

Synthesis and Structural Characterization of Methacrylic Acid/Octadecyl Acrylate-graft-Poly(methylhydrosiloxane) by Hydrosilylation

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ABSTRACT: Methylmethacrylate (MMA) and octadecyl acrylate (OA) were grafted to poly(methylhydrosiloxane) (PMHS) by hydrosilylation, respectively, with hexachloroplatinic acid as catalyst, and the former was further hydrolyzed to prepare methacrylic acid (MAA)-graft-PMHS under the alkaline condition. Through orthogonal experiment, main factors affecting the graft reaction between OA and PMHS were discussed and arranged in a decreasing order according to their abilities of the effect on the hydrosilylation of OA with PMHS: catalyst dosage, reaction temperature, reaction time, material ratio, and solvent dosage. It was found that the hydrosilylation of OA with PMHS was easier to that of MMA with PMHS. Under optimal conditions, the grafting ratios of MMA with PMHS and

OA with PMHS reached about 90 and 95%, respectively. FTIR and ¹H NMR spectra indicated that the hydrosilylation reactions followed the Markovnikov's rule and played a strong preference toward β -1,2-addition. The test of contact angle indicated that surface energy of a system was mainly dependent on the polar groups. The surface energy of OA-graft-PMHS (35.07 mN/m) was similar to those of PMHS (35.62 mN/m) and polyoctadecyl acrylate (36.57 mN/m), and lower than that of MAA-graft-PMHS (43.50 mN/m). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3773–3780, 2008

Key words: polysiloxanes; hydrosilylation reaction; FTIR; ¹H NMR; surface energy

INTRODUCTION

Polysiloxanes, which are usually known as “silicone” or “silicone elastomers,” have received widespread attention as a special family of polymers because of their unique properties, such as low glass transition temperature (T_g), low surface tension and surface energy, low solubility, low dielectric constant, transparency to visible and UV light, high resistance to ozone, and stability against atomic oxygen even oxygen plasmas.¹ In addition, hydrosilylation is the subject of ever-interesting attention and has been increasingly used for the synthesis of block and graft polymers and polymers of networks.^{2–7} One of the most dominant advantages of hydrosilylation is that the reaction could not be interfered by many active groups (C=O, CN, NR₂, Cl, COOR, etc.) in the molecule.

Recently, John and Patrica, and Ela'mma et al. have reported that when the mineral-tanned leather was treated with acrylic resin grafted with additional long alkyl ester group, it could attain excellent water repellency, softness, and strength.^{8,9} So, it is of great inter-

est to know whether the resulting product might possess the extra similar properties, if this group is attached to the polysiloxane backbone.^{10–12} At present, monomer silane or siloxane is usually used as raw material for the synthesis and modification of polysiloxane.^{13–15} The disadvantages of this scheme are that several processes are needed to gain the aim product, the yield is not always acceptable, and the structure of final product may be different to the designed one. Correspondingly, using macromolecule as reactant has the advantage of fewer side reactions. Meanwhile, the structure of long alkyl group, which contains eighteen or more than eighteen carbons, is similar to that of body fat. Therefore, it has better compatibility with human skin and could be used in cosmetic or textile as sheeny auxiliary agent, lubricant, etc.¹⁶ So, in this paper, octadecyl acrylate (OA) was selected to modify poly(methylhydrosiloxane) (PMHS) and the reaction conditions were studied and compared with those of methylmethacrylate (MMA)-modified PMHS. In practical application, MMA-graft-PMHS was usually hydrolyzed to produce carboxylic siloxane [methacrylic acid (MAA)-graft-PMHS] with excellent reactivity and adhesiveness, which would have good compatibility with other finishing materials (polyurethane, polyacrylate, etc.) used in leather-making process and could endow

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leather with good softness, pleasant handle, and preferable elasticity.¹⁷ The structures of grafted polymers were determined by FTIR and ¹H NMR spectra, and the surface energies of raw PMHS, two modified products (MAA-*graft*-PMHS and OA-*graft*-PMHS), and their mixture (mol ratio of MAA-*graft*-PMHS to OA-*graft*-PMHS was 7 : 3) were calculated by a contact-angle technique. To explain the similarity on the surface energies of PMHS and OA-*graft*-PMHS, homogeneous polyoctadecyl acrylate (POA) was also synthesized and the surface energy of it was obtained according to the same method.

EXPERIMENTAL

Materials and instruments

PMHS (*H*-value is 36.1 mL/g) was of industrial grade and supplied by Chenguang Chemical Research Institute, Chengdu, China; OA (C.P., > 99%) was purchased from Tianjin Tianjiao Chemical, Tianjin, China; methylmethacrylate, chloroplatinic acid, and other conventional chemicals, which were purchased from Kelong Chemical Company, Chengdu, China, were of reagent grade and used without further purification.

The grafting ratio of the product was calculated by the determination of the residual hydrogen value.¹⁸ The term "hydrogen value" refers to the number of milliliters of gas (at S.T.P.) liberated per gram of compound. The determination of it was carried out as follows: About 0.5 g reaction mixture was reacted with 15 mL potassium hydroxide/isobutanol/H₂O solution (4 : 1 : 0.35, by weight). After the vibration of the reaction system for 20 min, the volume of the liberated gas was measured at S.T.P. The blank experiment was carried out by replacing the reaction mixture with toluene. The grafting ratio was calculated according to the following formula:

$$\text{Grafting ratio (\%)} = 100 \times [(V_0/m_0 - V_g/m_g)/(V_0/m_0)]$$

where V_0 and V_g are the volumes (mL) of the liberated gas of raw PMHS and grafted polymer, respectively; and m_0 and m_g are the weights (g) of raw PMHS and grafted polymer used in the experiment, respectively.

Structures of obtained products were ascertained by FTIR (Perkin Elmer Spectrum One, Perkin Elmer, USA) and ¹H NMR (BRUKER 300 Ultrashield™, Bruker G. E.) spectra. Surface energies of films were measured by a contact-angle technique (JY-82, Chengde shiyANJI).

Synthesis and hydrolyzation of MAA-*graft*-PMHS

Synthesis and purification of MMA-*graft*-PMHS

MMA-*graft*-PMHS was synthesized and purified according to Ref. 19 under optimal conditions.

Namely, a mixture of PMHS (10 g), toluene (20 g, 0.8 times the mass of the reactants) and chloroplatinic acid (1.5×10^{-3} g, 60×10^{-6} times the mass of the reactants, dissolved in tetrahydrofuran, 5 g/L) was added to a flask equipped with a reflux condenser, a stirrer, and a gas inlet cock, and heated at 80°C for 5 min under nitrogen atmosphere. Then MMA (15 g) containing some thiodiphenylamine (0.15 g) was dripped within 1–1.5 h and heated at 140°C for 30 h. The resulting liquid was distilled under reduced pressure to remove the remaining MMA and toluene, and then the residue was dissolved in ethanol and centrifuged to remove thiodiphenylamine. The final product was obtained by drying in a vacuum oven.

Hydrolyzation of MMA-*graft*-PMHS

MMA-*graft*-PMHS was hydrolyzed according to Ref. 20. Some purified MMA-*graft*-PMHS was added to a flask containing a reflux condenser, a stirrer, and fraction equipment (to collect the distilled MeOH), and then the reactor was kept in a water bath and heated at 90°C. After dropwise addition of 12% NaOH (mol ratio of grafted MMA to NaOH was 1 : 1.5) within 80 min, the mixture was cooled to room temperature and neutralized with 10% HCl. Finally, white ropy material obtained was dewatered in a vacuum oven to get MAA-*graft*-PMHS. The hydrolyzation ratio of the grafted product was calculated according to formula 2, where the carboxylic value was defined as the mmol of carboxylic group per gram of polysiloxane and determined by titration with 0.14M KOH ethanol solution containing 0.2% phenolphthalein as an indicator (see formula 1)²¹:

$$\text{Carboxyl value (mmol/g)} = (V \times C) / m \quad (1)$$

$$\text{Hydrolyzation ratio (\%)} = (m_1 / m_2) \times 100 \quad (2)$$

Here, V and C are the volume (mL) and concentration (mmol/mL) of KOH in ethanol solution, respectively; m is the weight (g) of polysiloxane used in the titration; m_1 is the carboxyl value of hydrolyzed product; and m_2 is the mmol of methyl methacrylic group per gram of MMA-*graft*-PMHS.

Synthesis and purification of OA-*graft*-PMHS

In a flask, equipped with a reflux condenser, a stirrer, and a gas inlet cock, OA (10 g) containing some thiodiphenylamine (0.05 g), toluene, and chloroplatinic acid (dissolved in tetrahydrofuran, 5 g/L) were heated at 80°C for 5 min under nitrogen atmosphere. Then PMHS was dripped within 1–1.5 h. After stirring the solution at a preselected temperature within a range of 100–130°C for 5–12 h (detail reaction scheme was shown in Table II), the resulting liquid

was distilled under reduced pressure to remove the toluene. Then the mixture of methane trichloride and acetone (10/1, v/v) was used to extract the residual OA monomer, and the resulting precipitate was rinsed with *n*-C₆H₁₄ to remove the homopolymer of OA. Finally, the material was dried in a vacuum oven to remove the *n*-C₆H₁₄.

Synthesis and purification of POA

POA was synthesized by free radical polymerization according to the Ref. 22, with toluene as solvent. The synthesis conditions were as follows: The concentration of OA was 0.3M, mass ratio of OA to initiator azobisisobutyronitrile (AIBN) 100 : 1, the reaction temperature 70°C, and the reaction time 7 h. The resulting polymer was purified by washing with trichloromethane and ethanol thoroughly.

Determination of contact angles of liquids on films

PMHS, POA, two modified polymers (MAA-graft-PMHS, OA-graft-PMHS), and their mixtures (mol ratio of MAA-graft-PMHS to OA-graft-PMHS was 7 : 3) were dissolved in methane trichloride, respectively, and then certain amounts of their solutions were dropped on glass slices, respectively, and vibrated carefully to spread polymers completely. After the solvent was volatilized, the contact angles for water and glycerol on the formed films were measured.

RESULTS AND DISCUSSION

Orthogonal experiment for the synthesis of OA-graft-PMHS

To optimize the reaction conditions for the synthesis of OA-graft-PMHS, orthogonal test was adopted. Main controllable variables, viz. reaction temperature (*A*), reaction time (*B*), catalyst dosage (*C*), solvent dosage (*D*), and material ratio (*E*) were selected. Other factors, such as rotation speed (rpm) and nitrogen flux (cm³/min), were set at the proper values based on our previous experiment. For each

TABLE I
Factors and Levels of the Orthogonal Experiment L₁₆ (4⁵) of OA-graft-PMHS

Variables investigated	Levels of each variable			
	1	2	3	4
<i>A</i> : Temperature (°C)	100	110	120	130
<i>B</i> : Time (h)	5	7	10	12
<i>C</i> ^a : Catalyst (ppm)	30	40	50	60
<i>D</i> ^a : Solvent dosage (g)	0.8	1.1	1.5	1.8
<i>E</i> ^b : Reactants ratio (mol/mol)	1/1	1.1/1	1.3/1	1.5/1

^a Based on the quality of two reactants.

^b Mol ratio of OA to Si—H residue in PMHS.

TABLE II
Results of the Orthogonal Experiment L₁₆ (4⁵) of OA-graft-PMHS

Run	<i>A</i>	<i>B</i>	<i>C</i> ^a	<i>D</i> ^a	<i>E</i> ^b	Grafting ratio ^c (%)
1	1	1	1	1	1	57.85
2	1	2	2	2	2	82.15
3	1	3	3	3	3	88.00
4	1	4	4	4	4	91.65
5	2	1	2	3	4	80.30
6	2	2	1	4	3	63.15
7	2	3	4	1	2	96.65
8	2	4	3	2	1	91.90
9	3	1	3	4	2	93.55
10	3	2	4	3	1	96.20
11	3	3	1	2	4	67.70
12	3	4	2	1	3	88.00
13	4	1	4	2	3	99.00
14	4	2	3	1	4	96.20
15	4	3	2	4	1	90.25
16	4	4	1	3	2	78.10
<i>k</i> ₁	319.7	330.7	266.8	338.7	336.2	
<i>k</i> ₂	332.0	337.7	340.7	340.8	350.5	
<i>k</i> ₃	345.5	342.6	369.7	342.6	338.2	
<i>k</i> ₄	363.6	349.7	383.5	338.6	335.9	
<i>K</i> ₁	79.9	82.7	66.7	84.7	84.1	
<i>K</i> ₂	83.0	84.4	85.2	85.2	87.6	
<i>K</i> ₃	86.4	85.7	92.4	85.7	84.6	
<i>K</i> ₄	90.9	87.4	95.9	84.7	84.0	
<i>R</i>	11.0	4.7	29.2	1.0	3.6	

A: Temperature (°C); *B*: Time (h); *C*: Catalyst (ppm); *D*: Solvent dosage (g); *E*: Reactants ratio.

^a Based on the quality of two reactants.

^b Mol ratio of OA to Si—H residue in PMHS.

^c Average of two tested results.

selected factor, four levels were investigated and listed in Table I.

Reference to the experimental design theory, the orthogonal array L₁₆ (4⁵) was chosen to arrange the aforementioned synthesis conditions. For each experimental project, the grafting ratio of the resulting product was calculated by the determination of the residual hydrogen value. The tested results are listed in Table II.

In Table II, "*k*_{*i*}" (*i* = 1,2,3,4) is the sum of four grafting ratios in the corresponding column marked as level "*i*"; "*K*_{*i*}" (*i* = 1,2,3,4) equals to *k*_{*i*}/4 in the corresponding column; whereas "*R*" is the variance of "*K*_{*i*}" in the corresponding column. As shown in Table II, the grafting ratios ranged from 57.85% to 99.00%, which indicated that grafting ratio depended distinctly on the reaction conditions. The values of "*K*_{*s*}" in Table II and curves in Figure 1(a–c) showed that in the experimental range, grafting ratio of OA with PMHS enhanced with the increase of reaction temperature, reaction time, and catalyst dosage, respectively. Elevating the reaction temperature could enhance the reactivity of the reactants, prolonging the reaction time could guarantee their complete reaction, and increasing the catalyst

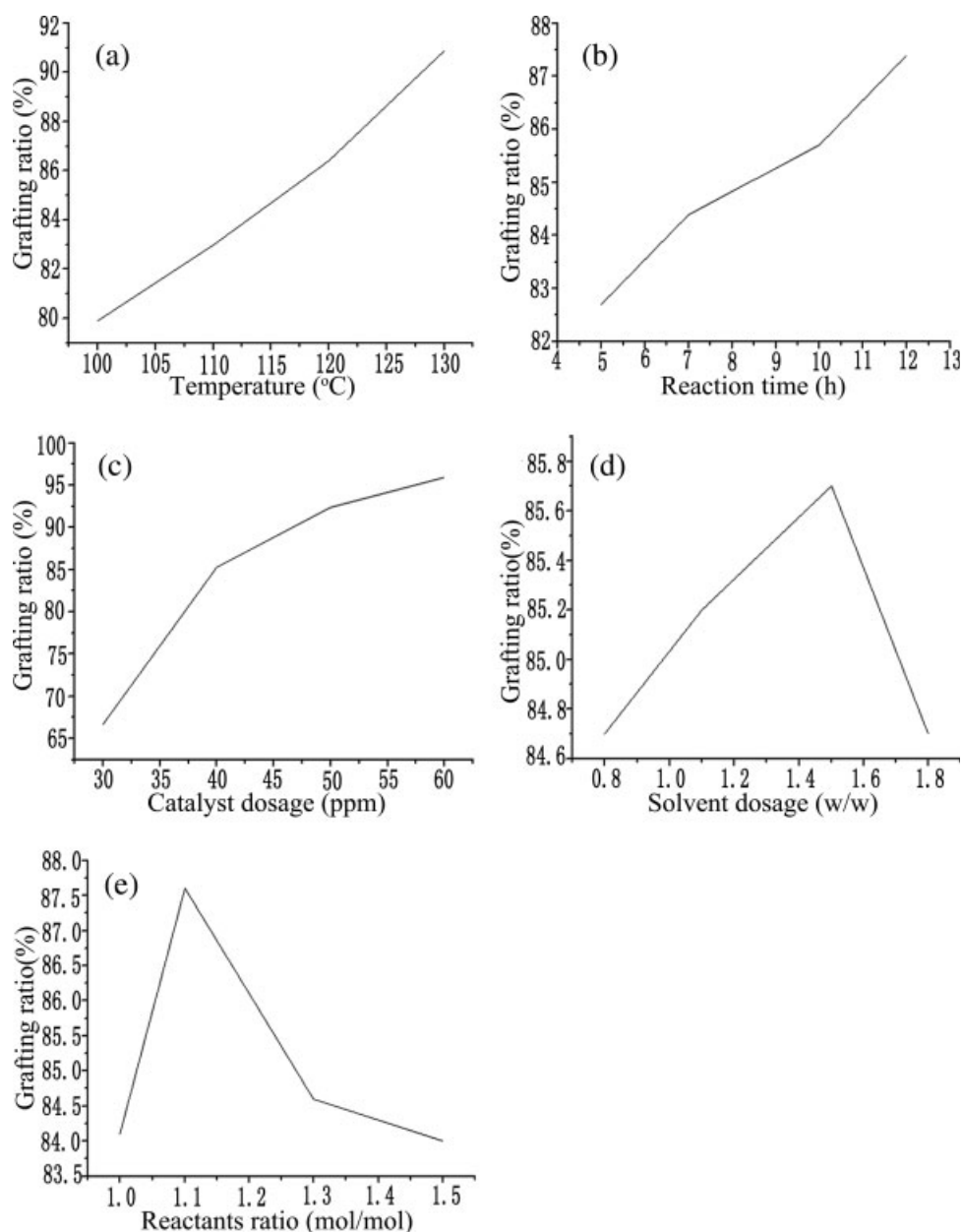
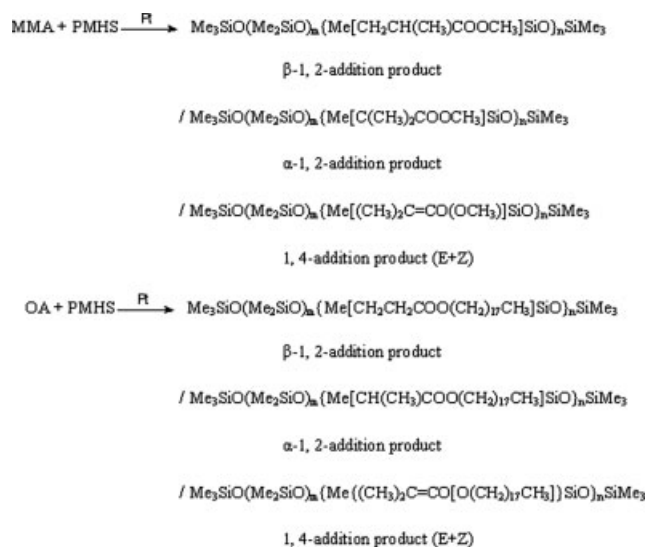


Figure 1 Influence of reaction temperature (a), reaction time (b), catalyst dosage (c), solvent dosage (d), and reactants ratio (e) on the grafting ratio of the OA with PMHS.

dosage would favor the formation of active site and increase of the reaction rate; so these factors were propitious to the hydrosilylation. In the case of solvent dosage [Fig. 1(d)], fixing other factors and increasing the solvent dosage (based on the quality of the reactants) from 0.8 to 1.5 would favor the grafting ratio of the product, but when the amount of solvent was further increased, the grafting ratio decreased. Generally speaking, increasing the solvent dosage could reduce the viscosity of the reaction system and favor the movement of the reagents, which could in turn facilitate the effective collision among them. But excessive solvent caused the addi-

tional dilution of OA and PMHS, which might enlarge the mean molecular distance and decrease the effectual impact probability among them, and thus the grafting ratio of the modified product decreased. Meanwhile, the ratio of OA to Si—H residue in PMHS [Fig. 1(e)] had a similar influence on the grafting ratio. The grafting ratio of the product increased when the mol rate of OA to Si—H residue in PMHS rose from 1 to 1.1, but subsequently heightening their ratio would decrease the grafting ratio. The reason for this might be that superfluous OA resulted in additional long flexible hydrophobic chains in the system, which could form enwrapping



Scheme 1 Processes for the reaction of MMA/OA with PMHS.

along PMHS backbones and inhibit the contiguity of the function groups of reactants.

The values of "Rs" in Table II showed that each factor had different effects on the hydrosilylation. The larger the value of *R* was, the greater the effect of the factor on the hydrosilylation was. According to this rule, factors could be arranged in the following order according to their decreasing ability of the effect on the hydrosilylation of OA with PMHS: $C > A > B > E > D$. Besides, the influence of solvent dosage could be omitted when its value was in the experimental range. The optimum level of each variable was $A_4B_4C_4D_3E_2$, i.e. reaction temperature 130°C, reaction time 12 h, catalyst dosage 60 ppm (based on the quality of the reactants), solvent dosage 1.5 (based on the quality of the reactants), and material ratio 1.1/1 (mol proportion of OA to the Si—H residue in PMHS). The grafting ratio of the final product could reach as high as 95%.

Comparison of two synthesis reaction conditions

Generally speaking, the reaction activity of ester or other alkyl materials decreases with the elongation of molecular chain length: molecule with flexible long chain may curl around itself or entangle with other chains, the active sites may involve in it, and the whole molecule exhibits a little or no activity at all. But in our study, we found that the synthesis reaction of MMA with PMHS (grafting ratio and reaction time were about 90% and 30 h respectively), which needed higher reaction temperature and much longer reaction time, was more difficult than that of OA with PMHS (under optimal conditions, the grafting ratio of the final product could reach as high as 95% within 12 h). This may be illuminated

from the structural differentiations between them and the reaction mechanism of hydrosilylation with hexachloroplatinic acid as catalyst.^{23,24} Comparing the molecule structure of MMA with OA, there is a methyl group linked on the second carbon atom (alkene carbon atom) of MMA, which forms a bigger steric hindrance to the alkene carbon atom than that of hydrogen atom linked on the alkene carbon atom of OA. Therefore, it is difficult for the alkene to approach to the active site of catalyst or to form a stable complex with catalyst, which in turn disturbed the reaction of MMA with PMHS. In conclusion, the reaction of OA with PMHS is easier than that of MMA with PMHS.

Structure analyses of grafted products

Several functional polysiloxanes may be prepared via the platinum-catalyzed hydrosilylation of MMA/OA with PMHS (Scheme 1). The reaction could be conveniently monitored by observing the disappearance of the characteristic Si—H absorption at about 2150 cm^{-1} by IR or chemical shift at 4.7 ppm by ^1H NMR.²⁵

Figures 2(a) and 2(b) showed the IR spectra of PMHS and MMA-graft-PMHS, respectively, both of which were dissolved in CCl_4 . The IR spectrum of PMHS in Figure 2(a) had a sharp peak at 2158 cm^{-1} , which is assigned to the Si—H vibration, and MMA should have two characteristic absorption regions (spectrum was not shown) at about 1710 cm^{-1} due to $\nu_{\text{C}=\text{O}}$ of unsaturated ester and at 1640 cm^{-1} due to $\nu_{\text{C}=\text{C}}$.²⁶ In Figure 2(b), the Si—H absorption at 2156 cm^{-1} and the C=C absorption at about 1640 cm^{-1} almost disappeared, and $\nu_{\text{C}=\text{O}}$

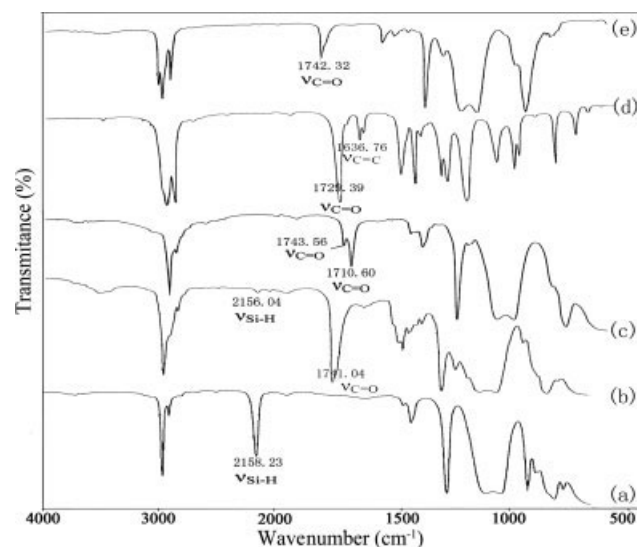


Figure 2 FTIR spectra of PMHS (a), MMA-graft-PMHS (b, reaction time is 30 h); hydrolyzation product of MMA-graft-PMHS (c); OA (d); and OA-graft-PMHS (e).

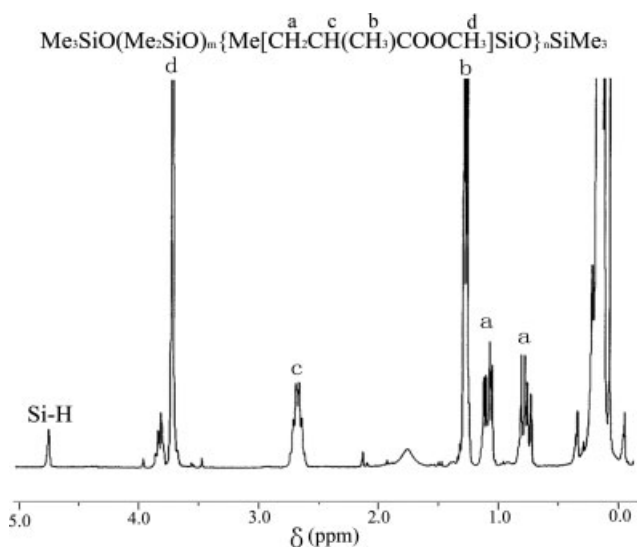


Figure 3 ^1H NMR spectrum of MMA-graft-PMHS.

shifted to 1741 cm^{-1} due to $\text{C}=\text{O}$ vibration of a saturated ester. All these confirmed that MMA functional group was chemically bonded to the Si atom of PMHS. The ^1H NMR spectrum of MMA-graft-PMHS (dissolved in CDCl_3) was shown as Figure 3. In Figure 3, the characteristic signal at 4.7 ppm assigning to the proton bonded to silicon atom almost disappeared. Signals at 0.7 and 1.0 ppm ($\text{Si}-\text{CH}_2$, m, 2) attributed to the protons of methylene linked to silicon of $\text{Si}-\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$. The split of these two peaks of methylene protons were attributed to the chiral carbon of methine next to methylene, which formed different chemical environment around the methylene protons. On the other hand, protons of methylene were spatially adjacent and coupled with each other; so each peak split into several extra distinguishable ones, which could further confirm the above proposed structure of MMA-graft-PMHS. Chemical shift at 1.2 ppm ($\text{CH}-\text{CH}_3$, d, 3) belonged to the methyl protons of $\text{Si}-\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$; response at 2.6 ppm (CH , m, 1) was due to the methane proton of $\text{Si}-\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$, and a strong peak at 3.7 ppm ($-\text{OCH}_3$, s, 3) was attributed to the methyl protons next to oxygen atom. The number of protons was calculated according to the corresponding peak or peaks area. In the spectrum, neither characteristic peaks of methyl protons bonded to $-\text{CHCOOR}$ group indicating the α -1,2-addition at about 1.1 ppm (different from that of the β -1,2-addition at 1.2 ppm in proton numbers and peak's split pattern) nor signals of methyl protons bonded to $\text{C}=\text{C}$ indicating the 1,4-addition at about 1.6 ppm could be observed (Scheme 1). As a result, the addition pattern of hydrosilylation of MMA with PMHS would be confirmed and displayed a strong preference toward β -

1,2-addition. Theoretically, this was because the space hindrance on α position was too large for silicon atom to approach, which could also illuminate that catalyst had a good selectivity, and hydrosilylation reaction followed the Markovnikov's rule. Similar result was gotten by Torrès et al. and Chujo et al.^{27,28} Figure 2(c) depicted the IR spectrum of hydrolyzed product of MMA-graft-PMHS. It represented that the vibration of carbonyl of saturated ester was greatly weakened and substituted with a peak at 1711 cm^{-1} . Meanwhile, there was a broad peak at about 3300 cm^{-1} . Both the changes of characteristic peaks clearly revealed the formation of carboxyl group. Therefore, the ester group in MMA-graft-PMHS had been hydrolyzed and turned into carboxyl group, namely, MAA-graft-PMHS was obtained.

Figures 2(d) and 2(e) showed the IR spectra of OA and OA-graft-PMHS, respectively, both of which were dissolved in CCl_4 . The spectrum of OA in Figure 2(d) showed two characteristic absorption regions: 1729 cm^{-1} due to $\nu_{\text{C}=\text{O}}$ of unsaturated ester and 1637 cm^{-1} due to $\nu_{\text{C}=\text{C}}$. In Figure 2(e), $\nu_{\text{Si}-\text{H}}$ band at 2150 cm^{-1} and $\nu_{\text{C}=\text{C}}$ at 1640 cm^{-1} disappeared completely, and $\nu_{\text{C}=\text{O}}$ shifted to 1742 cm^{-1} , which indicated a $\text{C}=\text{O}$ vibration of a saturated ester. In addition, there was a new $\text{Si}-\text{C}$ absorption at 1260 cm^{-1} . These results confirmed that OA functional group was chemically bonded to the Si atom of PMHS. The ^1H NMR spectra of OA and OA-graft-PMHS, both of which are dissolved in CDCl_3 , are shown in Figures 4(a) and 4(b), respectively. The ^1H NMR spectrum of OA in Figure 4(a) displayed three peaks at 5.8, 6.2, and 6.4 ppm ($\text{CH}_2=\text{CH}-$, m, 3) for the three alkene protons, respectively. In Figure 4(b),

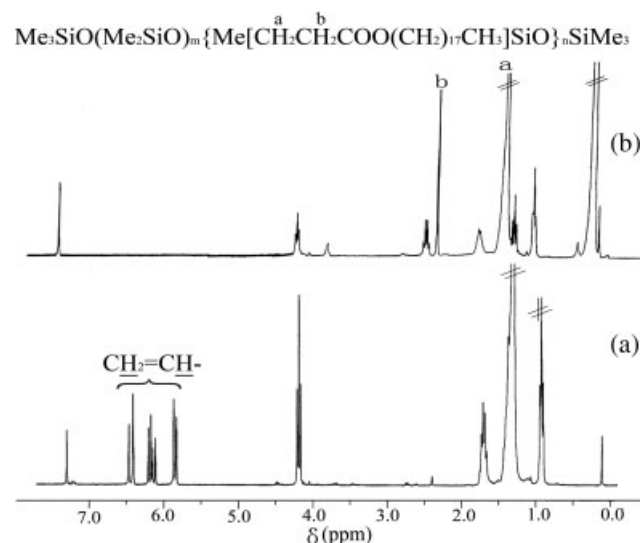


Figure 4 ^1H NMR spectra of OA (a) and OA-graft-PMHS (b).

TABLE III
Surface Energies of Water and Glycerol, and Polar Fractions and Nonpolar Fractions of Their Surface Energies

	Surface energy (mN/m)	γ_l^p (mN/m)	γ_l^d (mN/m)
Water	72.8	21.8	51.0
Glycerol	63.4	37.0	26.4

γ_l^p and γ_l^d : Polar and nonpolar fractions of surface energy, respectively.

all these peaks besides Si—H signal at 4.7 ppm disappeared. A new signal at 1.15 ppm (Si—CH₂—, m, 2) provided evidence for the introduction of Si—CH₂— group. Chemical shift at 2.35 ppm (Si—CH₂—CH₂—, m, 2) confirmed that the unsaturated carbon atom is attached to PMHS. In Figure 4(b), neither proton signals of Si—CH(CH₃)— at about 1.1 ppm indicating an α -1,2-addition product nor signals of C=C(CH₃)— at about 1.6 ppm suggesting a 1,4-addition product appeared (Scheme 1), which could further confirm that the hydrosilylation of OA with PMHS was β -1,2-addition.

Surface energies of films

The surface energy is also named surface free energy. The surface free energy of solid cannot be tested by experimental method directly, but could be calculated by measuring the contact angles of liquors on the surface of the solid.^{29–31}

Surface free energy of solid of organic compound is primarily composed of the polar (γ^p) and nonpolar (γ^d) fractions of surface tension. When there are polar and nonpolar forces in the interphase of solid and liquid, the surface free energy on the solid surface could be represented as follows:

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (3)$$

where γ_s (mN/m), γ_s^p (mN/m), and γ_s^d (mN/m) are surface tension, the polar fraction, and nonpolar fraction of surface tension, respectively.

When concerning the Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (4)$$

where γ_{sv} (mN/m), γ_{sl} (mN/m), and γ_{lv} (mN/m) are the surface tensions on the interfaces of solid–vapor, solid–liquid, and liquid–vapor, respectively; θ is a nonzero contact angle along the vapor–liquid and solid–liquid interfaces.

Formula 5 could be drawn through mathematical transformation:

$$\gamma_{lv}(1 + \cos \theta) = 2(\gamma_l^p \gamma_s^p)^{1/2} + 2(\gamma_l^d \gamma_s^d)^{1/2} \quad (5)$$

where γ_l^p (mN/m) and γ_l^d (mN/m) are the polar and nonpolar fractions of surface tension of the liquid used, respectively.

Table III represented the surface energies and their polar fractions and nonpolar fractions of water and glycerol.²⁹ Through testing the contact angles between the film and two control liquids (water and glycerol), respectively, the polar fraction (γ_s^p) and nonpolar fraction (γ_s^d) of the surface energy of the film could be obtained by replacing the parameters of water and glycerol in formula 5, respectively, and the surface energy (γ_s) of the film could be figured out according to formula 3. The results were listed in Table IV.

As shown in Table IV, each grafted group had different influence on the surface energy of polysiloxane. The γ_s of PMHS and OA-graft-PMHS were 35.62 and 35.07 mN/m, respectively, which were nearly the same as each other. This is owing to the low γ_s of POA (36.57 mN/m). Therefore, the introduction of weak polar group had little influence on the surface energy of polysiloxane. The γ_s of Me₃SiO(MeR-SiO)_nSiMe₃ changed with the number of carbon atoms of alkyl group R. If R residues were tetradecyl or octadecyl, the γ_s was 33.49 or 39.5 mN/m, respectively,³² indicating that OA-graft-PMHS might have a similar surface property to that of long alkyl-graft-polysiloxane. On the other hand, the γ_s of MAA-graft-PMHS, whose hydrolyzation ratio was about 90%, was quite large and equaled to 43.50 mN/m owing to the hydrophilic carboxyl group in the polysiloxane backbone. The mixture of MAA-graft-PMHS

TABLE IV
Contact Angles and Surface Energies of Films (20°C)

Kind of films	Water (θ_1)	Glycerol (θ_2)	γ_s^p (mN/m)	γ_s^d (mN/m)	γ_s (mN/m)
PMHS	87.7	69.2	2.34	33.28	35.62
OA-graft-PMHS	89.2	70.6	1.98	33.09	35.07
POA	95.7	74.9	0.44	36.13	36.57
MAA-graft-PMHS	62.6	49.1	16.23	27.25	43.50
MAA0-graft-PMHS/OA graft PMHS ^a	80.3	61.5	4.12	35.98	40.10

θ_1 : Contact angle between tested film and water; θ_2 : Contact angle between tested film and glycerol; γ_s : Surface energy of the film; γ_s^p and γ_s^d : Polar and nonpolar fractions of surface energy on the solid surface, respectively.

^a Mol ratio of MAA-graft-PMHS to OA-graft-PMHS is 7 : 3.

and OA-graft-PMHS had a γ_s of 40.10 mN/m, which was higher than the linear addition of their γ_s values, 37.81 mN/m by calculation. These results suggested that the influence of MAA residue on the surface energy of grafted product was higher than that of OA residue. The possible reason for these was that polysiloxane had excellent adherence to glass. When glass slice was used as a carrier for the test of the contact angle between the liquor and the film, polysiloxane main chain was abutted against glass and left grafted OA residue or MAA residue facing to the gas phase. Since OA residue was a hydrophobic group, the γ_s of OA-graft-PMHS was nearly the same as that of PMHS. Contrary to OA-graft-PMHS, the contact angles of MAA-graft-PMHS with water or glycerol were smaller due to greater compatibility of MAA residue with polar materials, and thus MAA-graft-PMHS had a higher γ_s value. For the same reason, the percentage of MAA residue facing to the vapor phase was higher than that of OA residue in the mixture of OA-graft-PMHS and MAA-graft-PMHS; so the γ_s of their mixture was higher than that of their linear addition one, which indicated that the surface energy of a system was mainly dependent on the residues of polar groups.

CONCLUSIONS

MMA and OA could be directly grafted to PMHS by hydrosilylation, respectively. The optimal reaction conditions for synthesizing OA-graft-PMHS are as follows: reaction temperature 130°C, reaction time 12 h, catalyst dosage 60 ppm (based on the quality of the reactants), solvent dosage 1.5 (based on the quality of the reactants), and material ratio 1.1/1 (mol proportion of OA to the Si—H residue in PMHS). Under optimum conditions, the grafting ratios of MMA with PMHS and OA with PMHS were about 90 and 95%, respectively. Through IR and ¹H NMR analyses, the structures of modified products were further confirmed. The hydrosilylation reaction followed the Markovnikov's rule, and both the grafted polymers were β -1,2-addition products. This was because the space hindrance of α position of MMA and OA was too large for silicon atom to approach, which could also illuminate that catalyst had a good selectivity.

The reaction of OA with PMHS was easier than that of MMA with PMHS. The possible reason was that the methyl group linked on the second carbon atom (alkene carbon atom) of MMA formed a bigger steric hindrance to the alkene carbon atom comparing with that of hydrogen atom linked on the alkene carbon atom of OA, hampered the approach of alkene carbon atom to the catalyst or the formation of a stable complex with catalyst, and in turn inhibited the reaction of MMA with PMHS.

Surface energies of PMHS and OA-graft-PMHS were 35.62 and 35.07 mN/m, respectively. The similarity in their surface energies would be explained by the low surface energy of POA (36.57 mN/m). MAA-graft-PMHS had a much higher γ_s value of 43.50 mN/m. Therefore, the introduction of weak polar group had little influence on the surface energy of PMHS, whereas the grafting of polar residue would change its surface properties. To the mixture of MAA-graft-PMHS and OA-graft-PMHS (mol ratio was 7 : 3), its γ_s value (40.10 mN/m) was higher than their linear-addition one (37.81 mN/m, by calculation). These results indicated that MAA residue had greater influence on the surface energy of PMHS than that of OA residue, and surface energy of a system was mainly dependent on the polar groups.

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