Silicone Acrylates through the Hydrosilation of Polyacryloyloxy Functional Monomers with Copolymers of Dimethyl and Hydrogen Methylsiloxanes

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SYNOPSIS

Silicone acrylates, as possible electron beam (EB) curable release coatings for paper, were prepared by the platinum-catalyzed hydrosilation of polyacryloyloxy functional monomers with copolymers of dimethylsiloxane and hydrogen methylsiloxane (PDMHMS). The hydrosilation of either 1,6-hexanediol diacrylate (HDDA) or trimethylolpropane triacrylate (TMPTA) with PDMHMS occurs to only one of the 2 or 3 available olefinic groups, respectively, as long as excess monomer is present. The amount of excess monomer needed to prevent gelation during hydrosilation or subsequent storage in excess of 1 month appears to be dependent on the hydrogen methylsiloxane content of the PDMHMS. A release coating having excellent cohesive and adhesive strength on paper was obtained by the EB curing of the product of hydrosilation of TMPTA with a PDMHMS containing 4 mol % hydrogen methylsiloxane at a dose-to-cure of 2 Mrad, but the aged release force was excessively high. The poor aged-release performance was likely due to dilution of the dimethylsiloxane content of the coating with excess monomer required to stabilize the silicone acrylate. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Numerous methodologies have been reported over the last 40 years for the preparation of silane and silicone acrylates. Silicone acrylates have been prepared through four different approaches: (1) condensation reactions,[1] (2) polymerization of silane acrylates,[1c] (3) displacement reactions,[1c,d,g,2] and (4) hydrosilation reactions.[1c,g,3] Surprisingly, no one has reported the hydrosilation of a polyacryloyloxy functional monomer with a dimethylsiloxane–hydrogen methylsiloxane copolymer (PDMHMS):

(1)
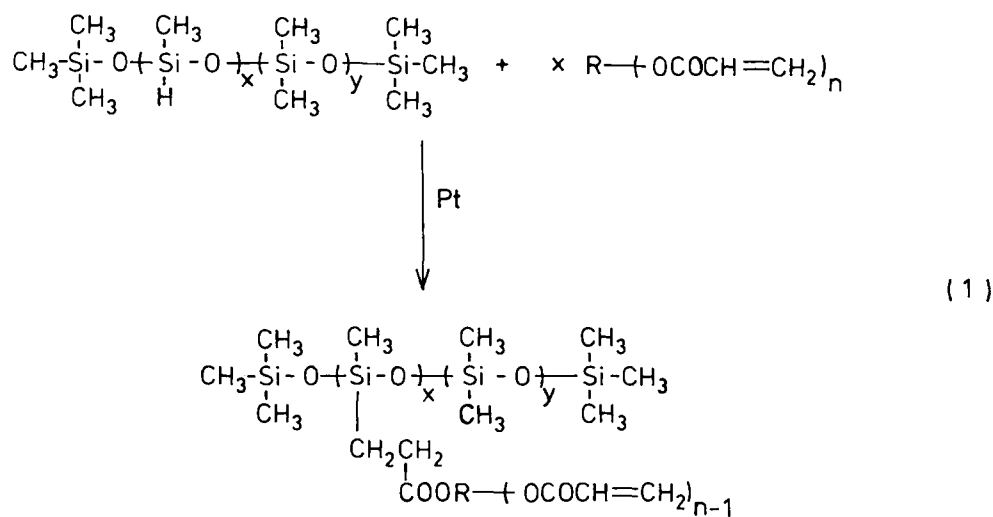
The only precedent for this reaction is the generation of a photopolymerizable composition through the hydrosilation of diethylene glycol dimethacrylate with a low molecular weight PDMHMS.[1c]

We were interested in using the reaction of eq. (1) to prepare silicone-release coatings that are curable with electron beams (EB) at low dose-to-cure (i.e., 1–2 Mrad), have reasonable shelf stability, and produce tough coatings with durable release characteristics on paper or polypropylene substrates. Since methacrylates do not cure with EB in reasonable times at the dose-to-cure levels sought, polyacryloyloxy functional monomers, as shown in eq. (1), were required. The characterization of silicone acrylates, prepared according to eq. (1), and the properties of the EB-cured release coatings resulting from them are presented herein.

EXPERIMENTAL

General

The monomers used in this study were obtained from Arco Specialty Chemicals and include 1,6-hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), triethylene glycol diacrylate (TEGDA), neopentyl glycol diacrylate (NPGDA), Chem Link-2000, tripropylene glycol diacrylate (TPGDA), Arco C-5000, and ethoxylated bisphenol A diacrylate. The PDMHMS used were 1.0 and 2.5 mol % SiH (Petarch Chemicals) and 4.0 mol % SiH (JR-Graphics, South Hadley). Dow Corning 7600, which is composed of a dimethylsiloxane–methyl vinylsiloxane copolymer, a poly(hydrogen methylsiloxane), and a platinum catalyst, was obtained from Dow Corning. The chloroplatinic acid hexahydrate was obtained from Strem Chemical Inc. and was dissolved in isopropanol (1 g/123 mL). The release liner used was a 42 lb/3000 ft^2 supercalendered bleached kraft paper from Plainwell. The SBR adhesive tape used in release evaluations was Zonas tape (Johnson and Johnson). ^{1}H-NMR spectra were taken on a Varian EM-360. Infrared spectra were taken on a Beckman 4230 infrared spectrometer. Ultracentrifugation was done with a L-5 Beckman ultracentrifuge. High-pressure liquid chromatography (HPLC) was done with a Varian Model 5020 HPLC, with an Upchurch C-135B pellicular packed precolumn and a Zorbax C RP-HPLC column. EB curing was done with an Energy Sciences EB lab processor. An Instron was used to measure release forces.

Hydrosilations

Reaction of HDDA and PDMHMS

A 10 g sample of PDMHMS (2.5 mol % SiH; 3.4 mmol SiH) was mixed with 1.13 g HDDA (1.47 equiv based on SiH), 6 drops of Pt catalyst solution, and heated at 80°C with vigorous stirring for 2 h, at which time reaction was complete (i.e., the SiH band at 2180 cm^{-1} was absent). The resultant cloudy fluid was diluted in chloroform and chromatographed isocratically with HPLC, at a pressure of 54 atm and a flow rate of 0.5 mL/min. The residual level of HDDA was found to be 0.029 ± 0.001 g/g product.

Reaction of TMPTA and PDMHMS

A 10 g sample of PDMHMS (2.5 mol % SiH; 3.4 mmol SiH) was mixed with 1.48 g TMPTA (1.47 equiv based on SiH), 2 mL toluene, and 6 drops Pt catalyst solution and heated at 80°C with vigorous stirring for 4 h, at which time reaction was complete (i.e., the SiH band at 2180 cm^{-1} was absent). The toluene was removed *in vacuo*, and the product was centrifuged for 210 min at 10°C and 20,000 rpm (43,700 G) to provide two fluid layers. Top layer: IR (neat) 2940, 1725, 1605, 1405, 1250, 1040, 785 cm^{-1}. ^{1}H-NMR (60 MHz) δ 6.2 (m, 6H), 4.2 (s, 4H), 4.1 (s, 2H). Bottom layer: IR (neat) 2950, 1720, 1620, 1610, 1460, 1400, 1290, 1260, 1175, 1055, 980, 800 cm^{-1}.
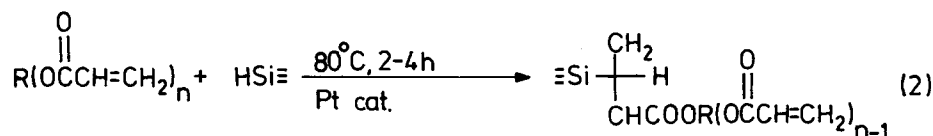
Release Testing

Unpurified silicone acrylate samples were coated on the release liner to a weight of 0.6 lb/3000 ft^2 EB-treated at a dose (Mrad) required to provide complete cure (no rub off, no smear, and no loss in tape adhesion), laminated with Zonas tape, and aged at 70°C under 0.25 psi for 28 days. Delamination (release) force was determined at 12 in/min, and adhesive subsequent adhesion was determined against a 280 grit stainless-steel plate.

RESULTS AND DISCUSSION

Synthesis of Silicone Acrylates

A polydimethylsiloxane having pendent monoacryloyloxy groups [$n = 2$ in eq. (1)] along the polymer chain was prepared through the hydrosilation of 1.47 equiv HDDA (based on moles SiH) with PDMHMS containing 2.5 mol % SiH under the following conditions:

$$R(O\overset{\overset{O}{\|}}{C}CH{=}CH_2)_n + HSi{\equiv} \xrightarrow[\text{Pt cat.}]{80^{\circ}C,\ 2{-}4h} {\equiv}Si{-}\overset{\overset{CH_2}{|}}{\underset{CHCOOR(O\overset{\overset{O}{\|}}{C}CH{=}CH_2)_{n-1}}{|}}H \qquad (2)$$

The reaction was complete (disappearance of SiH band at 2180 cm^{-1}) after 2 h and provided a cloudy fluid product. The residual HDDA was determined, by HPLC, to be 0.029 ± 0.001 g/g product. Since the calculated residual HDDA level, for a reaction stoichiometry of 1, is 0.033 g/g product, it appears that only one of the two acrylate double bonds of the HDDA was hydrosilated.

A carbonyl band at 1725 cm^{-1} is seen in the IR spectrum of the product mixture from the above reaction with HDDA. The position of this carbonyl band is purportedly the result of α-regioselective hydrosilation of an acrylate double bond[4]:

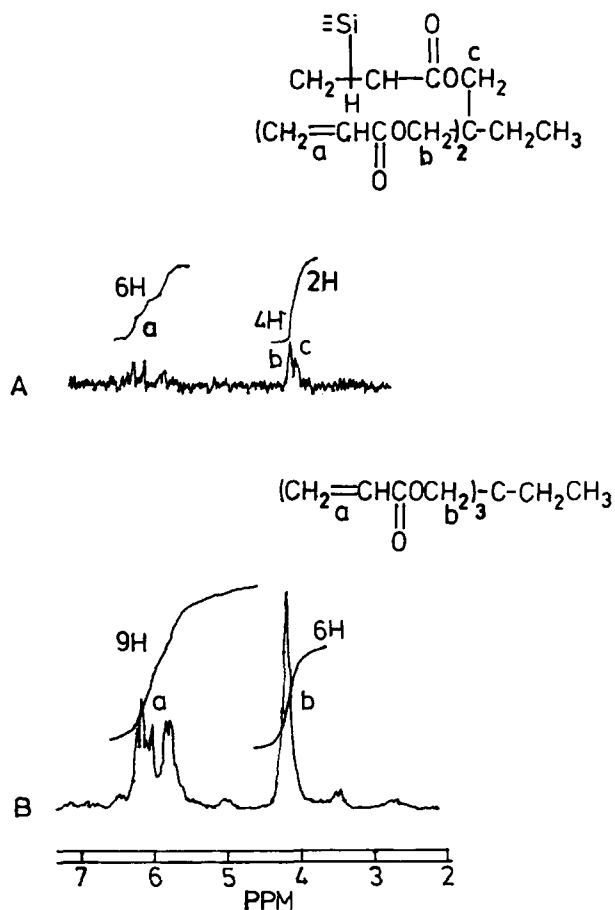$$R_3SiH + CH_2{=}CHCO_2R' \rightarrow$$

$$CH_3{-}CH(SiR_3)CO_2R'$$
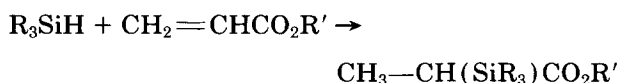
A recent study, however, showed that the hydrosilation of monoacrylates by poly(hydrogen methylsiloxanes) was generally not regioselective.[5] In those cases where regioselectivity was realized (i.e., acrylates having bulky ester groups), the β-regioisomers were favored.[5] There are not enough data to firmly establish the regiochemistry of the reactions in the present study.

A polydimethylsiloxane having pendent diacryloyloxy functional groups [n = 3 in eq. (1)] along the polymer chain was prepared by the hydrosilation of 1.47 equiv TMPTA (based on moles SiH) with PDMHMS containing 2.5 mol % SiH under the conditions of eq. (2). The reaction was complete (disappearance of SiH band at 2180 cm^{-1}) after 4 h and provided a milky fluid product. Unlike the HDDA reaction, hydrosilation of TMPTA would not occur unless a small amount of toluene was added to the reaction mixture. Presumably, the toluene provided some compatabilization of the reactants. The milky product was ultracentrifuged into two layers. The bottom layer was unreacted TMPTA. The IR spectrum of the clear fluid top layer is shown in Figure 1. The bands at 1725 and 1610 cm^{-1} are due to the acrylate carbonyl carbon–oxygen and olefinic carbon–carbon stretches, respectively. The bands at 1250 and 1040 cm^{-1} are due to a silicon–carbon deformation and a silicon–oxygen stretch, respectively. The ^{1}H-NMR spectrum of the top layer is compared with that for pure TMPTA in Figure 2. The singlet for the equivalent ester methylene groups at 4.2 ppm for TMPTA (spectrum B) re-
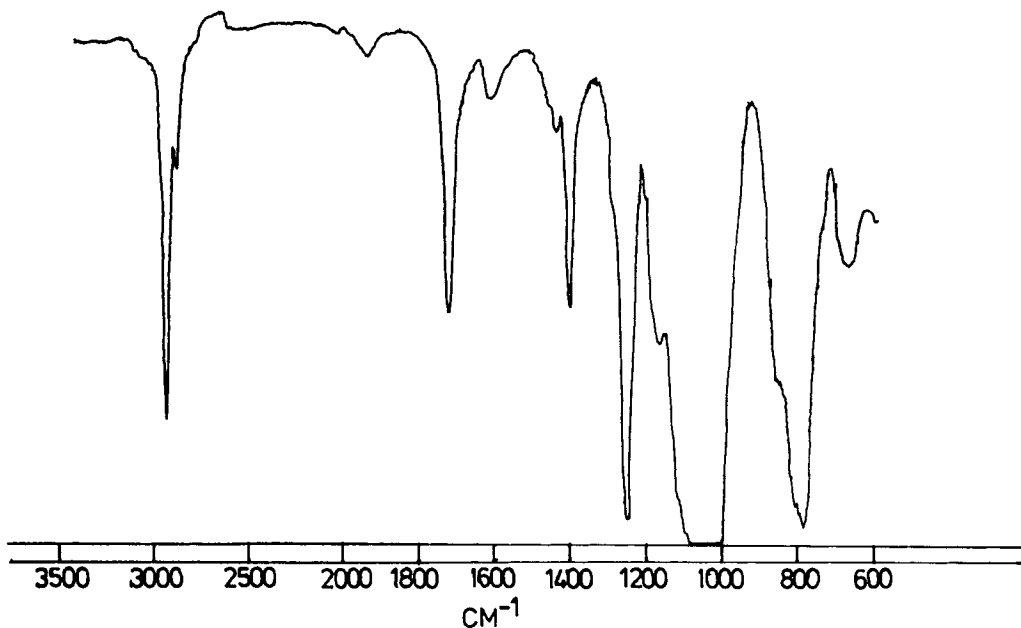
Figure 1   IR spectrum of silicone acrylate prepared by the hydrosilation of TMPTA with PDMHMS (2.5 mol % SiH).

$\equiv$Si   O
  | || c
CH$_2$$-CH-$COCH$_2$
      |
      H
(CH$_2$=CHC OCH$_2$)C-CH$_2$CH$_3$
   a || b 2
            O

6H / a   /2H
        4H / c
          b

A

(CH$_2$=CHCOCH$_2$)$-$C-CH$_2$CH$_3$
   a || b 3
            O

9H   6H
    a   b

B

7   6   5   4   3   2
        PPM

Figure 2 ^{1}H-NMR spectra of (A) silicone acrylate from the hydrosilation of TMPTA with PDMHMS (2.5 mol % SiH) and (B) pure TMPTA.

solved into two singlets after the hydrosilation reaction (spectrum A). The downfield singlet (4.2 ppm of spectrum A) is attributed to the ester methylene groups of the unreacted double bonds, and the upfield singlet (4.1 ppm), to the ester methylene groups of the hydrosilated double bonds. The ratio of protons, 3-2-1, from the integration of the vinylic (6.2 ppm), and the different methylene protons (4.2 and 4.1 ppm), respectively, suggests that hydrosilation occurred to only one of the three available double bonds of TMPTA.

The possibility that the two methylene signals in spectrum A of Figure 1 were due to β- and α-regioisomers is unlikely because of the observed integration. For example, in the case where the β- and α-regioisomers are formed in equal amounts and the upfield singlet (4.1 ppm of spectrum A) is due to the α-regioisomer,[5] the ratio of vinylic protons to the different ester methylene protons would be 6-5-1, instead of the observed ratio of 3-2-1 (above). Furthermore, if the hydrosilation is β-regioselective,

the ratio of the vinylic protons to the protons of the ester methylene group of the α-regioisomer would be > 6.

Attempts were made to hydrosilate other polyacryloyloxy functional monomers with PDMHMS under the conditions of eq. (2). The following monomers were successfully hydrosilated*: TEGDA, NPGDA, TPGDA, and Chem Link-2000 (a C$_{14}$ diol diacrylate). As with TMPTA, toluene had to be added to the reaction mixtures of the polyether acrylates to effect hydrosilation. Arco C-5000 (a polybutadiene diol diacrylate) could not be hydrosilated without gelation of the product. Ethoxylated bisphenol A diacrylate could not be hydrosilated under the conditions of eq. (2).

The success* of the reaction of eq. (2) is dependent on the mol ratio of monomer to SiH. For example, if the mol ratio of TMPTA to SiH is lower than 1.47 (above), the product jells. As the SiH content of the PDMHMS is increased, the mol ratio of monomer to SiH must also be increased to effect successful hydrosilation of either HDDA or TMPTA. Thus, hydrosilations involving silicones having SiH contents of 1.0, 2.5, and 4.0 mol % require monomer to SiH mol ratios of 1.0, 1.47, and 2.25, respectively, to avoid gelation.

The shelf stability of the silicone acrylates obtained by the reaction of eq. (2) is also dependent on the SiH content of the PDMHMS. Silicone acrylates prepared from PDMHMS having 2.5 mol % SiH have shelf lives greater than 1 month, whereas those silicone acrylates from PDMHMS having 4.0 mol % SiH jelled within 1 week.

The cause of these stability effects are unknown, but may be the result of Pt-mediated oligomerization of acrylates,[4,6] the mechanism of which must be different from that for hydrosilation since the inclusion of usual Pt poisons to the product mixtures did not prolong shelf life.

Characterization of Release Coatings

Unpurified silicone acrylates, prepared with either HDDA or TMPTA under the conditions of eq. (2), were coated on a bleached kraft release liner and cured by EB. As shown in Table I, the dose-to-cure decreases with increasing SiH content of the PDMHMS. Furthermore, silicone acrylates from HDDA required higher dose-to-cure than those from

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* Success is judged by disappearance of SiH band at 2180 cm^{-1} and no gelation. These silicone acrylates were not characterized further.

Table I   Dose-to-Cure Data for Silicone Acrylates Prepared by the Reaction of Eq. (2)[a]

Mol % SiH	Monomer	Equiv Monomer[b]	Wt % PDMS[c]	Dose-to-Cure (Mrad)
1.0	TMPTA[d]	1.00	97.1	> 12
2.5	HDDA[e]	1.47	89.9	12
2.5	TMPTA	1.47	87.1	4
4.0	HDDA	2.25	78.2	6
4.0	TMPTA	2.25	73.2	2

[a] Pt-catalyzed hydrosilation of monomer with PDMHMS having indicated mol % SiH at 80°C for 2–4 h.
[b] Based on mol SiH.
[c] (Wt silicone/wt silicone + wt monomer) × 100.
[d] Trimethylolpropane triacrylate.
[e] 1,6-hexanediol diacrylate.

TMPTA. A silicone acrylate having an acceptable dose-to-cure of 2 Mrad was prepared through the hydrosilation of TMPTA with PDMHMS containing 4.0 mol % SiH.

The coatings of the EB-cured silicone acrylates based on TMPTA (Table I) on paper were evaluated for aged-release performance and the results are shown in Figure 3. As can be seen, neither of the silicone acrylates provided acceptable aged release, as judged against a standard thermally cured release coating (Dow Corning 7600). The release performance of the coating based on PDMHMS having 2.5 mol % SiH is better than that for PDMHMS having 4.0 mol % SiH. However, the cohesive strength of the former coating is low, so the low release may be due to excessive silicone transfer to

the adhesive tape. Indeed, tape subsequent adhesion was low from the 2.5 mol % SiH-based coating.

One explanation for the failure to achieve acceptable release coatings through the EB curing of silicone acrylates, prepared according to reaction of eq. (2), is the low levels of polydimethylsiloxane (PDMS) attained when optimizing dose-to-cure. Increased functionality leads to lower dose-to-cure (above), but also results in lower percentages of PDMS (Table I). According to the industry standard, a coating must be composed of ≥ 90% PDMS before durable release in the range of 0–20N/m can be achieved. Thus, while the EB-cured coating based on the hydrosilation product of TMPTA and PDMHMS containing 4.0 mol % SiH had excellent cohesive and adhesive strength, the PDMS content
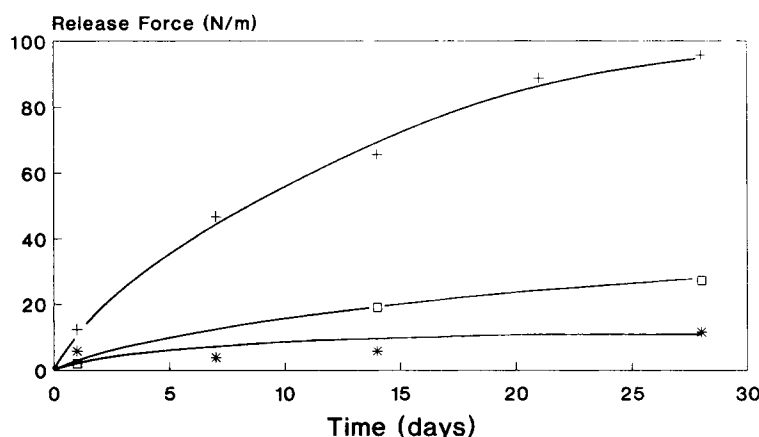
Figure 3   A plot of release force vs. the time of aging laminates of Zonas tape with release coatings prepared by (□) EB curing a silicone acrylate from the hydrosilation of TMPTA with a PDMHMS having 2.5 mol % SiH at 4 Mrad, (+) EB curing a silicone acrylate from the hydrosilation of TMPTA with a PDMHMS having 4.0 mol % SiH at 2 Mrad, or (*) thermal curing of the Dow Corning 7600 Pt cure release system.

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was only 73% (Table I) and tight (high release force) aged release was observed.

CONCLUSIONS

EB-curable silicone acrylates can be obtained through the hydrosilation of polyacryloyloxy functional monomers with PDMHMS. Versions having shelf lives in excess of 1 month can be prepared, but the SiH content of the PDMHMS and the mol ratio of monomer to SiH must be carefully monitored. A release coating having excellent cohesive and adhesive strength on paper was obtained through the EB curing of a silicone acrylate, from the hydrosilation of TMPTA with PDMHMS containing 4.0 mol % SiH, at a dose-to-cure of 2 Mrad, but the aged-release performance was excessively tight. The poor aged-release performance was likely due to dilution of the PDMS content in the coating with excess monomer required to stabilize the silicone acrylate.

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