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Preparation and properties of UV-curable acrylate compositions containing silicon

Summary — Some di- and triacrylates were subjected to Michael addition reaction with *N*-cyclohexyl- γ -aminopropylmethyldimethoxysilane (CAMS). FT-IR method has been used to follow the course of the reaction of -NH group in CAMS with double bond in an acrylate. Post-reaction mixtures obtained underwent UV-curing in the presence of a photoinitiator (2-hydroxy-2,2-dimethyl-1-phenylethane-1-one, trade name "Darocur 1173") and formed thin films on the glass or plastic substrate. Dependence of the thermal stability of cured material on its initial composition was characterized using thermogravimetric method. There were determined the effects of non-reacted acrylic groups' part in the post-reaction mixture as well as of irradiation time (crosslinking degree) on hardness and brittleness of the coatings cured. Silicon atoms presence in the compositions improves their elasticity but deteriorates thermal stability.

Key words: Michael addition reaction, di- and triacrylates, *N*-cyclohexyl- γ -aminopropylmethyldimethoxysilane, photocured coatings, hardness, brittleness, thermal stability.

Since its commercial introduction over 30 years ago, radiation curing has steady grown in demand and usage and has become one of the fastest developing coatings technologies in the world [1, 2]. Radiation curing can be performed by electron beam (EB) and ultraviolet (UV) irradiation, and it is known to be one of the most efficient methods for producing *quasi*-instantly highly cross-linked polymer materials. Due to its unique advantages of fast reaction rate, solvent-free formulation and excellent physical properties, this technology has found a large number of industrial applications, such as fast drying varnishes and inks, optical fibers, electronic components and printing plates, and restoration materials [3–7].

To produce the surface coatings showing particular properties, an appropriate oligomer functionalized with acrylate groups in combination with a polyfunctional acrylate to reduce the viscosity of an oligomer is used [8, 9]. Because of the peculiar characteristics given by silicon presence, the use of monomers and oligomers containing silicon is very attractive, and their characteristics

include a wide working temperature range, increased impact strength, good release properties, hydrophobicity, good thermal and chemical stability, weather resistance, a low coefficient of friction, incompatibility with majority of organic compounds and excellent dielectric insulating properties. Because of their low surface energy, the siloxane segments tend to migrate to the air-polymer interface. Besides, siloxanes are also of interest as possible biomaterials because they are physiologically inactive, of very low toxicity, and present no health hazards [10–15].

Several methods of the preparation of radiation curing siloxane monomers and oligomers have been used. Silanes and siloxanes modified by epoxy compounds have been synthesized *via* the hydrosilylation of vinyl epoxy resins using various Si-H functional silanes or siloxanes and their curing with cationic photoinitiators [16]. A method of the acryl functional silicone compounds preparing is a reaction of hydroxyalkylacrylate with chlorosilane to produce the acryl functional siloxane compound with HCl as a by-product. The reaction can run in the presence of an acid acceptor, such as amine which produce amine hydrochloride salt, or it can run under partial vacuum to remove HCl by-product, as it is formed [8, 9]. Another process of photopolymerizable organopolysiloxanes preparing by reaction of hydrosiloxanes with allyl acrylates in the presence of a platinum catalyst has been described. They are mixed with urethane acrylate and epoxy acrylate to be applied to the optical fibers [17, 18]. Photopolymerizable

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organopolysiloxane acrylate has also been made by reaction of hydroxy-terminated diorganopolysiloxanes with an acrylate-functional alkoxysilane [6, 19].

In this paper, to obtain the composition of acrylates containing silicone compounds, *N*-cyclohexyl- γ -aminopropylmethylmethoxysilane (CAMS) and di- or multi-functional acrylates were used as raw materials and Michael-type addition reaction was applied. Because no catalysts were used and no by-products were formed, the acrylates containing silicone obtained this way were purer than when other methods were used. Kinetics of photopolymerization of synthesized acrylates as well as the estimation of the properties of the coatings obtained have been also studied.

EXPERIMENTAL

Materials

Dipropylene glycol diacrylate (DPGDA), neopentyl glycol diacrylate (NPGDA), propoxylated neopentyl glycol diacrylate (PO-NPGDA), pentaerythritol triacrylate (PETA), trimethylolpropane triacrylate (TMPTA), ethoxylated trimethylolpropane triacrylate (EO-TMPTA), 1,4-butanediol diacrylate (BDDA), phthalic tripropylene glycol diacrylate (PDTPGDA), ethoxylated bisphenol diacrylate (EO-BPDA), 1,6-hexanediol diacrylate (HDDA) and propoxylated glycerol diacrylate (PO-GTA) were supplied by Tianjiao Paint Ltd. Tripropylene glycol diacrylate (TPGDA), phthalic diglycol diacrylate (PDDA), diglycol diacrylate (DGDA) and triglycol diacrylate (TGDA) were supplied by Beijing Eastern Acrylic Chemical Technology Ltd.

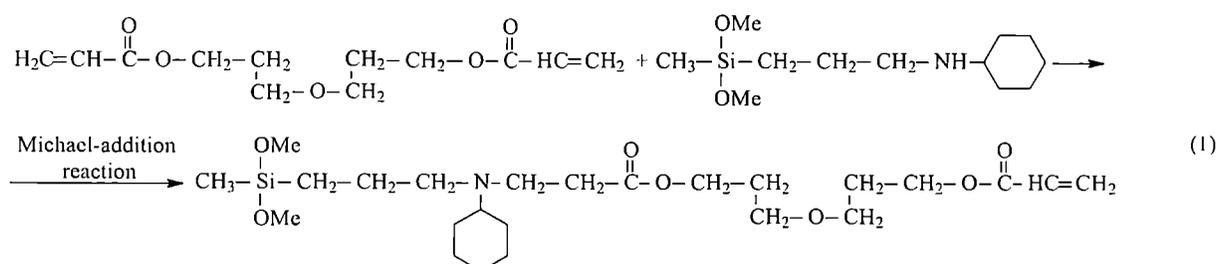
N-cyclohexyl- γ -aminopropylmethylmethoxysilane (CAMS) were delivered by Hangzhou Dalu Industry Ltd.

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

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

Synthesis of the compositions

Compositions from acrylates and organosiloxane were prepared by mixing of defined acrylate with CAMS in molar ratio given in Table 2.



The mixture was heated up to 70 °C and maintained for 12 hours. The equation (1) illustrates this reaction course on the example of DPGDA + CAMS system.

Preparation of the coating compositions and their UV curing

Photoinitiator was dissolved in the monomer prepared at constant concentration equal 4 wt. %. The solutions were coated onto a glass plate or a plastic piece with a special frame as a support. Then the samples were cured (see Table 2) using the Ultraviolet High Pressure Mercury Lamp (1 kW, 80 W/cm, Huiyixin Electrical Light Source Technology Development Ltd., Beijing).

Methods of products characterization

Conversion of unsaturation [8, 20]

The conversion of acrylic groups measured as residual unsaturation in the UV cured films approximately 6 μm thick was determined using RFX-65A FT-IR Spectrophotometer (Analect, USA). Absorptions due to the acrylic double bonds appear at 1729, 1637, 1619 and 810 cm^{-1} . Using 810 cm^{-1} (out of plane deformation vibration) as a baseline method, the spectra was normalized using the carbonyl peak at 1729 cm^{-1} as an internal standard to account for variations in sample thickness and instrument recording. Thus the ratio of the acrylate peak at 810 cm^{-1} and at 1729 cm^{-1} was determined for the film prior to irradiation and after irradiation. Acrylic double bonds content in the uncured solutions was defined as 100 %.

The pencil hardness

The pencil hardness of the cured film was evaluated by drawing the coated substrate using a pencil with changeable 0.5 mm flat-ended leads. Pencils of various hardness were held firmly against the film at a 45° angle and pushed away in a 5 cm stroke, and the point at which the film was etched was recorded. The film was applied on glass plates by a coater with a 60 μm thick.

Brittleness [9]

Brittleness of the cured film was measured by 180° folding of a coated substrate and assessed the amount of debris along the crease. An arbitrary scale from 1 (no

debris, flexible) to 5 (large amount of debris, very brittle) was used to assess the brittleness.

Thermal properties

The decomposition temperature of UV cured films was determined using Netzsch thermal analyzer at a heating rate of 10 °C/min and a test range of 20–700 °C under a nitrogen purger. The sample weights were about 8 ± 2 mg.

RESULTS AND DISCUSSION

A series of silicon containing products synthesized by Michael-type addition reaction were transparent liquids.

Typical example of the changes appearing in IR spectra of the substrates after Michael reaction is given in Fig. 1 for DPGDA/CAMS system.

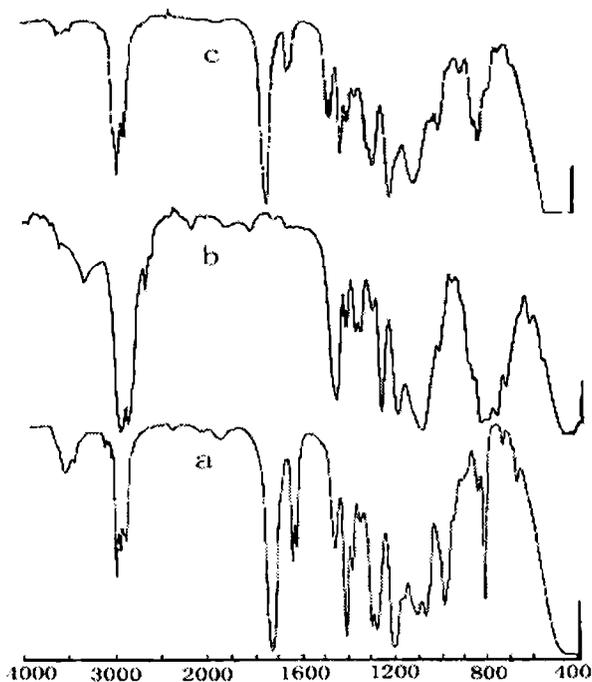


Fig. 1. FT-IR spectra of DPGDA (a) and CAMS (b) before the reaction, and DPGDA + CAMS (c) after the reaction

FT-IR spectra of such a system tend to be changed when the mixture was maintained at 70 °C. There are evident absorption peaks of -NH group of CAMS at 3300 cm^{-1} and 1300 cm^{-1} . The absorption peak of -NH group at 3300 cm^{-1} decreased with increasing the reaction time as -NH group of CAMS was reacting with the acrylic group of DPGDA gradually. The reaction of synthesis had been finished when the absorption peak at 3300 cm^{-1} had completely disappeared after 12 h.

The silicon-containing acrylates are rapidly cross-linked by free-radical polymerization mechanism in the

presence of an effective photoinitiator. A remarkable feature of these materials, which may influence their reactivity is that triacrylates and diacrylates with high part of double bonds are used. As it can be seen from Fig. 2, the conversion of double bonds in all cured films increased extensively, to 38 % for cured pure TMPTA film, 43 % for cured TMPTA + CAMS (3:1) film, 48 % for cured TMPTA + CAMS (2:1) film, 50 % for cured TMPTA + CAMS (1:1) film after first 5 s of irradiation, respectively. When cure time was growing up to 40 s, there were 30, 12, 15, and 10 % of unreacted double bonds remaining in the cured films in the four cases, respectively. Complete saturation is never obtained because small amounts of the acrylic groups may be hidden inside the crosslinked networks of the cured resins so unable to react in the three-dimensional polymer matrix formed [21].

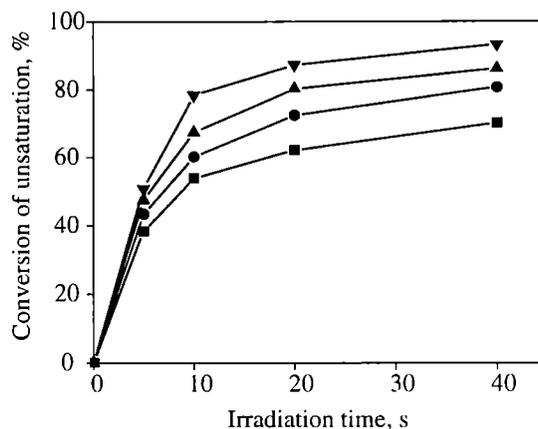


Fig. 2. Effect of irradiation time and molar ratio of the reagents on the conversion of unsaturation of TMPTA (■), TMPTA + CAMS (1:1, ▼), TMPTA + CAMS (2:1, ▲) and TMPTA + CAMS (3:1, ●)

These results would indicate the silicon-containing acrylates form tack-free films at shorter irradiation time than TMPTA does. It would appear that, within the structure of the polymerizing silicon-containing acrylates, there are some double bonds reacting with -NH in CAMS and conformational mobility is greater, thereby allowing the radical at the growing chain to explore a greater volume than is the case of TMPTA. Consequently, a larger proportion of acrylic groups is used up. At the same time, curing of TMPTA led to so much shrinkage that the films exhibited severe reticulation and as a consequence it proved impossible to submit them to the standard physical testing procedure.

The results of TGA analyses of UV-cured films, on TMPTA example, are shown in Fig. 3. So the temperature of start of thermal decomposition of UV-cured films remarkably decreased with increase in silicon concentration in acrylates. The temperature of thermal decomposition beginning of UV-cured TMPTA films is 204.1 °C ,

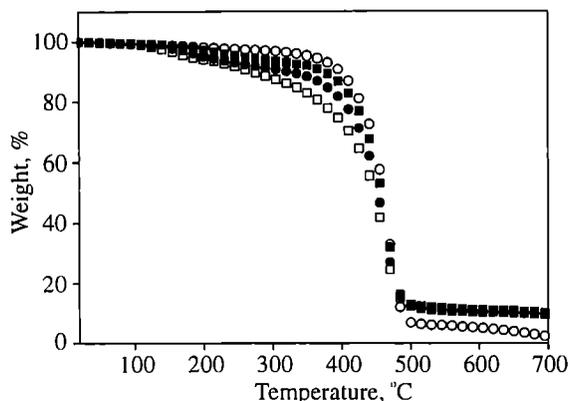


Fig. 3. Thermal decomposition of TMPTA (O), TMPTA + CAMS (1:1, □), TMPTA + CAMS (2:1, ●) and TMPTA + CAMS (3:1, ■); curing time 40 s

however, the UV-cured TMPTA + CAMS (1:1) film start to decompose at 131.4 °C. The results may be interpreted this way: C-C and C-O bonds (342 and 343 kJ/mol respectively) are considerably stronger than C-N and Si-C bonds (293 and 318 kJ/mol respectively) in silicon-containing acrylates [9]. C-N and Si-C bonds start to decompose at lower temperature than C-C and C-O.

Table 1. Thermogravimetric analysis: decomposition temperature (°C) at certain residues (wt. %)

Sample	Temperature (°C) related to the residue:						Residue at T = 700 °C, %
	98 %	90 %	80 %	50 %	20 %	10 %	
TMPTA	204.1	399.5	427.6	460.2	478.0	487.8	2.20
TMPTA + CAMS (1:1)	131.4	269.8	368.9	447.1	475.3	—	10.20
TMPTA + CAMS (2:1)	147.1	324.1	401.8	452.4	477.5	672.6	9.70
TMPTA + CAMS (3:1)	178.8	374.3	417.2	457.4	480.1	657.5	9.40
NPGDA	169.8	391.6	428.1	462.7	477.8	487.2	3.60
NPGDA + CAMS (2:1)	119.1	216.5	346.3	442.4	482.8	—	10.12
PO-NPGDA + CAMS (2:1)	152.5	288.8	364.2	418.2	453.1	—	10.18

Table 1 presents the results of thermogravimetric analyses of three selected types of compositions, namely one based on triacrylate (TMPTA) and two based on diacrylate NPGDA (non-propoxylated — NPGDA or propoxylated — PO-NPGDA). CAMS presence in the composition deteriorates thermal stability of the system. Beginning of the decomposition (up to 20 %) of diacrylate based composition is placed in lower temperature range than of triacrylate based one. Propoxylation of

Table 2. Physical test data of the films investigated

Sample	Initial components of the composition	Molar ratio	Irradiation time, s	Pencil hardness	Brittleness
1	DPGDA + CAMS	2:1	20	H	1
			40	3H	2
2a	TMPTA + CAMS	1:1	20	4H	1
			40	5H	2
2b	TMPTA + CAMS	2:1	20	4H	1
			40	5H	2
2c	TMPTA + CAMS	3:1	20	5H	2
			40	5H	3
2d	EO-TMPTA + CAMS	1:1	20	4H	1
			40	5H	2
3a	NPGDA + CAMS	2:1	20	H	1
			40	3H	2
3b	PO-NPGDA + CAMS	2:1	20	H	1
			40	2H	1
4	TPGDA + CAMS	2:1	20	HB	1
			40	2H	1
5a	PETA + CAMS	1:1	20	4H	2
			40	5H	3
5b	PETA + CAMS	2:1	20	4H	2
			40	5H	3
5c	PETA + CAMS	3:1	20	5H	3
			40	5H	3
6	BDDA + CAMS	2:1	20	H	1
			40	2H	1
7	PDTPGDA + CAMS	2:1	20	2H	1
			40	4H	2
8	EO-BPDA + CAMS	2:1	20	3H	1
			40	5H	2
9	HDDA + CAMS	2:1	20	H	1
			40	2H	1
10	PO-GTA + CAMS	2:1	20	H	1
			40	3H	1
11	PDDA + CAMS	2:1	20	H	1
			40	3H	2
12	DGDA + CAMS	2:1	20	H	1
			40	3H	1
13	TGDA + CAMS	2:1	20	H	1
			40	2H	1

diacrylate significantly shift this range to higher temperature.

Characteristic of functional properties of the coatings obtained from various post-reaction mixtures is given in

Table 2. These materials were coated onto a glass plate or a plastic piece and then exposed to UV radiation. The films formed were submitted to physical testing. The results of testing of pencil hardness and brittleness are collected in Table 2. In our case they are only a guide to the properties of films because it is difficult to obtain uniform coatweights of the films. The pencil hardness is one of the important properties of UV cured films and it is related to the crosslinking network density and the conversion of acrylic groups in the molecular chain. The pencil hardness of our films depends on irradiation time. It can be seen that irradiation time prolongation usually leads to an increase in the pencil hardness because more light energy causes higher conversion of acrylic groups.

Two important functional features of the coating, namely pencil hardness and brittleness, depend on the coating crosslinking degree related to the part of non-reacted acrylic groups in the composition. The higher this part (= increase in crosslinking degree) the bigger values of pencil hardness and brittleness. It can be observed when the compositions either made of the same components but with higher acrylates' concentrations (samples 2b and 2c) or of the same molar ratio of the components but based on di- or triacrylates (e.g. samples 1 and 5b) are compared.

CONCLUSIONS

Michael-type addition reaction was carried out in the absence of solvent and catalyst. The reactivity of -NH groups of CAMS with the acrylic groups of diacrylates and triacrylates could be analyzed by the change of the characteristic absorption peak in the IR-spectrum at 3300 cm^{-1} .

Functional properties of the cured films namely pencil hardness and brittleness, can be changed by irradiation time varying. The curing rate and unsaturation conversion increased with the CAMS added. All these materials can be cured at short time to give (oppositely to acrylates themselves, without CAMS) hard, flexible films, and furthermore film formation was not accompanied by noticeable shrinkage. However, CAMS presence

leads to thermal stability deterioration. The properties of the coatings obtained were attributed to silicon atom presence in the products investigated.

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