confirmed the reactivity of N-H groups of MCAPS with the acrylic groups of HDDA. UV-curable resin films were prepared by introduction of POSA into the formulation. XDS measurements proved that POSA enriched the air side of UV-cured films, so their surfaces show sharply outlined hydrophobic character (in spite of the presence of many polar OH groups in the polymeric network) and a high hysteresis of contact angle. The highest contact angle of UV-cured films with water reached 101°. UV-cured films with POSA show higher surface resistance and lower specular gloss, in comparison with the pure epoxy-acrylic films.

REFERENCES

1. Burak L.: *J. Coat. Tech.* November 1997, **69**, No. 874, 29.
2. Golden R.: *J. Coat. Tech.* 1997, **69**, No. 871, 83.
3. Yu Q., Nauman S., Santerre J. P., Zhu S.: *J. Appl. Polym. Sci.* 2001, **82**, 1107.
4. Dvorehak M. J., Riberi B. H.: *J. Coat. Tech.* 1992, **64**, No. 808, 43.
5. Decker Ch., Moussa K.: *J. Coat. Tech.* 1993, **65**, No. 819, 49.
6. Priou C., Soldat A., Cavezzan J.: *J. Coat. Tech.* 1995, **67**, 71.
7. Bongiovanni R., Malucelli G., Messori M., Pilati F., Priola A., Tonelli C., Toselli M.: *J. Appl. Polym. Sci.* 2000, **75**, 651.
8. Bowling K., Adams J., Struck S.: *J. Coat. Tech.* 1996, **68**, No. 854, 91.
9. Idriss K. M., Mubrak A. K., Mokhlesur R., Mahmuda G.: *J. Appl. Polym. Sci.* 1997, **66**, 1997.
10. Davidson R. S., Ellis R., Tudor S., Wilkinson S. A.: *Polymer* 1992, **33**, 3031.
11. Batten R. J., Davidson R. S., Ellis R. J., Wilkinson S. A.: *Polymer* 1992, **33**, 3037.
12. Liu H., Chen M., Zhang X., He T., Wang Z.: *Polimery* 2004, **49**, 168.
13. Sun Y. P., Zheng C. R.: *Re Gu Xing Shu Zhi* 1999, **3**, 16.