

Synthesis of Ultraviolet-Curable Modified Polysiloxane and Its Surface Properties

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ABSTRACT: A novel ultraviolet (UV)-curable monomer α,ω -dichloropolysiloxane was synthesized by the telomerization of dichlorodimethylsilane and octamethylcyclotetrasiloxane (D_4). The products with very low peel strength (<0.332 N/cm) could be used as release agents in pressure-sensitive adhesives. Moreover, the values of the dispersion component of surface energy (γ_s^d) from the films of UV-

curable prepolymers (26.40–33.75 mJ/m²) were determined and the effects of γ_s^d on the reduction of adhesion were investigated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2135–2139, 2002

Key words: modified polysiloxane; ultraviolet (UV) curable; curing of polymers; release agent; surface energy

INTRODUCTION

Silicone release coatings are very important in the tag and label industries and for other compounds that could not exist in their present forms without reliable release agents for pressure-sensitive adhesives (PSAs). Because of an increase in the sophisticated and demanding requirements, silicones remain the only authentic means of providing necessary low surface energy, nonpolarity, chemical inertness, and long-term release stability for today's PSA products.¹

The desirable release characteristics are dependent on the linear polydimethylsiloxane structure. In contrast to the typical polar organic PSAs (PSA with surface energy >30 dyne/cm), the low surface energy of a nonpolar cross-linked polydimethylsiloxane surface (usually at 22 dyne/cm) prevents tight physical bonding of the adhesives to the silicone.

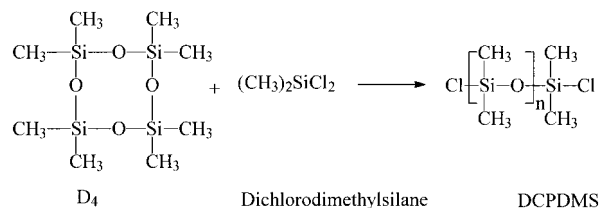
First, the thermally cured, solvent-borne coatings were applied in liquid form to a release liner. Then, they were irreversibly converted to cross-linked films by thermally accelerated chemical reactions between reactive silicone polymers and cross-linkers. Condensation-cure systems for paper release applications were an initial development of this technology. These systems are applied as solutions in organic solvents (toluene or *n*-heptane) or as oil-in-water emulsions.

Addition-cure silicones resemble condensation-cure types in some respects. Both systems rely on thermally accelerated cross-linking reactions between polymethylhydrogen siloxane cross-linker molecules and a separate reactive dimethylsiloxane polymer. Polymers in use are vinyl-functional silicones, and the curing reaction, also known as hydrosilation process, is an addition of the SiH group across the olefinic double bond. The most widely used catalysts for the hydrosilation process are based on precious metals. Inhibitors function by binding with the catalyst at lower temperature while still allowing rapid curing at elevated temperatures. Hydrosilation can also be triggered by peroxides, azonitriles, and high-energy ultraviolet (UV) or gamma radiations. These reactions are free radical in nature and therefore are not well suited for conventional coating techniques because the radicals so generated are quenched by atmospheric oxygen.

The new technology combines functional dimethylsiloxanes with a proprietary photocatalyst. Cross-linking is initiated by UV light, and curing normally takes place in <1 s at room temperature. Oxygen does not inhibit the curing process because no free radicals are generated during the curing process, thereby, eliminating the use of inert conditions.

In the present study, the novel monomer α,ω -dichloropolysiloxane was synthesized by the telomerization of dichlorodimethylsilane with octamethylcyclotetrasiloxane (D_4), which was then reacted with acrylates containing hydroxyl groups. In this way, several UV-curable prepolymers were obtained. The effect of the prepolymer structures on surface energy and release properties of solid film were investigated.

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Scheme 1

EXPERIMENTAL

Materials

Dichlorodimethylsilane, octamethylcyclotetrasiloxane (D_4), β -hydroxyl propyl acrylate (HPA), hydroxy ethyl methacrylate (HEMA), and pentaerythritol triacrylate (PETA) were of technical grade, benzoin isopropyl ether was of chemical grade, and diiodomethane was of analytical grade.

Determination of polymerization degree of α,ω -dichloropolydimethylsiloxane (DCPDMS)

Using end group determination method, 30–40 mL of (exact volume measurement) of 0.1 N NaOH solution was taken in a conical flask with a stopper, and exactly 0.15–0.7 g of the sample was added. The mixture was shaken, and 2–3 drops of phenolphthalein solution were added as an indicator and titrated against standard solution of 0.1 N HCl until the red color disappeared. The chlorine contents could then be calculated with the following formula:

$$\text{Chloro content (\%)} = \frac{(N_1V_1 - N_2V_2) \times 35.5}{G \times 10^3} \times 100\% \quad (1)$$

where N_1 is the concentration of standard NaOH solution, N_2 is the concentration of standard HCl solution, V_1 is the volume of standard NaOH solution (mL), V_2 is the volume of standard HCl solution (mL), and G is the sample weight (g). From the chlorine contents, the polymerization degree could be calculated.

Infrared spectroscopy

Infrared (IR) spectra were obtained from KBr pellets and recorded on a Perkin-Elmer Mode 1730 IR spectroscopy.

Preparation of solid film

In a dark box, prepolymer containing 3% benzoin isopropyl ether was irradiated by a 500 W high-pressure mercury lamp (the distance between sample surface and lamp was 10 cm) to obtain a solid film.

TABLE I
The Effect of the $\text{D}_4:(\text{CH}_3)_2\text{SiCl}_2$ Mole Ratio on the Synthesis Process

$\text{D}_4:(\text{CH}_3)_2\text{SiCl}_2$	Conversion (%)	Polymerization degree (theoretical)	Polymerization degree (observed)
2.00	91	9	11
3.75	93	13	14
5.00	97	21	21
8.00	96	33	32
10.00	93	41	39

Determination of contact angle

By using a CA-A type contact angle analyzer, the contact angles (CAs) of testing liquids (distilled water and CH_2I_2) on the surface of release agent were detected at $25 \pm 2^\circ\text{C}$.

Measurement of peel strength

A sheet of commercial polyacrylate pressure-sensitive tape was bonded to the surface of polypropylene film, and cured release agent was applied at its surface. The resulting laminate was pressed with a 2-kg rubber-coated roller. The test laminate was then aged at room temperature and cut into 200×25 -mm tapes for the T peel test. The laminate was pulled apart at a rate of 1.2 mm/s in an L & W tensile machine.

Measurement of viscosity

Viscosity was measured with a rotational viscometer at 25.0°C .

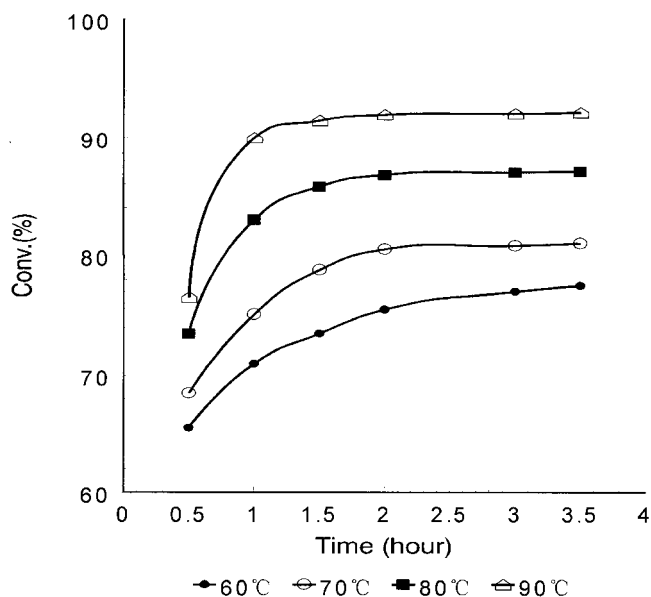


Figure 1 Effects of reaction temperature and time on product polymer degree.

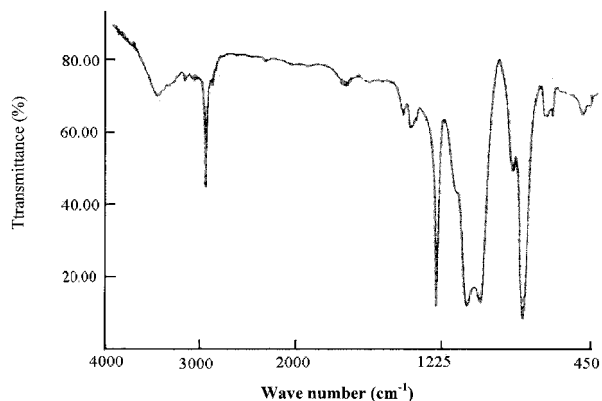


Figure 2 Infrared spectrum of DCPDMS.

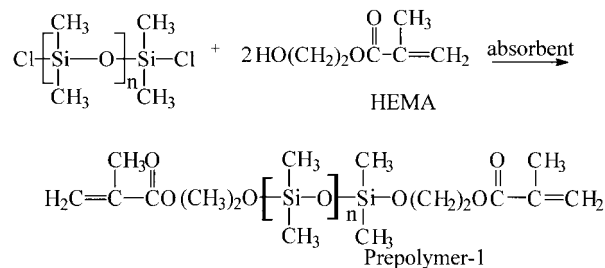
RESULTS AND DISCUSSION

Synthesis of α,ω -dichloropolydimethylsiloxane

α,ω -Dichloropolydimethylsiloxane (DCPDMS) was an important intermediate in this study and was synthesized by the telomerization of dichlorodimethylsilane with D_4 (see Scheme 1).²⁻⁵

Product properties are affected by the molar ratios of monomers (i.e., D_4 and $(CH_3)_2SiCl_2$), reaction temperature, and reaction time. These parameters were studied and the effect of monomer ratio on reaction products is shown in Table I and the effect of reaction temperature and reaction time on the polymerization degree of products are shown in Figure 1.

From the data in Table I, it is evident that the degree of polymerization of the product increases with an increase in the $D_4:(CH_3)_2SiCl_2$ molar ratio. However, the data in Table I also indicate that at low $D_4:(CH_3)_2SiCl_2$ molar ratio, the polymerization degree of the product was smaller than that of the theoretical calculation. On the contrary, at higher molar ratio, the polymerization degree was greater than that of the theoretical value. This result may be because dimethyldichlorosilane may react with the water in the air, when present in excess, because it is very reactive and volatile. This suggestion is further supported by the



Scheme 2

formation of fog in the reaction vessel at higher molar ratios of dimethyldichlorosilane.

The polymerization degree was calculated to be 37 from the IR spectrum of DCPDMS shown in Figure 2. In Figure 2, the peaks were assigned as follows: 2980 cm^{-1} for the C—H stretch vibration, 1260 cm^{-1} for the Si—CH₃ stretch vibration θ , 1023 cm^{-1} for the Si—O—Si stretch vibration, 805 cm^{-1} for the Si—CH₃ bending vibration, and 520 cm^{-1} for the Si—Cl stretch vibration. The characteristic peaks just described contribute towards the confirmation of the structure of the reaction products.

Synthesis of α,ω -dimethylacrylicsiloxane

In this article, the release agent prepolymer, polydimethylsiloxane containing methyl groups, was synthesized by the reaction of DCPDMS and acrylate containing a hydroxyl group.⁶ For example, the reaction of DCPDMS and HEMA is as shown in Scheme 2.

The reaction of DCPCM with PETA and HPA was similar to that with HEMA (see Scheme 2). The reaction products were named prepolymer-2 and prepolymer-3, respectively. When dichlorodimethylsiloxane was reacted with HEMA, HPA, and PETA, products of different viscosities were obtained with a varying degree of polymerization (8.8–37.2). In present study, reaction products with different viscosity were obtained by mixing dichlorodimethylsiloxane, which had low polymerization degree ($n = 8.8$) or high po-

TABLE II
Properties of Prepolymer for the Release Agent

Sample	Material					Pre-polymer	
	DCPDMS	Viscosity, cps	HEMA viscosity, cps	HPA viscosity, cps	PETA viscosity, cps	Appearance	Viscosity, cps
Poly.deg.							
M1	37.2	64	5	—	—		110
M2	8.8	17	5	—	—		18
A1	37.2	64	—	—	550		540
A2	37.2	64	—	6	—		120
A3	8.8	17	—	—	550		480
A4	8.8	17	—	6	—		20
A5			50% A1 + 50% A2			Opal and	370
A6			50% A3 + 50% A4			transparent	120

lymerization degree ($n = 37.2$), with equal weight HEMA, HPA, and PETA, respectively. The main results are shown in Table II.

We analyzed the purified A3 and unreactive PETA sample by IR, and the spectra are shown in Figures 3 and 4, respectively.

In Figure 3, the peaks were assigned as follows: 2963 cm^{-1} for the C—H stretch vibration, 1733 cm^{-1} for the C=O stretch vibration, 1023 cm^{-1} for the Si—O—Si stretch vibration, 1262 cm^{-1} for the Si—CH₃ stretch vibration, and 806 cm^{-1} for the Si—CH₃ bending vibration.

In Figure 4, the peaks were assigned as follows: 3431 cm^{-1} for the —OH stretch vibration, 1724 cm^{-1} for the C=O stretch vibration, 1637 cm^{-1} for C=C stretch vibration, and 2980 cm^{-1} for the Si—H stretch vibration.

By comparing Figure 3 with Figures 4 and 2, we see that the peaks intensities in Figure 3 (IR spectra of reaction products) are almost sum of both the peak intensities in Figure 2 and those in Figure 4, except the peak at 3141 cm^{-1} due to the —OH group and peak at 520 cm^{-1} due to the Si—Cl group have disappeared. All these data from IR spectra confirm the formation of the product.

Surface energy and release properties of UV-curable polysiloxane

In this paper, we calculated the dispersion surface energy (γ_s^d) of the solid release agent film by determining the contact angle on a nonpolar solid. Thomas Young discussed the contact angle of a drop of liquid on a plane solid surface, at equilibrium, under the action of the three surface tensions. Here, γ_{LV} is the surface tension at the interface of the liquid and vapor phases, γ_{SL} is the interface of the solid and the liquid, and γ_{SV} is the interface of the solid and vapor. Hence,

$$\gamma_{SL} = \gamma_s - \gamma_{LV} \cos \theta \quad (2)$$

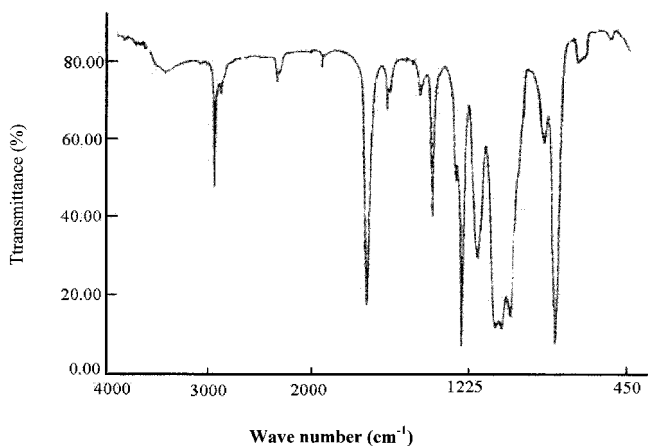


Figure 3 Infrared spectrum of A3.

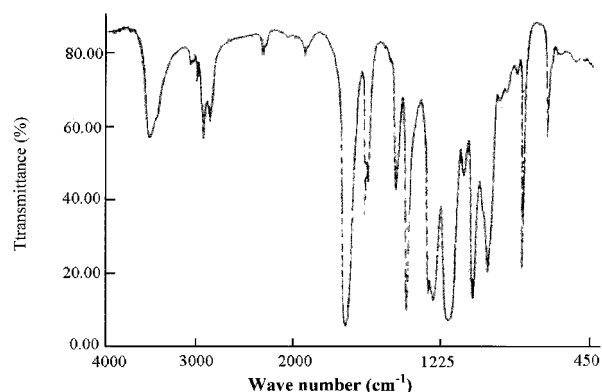


Figure 4 Infrared spectrum of PETA.

According to Fowkes' study, the interface tension could also be calculated by the following formulation:

$$\gamma_{SL} = \gamma_s + \gamma_{LV} - 2(\gamma_L^d \gamma_s^d)^{1/2} \quad (3)$$

Equations 2 and 3 give

$$\gamma_s^d = \frac{1}{4\gamma_L^d} [\gamma_{LV}(1 + \cos \theta)]^2 \quad (4)$$

H₂O ($\gamma_{LV} = 72.7\text{ mN/m}$, $\gamma_L^d = 23.9\text{ mN/m}$), and CH₂I₂ ($\gamma_{LV} = \gamma_L^d = 51.0\text{ mN/m}$) were used as the testing liquids. The CAs (θ) of the testing liquids on plane release agent film were measured. From θ , the γ_s^d values can be calculated with eq. 3, and values of γ_s^d are given in Table III. The release properties and γ_s^d values of release agent films are shown in Table III. The following conclusions can be drawn from these data:

1. The higher the content of siloxane, the smaller is the γ_s^d value of the release agent prepolymer. This result may be due to low surface energy of polysiloxane.
2. The γ_s^d value calculated from the CA of H₂O on release agent film was slightly greater than that calculated from the CA of CH₂I₂ on the release agent film.
3. The peel strength of the pressure sensitive band decreased with the decreasing of γ_s^d value. However, in the release agent prepolymer, an increase in the amount of polysiloxane would result in incomplete curing of release agent film because of a decrease in the amount of methacrylate.

CONCLUSIONS

1. α , ω -Dichloropolydimethylsiloxane (DCPDMS) was synthesized by the telomerization of dichlorodimethylsilane and D4. In this reaction, the

TABLE III
Release Properties and γ_s^d Value of the Release Agent Film

Property	Release agent								
	A3	A1	A4	A2	50% A3 + 50% A4	50% A1 + 50% A2	M1	M2	Blank
θ (H ₂ O)	99	106	104	108	103	106	107	103	—
θ (CH ₂ I ₂)	49	63	57	64	53	62	64	52	—
γ_s^d (H ₂ O)	37.35	29.00	31.77	26.40	33.21	29.00	27.80	33.21	—
γ_s^d (CH ₂ I ₂)	34.96	26.95	30.42	26.37	32.71	27.53	26.37	33.10	—
Peel strength (N/2.5cm)	0.87	0.061	0.056	Cured incompletely	0.082	0.044	Cured incompletely	0.071	220

ratio of D4 to (CH₃)₂SiCl₂, reaction temperature, and reaction time would obviously affect conversion rate and polymerization degree.

- By the reaction of α, ω -dichloropolydimethylsiloxane (DCPDMS) with acrylate (HEMA, HPA, and HETA) containing a hydroxyl group, the release agent prepolymer terminated with a methacryloyl group containing UV-sensitive groups was synthesized. The reaction process was explained by IR spectroscopy.
- The CAs of testing liquids (H₂O, CH₂I₂) on the surface of release agent solid film were detected and γ_s^d values of release agent solid film were calculated. Moreover, release properties were verified by measuring the peel strength of the PSA band from the surface of release agent film.

The results indicated that the value of the release agent and release property had a close relationship with the polysiloxane content in the release agent. In common, the higher the polysiloxane content, the lower the γ_s^d value, the better release property.

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