

Crosslinking effects on the release force of addition cure silicone release agents in model systems

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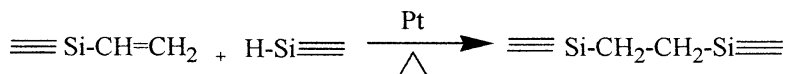
Summary

Crosslinking effects on the release force of some addition curable silicones in a model system have been investigated. The release force at several release speeds and the contact angles of ethyleneglycol on release papers coated by release agents having different crosslinking densities were estimated. Physical properties of model release agents in the bulk were also measured in bulk. We found that release force at a low speed is affected by the wettability of the surfaces and release force at a high speed is affected by the bulk crosslinking density.

Introduction

Silicone release agents are widely used by the pressure-sensitive adhesive industry for labeling and adhesive tape applications because of their low surface energy(1-4). There have been many recent investigations of polydimethylsiloxane-organic copolymer surfaces because of poor miscibility of silicones and organic polymers(5-10).

There are two kinds of silicone release agents now used by industry, ultraviolet/electron beam(UV/EB) cure types and heat cure types. Addition cure type utilizing hydrosilylation in the heat cure systems is mainly used nowadays. The reaction scheme of the hydrosilylation is shown below(11, 12). $-\text{CH}_2-\text{CH}_2-$ is formed by the addition reaction of a vinyl group linked to a silicon with a hydrogen linked to a silicon in the presence of a platinum catalyst.



The addition reaction generally used for silicone release agents requires a methylvinylsiloxane-dimethylsiloxane copolymer as a base polymer, a polymethylhydrogensiloxane as a crosslinker, and a platinum catalyst.

Pressure-sensitive adhesives have been thoroughly investigated because of their industrial importance. They are usually treated as a viscoelastic material and studied by separating the adherent wetting process from the fracture process. However, there have not been through studies of silicone release agents in spite of their practical importance. The surface energy of silicone release agents have been investigated, but the relationship between release force and bulk properties have not been understood clearly.

Shibano showed that the release force from silicone release agents is not only based on low critical surface tension but also low elastic modulus of cured silicone(13). Since cured silicone release agents are also viscoelastic materials, they should also be investigated by separating the wetting process and fracturing process of silicone release agents as well as pressure sensitive adhesives. Silicone release agents are generally coated under 1 μm , whereas pressure sensitive adhesives are coated from 30 to 40 μm thickness. Treatment of silicone release agents therefore are not same as that of pressure sensitive adhesives. It is also very important to certify the relationship between silicone composition and release properties since there are many kinds of release agents with various release properties.

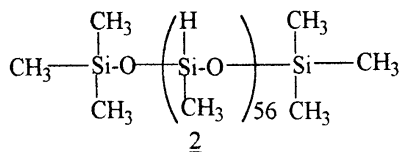
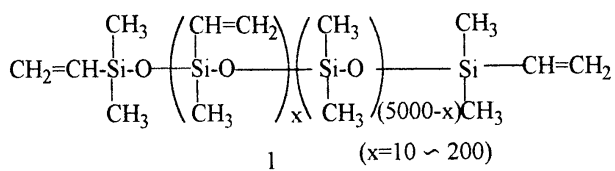
We are interested not only in the surface energy but also the crosslinking effects on the release force from cured silicone release agents. In particular, it is useful to study the release behavior as a function of the peeling speed, since the release behavior at high speed peeling(over 30 m/min) which is important in the process of removing unnecessary parts of cut labels differs from release performance in low speed peeling(under 5 m/min).

In this paper, many kinds of base polymers and crosslinker were synthesized and their structures were identified. Model systems of addition cure silicone release agents were also prepared and measured their surface properties and bulk properties. Thus, the relationship between release force and the bulk properties of release agents have been studied.

Experimental

Materials:

The structures of copolymers(1) and a crosslinker(2) in the model release agents are shown below.



The copolymers(1) were prepared by equilibrium polymerization of octamethylcyclotetrasiloxane(D_4), tetramethyltetravinylcyclsiloxane(D_4^{vi}), and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane(M_2^{vi}) with KOH(10 ppm) at 140°C for 4 h, being neutralized by phosphoric acid(20 ppm), and removing volatile components at 140°C for 4 h under 20 mmHg.

Polymethylhydrogensiloxane(2) used as a crosslinker was prepared by equilibrium polymerization of tetramethyltetrahydrocyclosiloxane(D_4^{H}) and 1,1,1,3,3,3-hexamethyldisiloxane(M_2) with acid clay(1.0 wt%) at 70°C for 4 h. Then volatile components were removed by heating at 120°C for 1 h under 20 mmHg after filtering acid clay.

Preparation of the model release agents and the model release papers:

Copolymers(30 g) were dissolved by stirring in toluene(70 g) at 70 °C for 3 h and cooled to room temperature. The crosslinker(Si-H/Si-Vi ratio = 2.0), a reaction inhibitor(0.03 g), and toluene were added to the copolymer solution and stirred for 10 min at room temperature. The concentration of nonvolatile component was controlled to 30 wt% by adjusting the amount of additional toluene.

Platinum catalyst(100 ppm as Pt) was added just before preparing each release coating solution. 3-methyl-1-butyn-3-ol inhibitor and platinum chloride coordinated by tetramethyltetravinyldichlorosiloxane catalyst were used in this investigation.

The model release papers were prepared by coating 5 wt % silicone release agents in toluene on the polyethylene laminated papers(Fujimori Kogyo, 75 g/m²). They were coated with 0.8 μm thickness of release agents by using #7 meyer bar then cured at 140°C for 30 sec. The release papers were estimated for release force and contact angles on the surface after aging in A4 size envelopes at 70°C for 20 h. The silicone coating thickness was confirmed by x-ray fluorescence method using Rigaku MINI-X.

Preparation of bulk specimens of model release agents:

Silicone solution(20 wt%) in toluene of each model release agent was prepared. The solution(45 g) was poured to a metal mold coated by polytetrafluoroethylene(15 cm x 15 cm x 0.5 cm). Sheets(0.4 mm thickness) for measurement of bulk properties were prepared by drying at 50 °C for 20 h and curing for at 70°C for 20 h.

Measurement:

(1) Molecular weight:

Gel permeation chromatographic(GPC) analyses were carried out using a Toyo Soda HLC-802UR equipped with a refractive index detector (column : GMH6 x 2). Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. The molecular weights were determined by polystyrene standards.

(2) Methylvinylsiloxane unit content:

Methylvinylsiloxane units in each poly(dimethylsiloxane-co-methylvinylsiloxane) were measured by near infrared spectroscopy method at 2148 nm based on vinyl groups(Hitachi self recorded photometer U-3500).

(3) Bulk properties of release agents:

The rubber properties were determined according to JIS K6301 and estimated elongation and break strength were measured using a Shimatzu autograph AG-500B.

Differential scanning calorimetry(DSC) was carried out by Seiko SSC5200/DSC120 system.

(4) Contact angles:

The contact angle in each model release paper was measured by Kyowa Kagaku CA-A using ethylenegrycol at 20°C. Work adhesion of each release paper was calculated by measuring contact angle below.

$$W = \gamma(1 + \cos\theta)$$

where,

W : work of adhesion

γ : surface tension(ethylene glycol : 47.7 mJ/m² at 20°C)

θ : contact angle

(5) *Release force:*

BPS8170(Toyo Ink), an acrylic pressure sensitive adhesive, was coated on each release paper to 128 μ m wet thickness and dried at 100°C for 3 min. Then the adhesive sheets were cut to 2.5 x 15 cm after laminating papers(65 g/m²) were applied to the adhesive layer. Release force at 0.3 m/min was measured by Autograph AG-500B(Shimadzu) and peel at high speed(60 and 200 m/min) was measured by Fast Peel Tester(Tester Sangyo) after aging in 50 %RH at 25°C for 20 h under 20 gf/cm².

(6) *Crosslinking density:*

The weight of each sample was measured after each silicone sheet(0.1 g) was swollen in cyclohexane(10 g) at 25 °C for 48 h. Then crosslinking densities were calculated as follows(14):

$$\frac{v_c}{V_0} = \frac{-2[v + \chi v^2 + \ln(1 - v)]}{V_1(2v^{1/3} - v)}$$

where,

v_c : mole number of crosslinking in the cured silicone

V_0 : volume of dried polymer

V_1 : molar volume of solvent (cyclohexane = 100.936)

v : volume percent of polymer in the gel

χ : polymer-solvent interaction parameter (silicone-cyclohexane at 25 °C = 0.42)

Results and discussion

Five kinds of model release agents having different crosslinking densities based on vinyl group content were prepared for this investigation.

Table 1 shows methylvinylsiloxane unit content, weight average molecular weight and molecular weight distribution of five kinds of copolymers. Investigation was carried out with copolymers of average molecular weight 3.0 x 10⁵ to 3.5 x 10⁵ and methylvinylsiloxane unit content from 0.2 mol% to 4.0 mol%. The viscosity of the used crosslinker was 17.5 cSt at 25°C and the hydrogen content was 1.59 wt%.

Fig. 1 shows the relationship between release speed and release force in each release agent controlled from 0.2 to 4.0 mol% by methylvinylsiloxane content. It is clear that the release force at high speed release (60 ~ 200 m/min) is extremely high while the release force at 0.3 m/min(low speed release) is low in the range of methylvinylsiloxane content from 0.2 to 0.5 mol%. The higher the crosslinking density is, the less the release force is affected by release force speed.

The release force at the low release speed(0.3 m/min) increases very slightly with increase of crosslinking density(Fig. 1).

Table 1 Methylvinylsiloxane content and \bar{M}_w of poly(dimethylsiloxane-co-methylvinylsiloxane)

Samples	Methylvinylsiloxane content (mol%)	Weight average molecular weight and its distribution	
		$\bar{M}_w (\times 10^{-5})$	\bar{M}_w/\bar{M}_n
A	4.00	3.51	2.12
B	2.00	3.44	2.20
C	1.00	3.02	2.19
D	0.50	3.43	2.26
E	0.20	3.56	2.45

In order to clarify this finding, the relationship between methylvinylsiloxane content and the release force at 0.3 and 200 m/min is shown in Fig.2. It is obvious that the release force at a low release speed(0.3 m/min) increases but the release force at a high release speed(200 m/min) decreases as methylvinylsiloxane content increases. Results apparently demonstrate that the degree of crosslinking strongly affects release force. Then calculation of the work of adhesion was made by measuring the contact angle of ethyleneglycol on each release paper. The relationship between methylvinylsiloxane content and work of adhesion is shown in Fig.3. The relationship between work of adhesion and the release force at 0.3 m/min is shown in Fig.4. The results apparently reveal that the greater the work of adhesion is, the higher the release force at a low release speed will be. In particular, it is clear that release force at 0.3 m/min significantly increases above 48 mJ/m² work of adhesion. This implies that release force at a low release speed(0.3 m/min) is highly affected by wettability of pressure sensitive adhesives to the surface of each release paper. Therefore, release force at a low release speed(0.3 m/min) increases with better wettability of the pressure sensitive adhesives(low contact angle of ethyleneglycol). One can postulate that increase of the surface energy is caused by generation of $-\text{CH}_2-\text{CH}_2-$ during crosslinking of methylvinylsiloxane and methylhydrogensiloxane. Adhesion theory is also suitable for the case of pressure sensitive adhesive-release since wettability of the surface relates to adhesion.

The bulk properties were investigated after preparation of cured sheet of each model release agent. The relationship between logarithm of crosslinking densities measured and elongation of the dumbbell cut is shown in Fig.5. It is apparent that elongation of the dumbbell decreases with the increase of crosslinking density.

The relationship between the logarithm of crosslinking density and logarithm of release force at high release speed(200 m/min) is given in Fig.6. It is evident that the release force at high release speed decreases as the crosslinking density increases. The relationship between elongation and release force at high release speed(200 m/min) may be seen in Fig.7. The logarithm of release force at high release speed highly correlates with logarithm of crosslinking density($r^2=0.98$). Release force increases in a low crosslinking density system because of more deformation of the cured silicone at high speed release condition, but release force does not increase in a high crosslinking density system such silicones are very rigid.

DSC thermograms of each cured silicone are given in Fig.8. Tg in the high crosslinking density is shown in around -120°C , but Tg in the low crosslinking density is unclear. Endothermic peaks from -50 to -40°C are due to the melting transition temperature(Tm). The relationship between logarithm of crosslinking density and Tm is shown in Fig.9.

It is clear that the melting transition temperature decreases when crosslinking density increases. This reveals that the melting transition temperature decreases because of the limitation of the movement of polymer chain as crosslinking density increases(15).

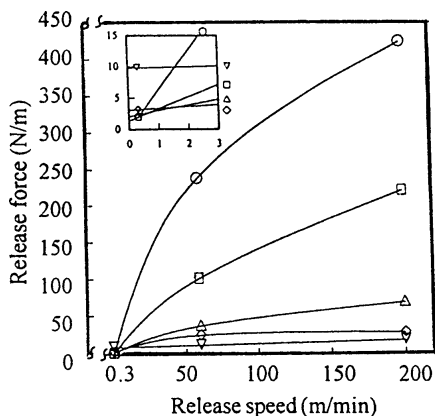


Fig.1 Relationship between release speed and release force
methylvinylsiloxane content (mol%);
○: 0.2 □: 0.5 △: 1.0 ◇: 2.0 ▽: 4.0

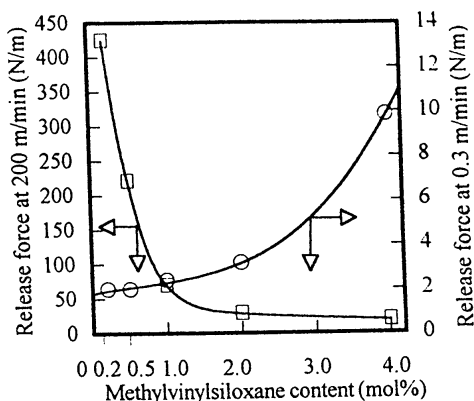


Fig.2 Relationship between methylvinylsiloxane content and release force at 0.3 and 200 m/min

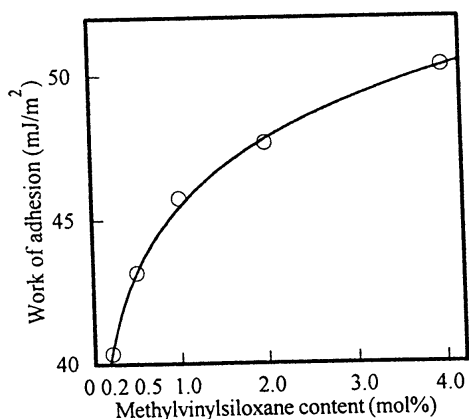


Fig.3 Relationship between release force at 0.3 m/min and work of adhesion

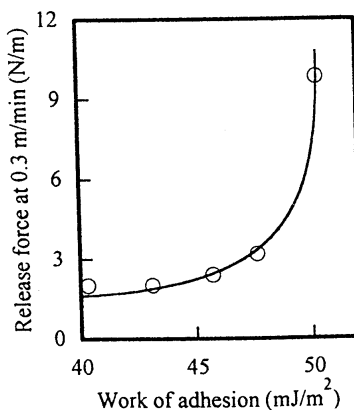


Fig.4 Relationship between release force at 0.3 m/min and work of adhesion

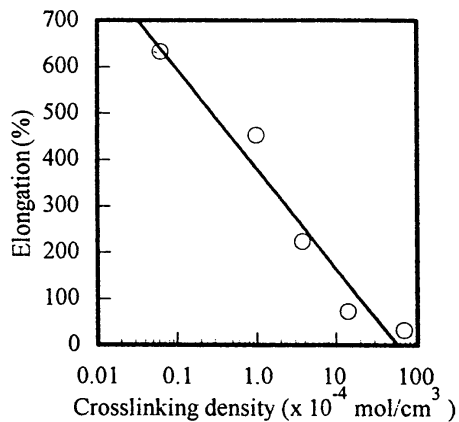


Fig.5 Relationship between crosslinking density and elongation

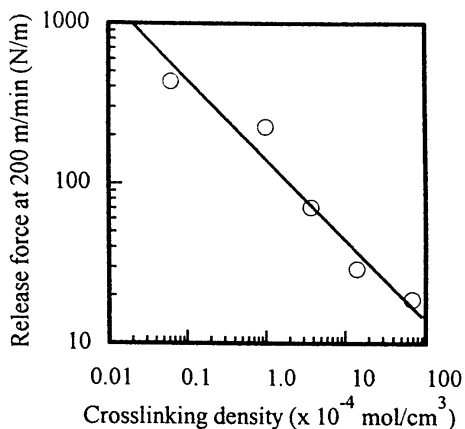


Fig.6 Relationship between crosslinking density and release force at 200 m/min

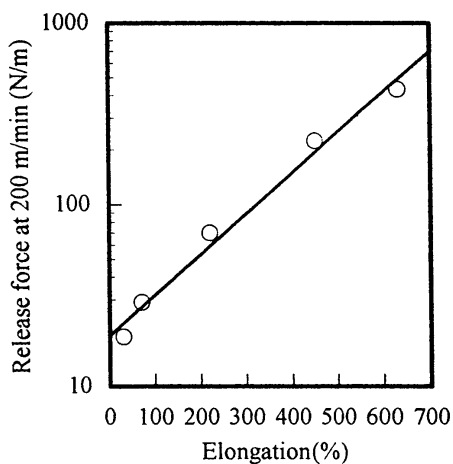


Fig.7 Relationship between elongation and release force at 200 m/min

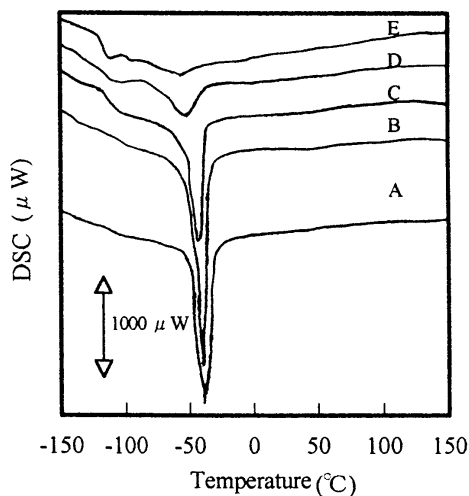


Fig.8 DSC thermograms showing the melting transition temperature for each cured silicone sample
Methylvinylsiloxane content(mol%);
A:0.2 B:0.5 C:1.0 D:2.0 E:4.0

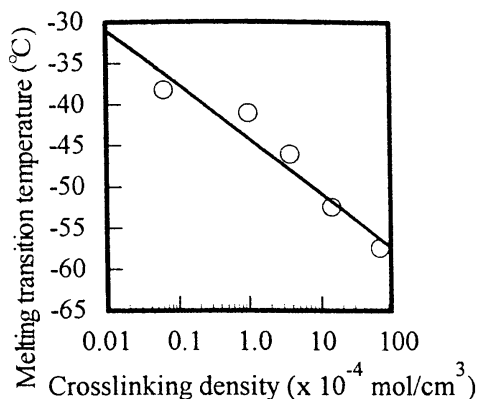


Fig.9 Relationship between crosslinking density and melting transition temperature

Conclusion

Crosslinking effects on release force of model silicone release agents were investigated. Our results were as follows:

- (1) Both the work of adhesion of the surface and the release force at low release speed (0.3 m/min) increase with increased crosslinking density.
- (2) Release force at high release speed (200 m/min) considerably decreases with increase in crosslinking density. It is highly correlated with bulk elongation.

Acknowledgments

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