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Ice releasing block-copolymer coatings

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The problem of ice adhesion is a very important one and presents a variety of interesting aspects (1, 7). The present paper deals with poly(dimethyl-siloxane)-bisphenol-A-polycarbonate block-copolymer films as abhesion coatings for ice. Not only the hydrophobic properties of the surfaces of such films are of significance for ice adhesion but also their mechanical and rheological properties. Experiments, reported here, show that the conditions for adhesion depend on the siloxane content and its block lengths, the glass temperature of the copolymer, and the hydrophobic properties of the film surfaces; i.e., the polysiloxane block is preferentially situated in the film surface. A practical result of this work consists of establishing the excellent adhesive properties of a particular block-copolymer; ice could very easily be removed from lock walls as large scale tests showed (2).

Experimental

(a) Apparatus

Adhesive strength is measured by shear experiments. The apparatus is schematically indicated in figure 1. It was supplied by the U. S. Army Corps of Engineers, CRREL, and designed by *K. Itagaki*. It was modified in our laboratory to make it suitable for the present purpose.

Boiled out distilled water was frozen in a cylindrical aluminium sleeve (a) resting on a plate coated with the polymer film. This plate resting on ball bearings was pulled to the left (d) by a compressed air piston device while the force was measured by the strain gauge (e). At first the force increases, but at the point where abhesion occurs the force decreases rapidly to zero. The force-time diagram is recorded and maximum force represents the adhesive force. The whole apparatus is thermostated (± 0.3 °C) in an air bath.
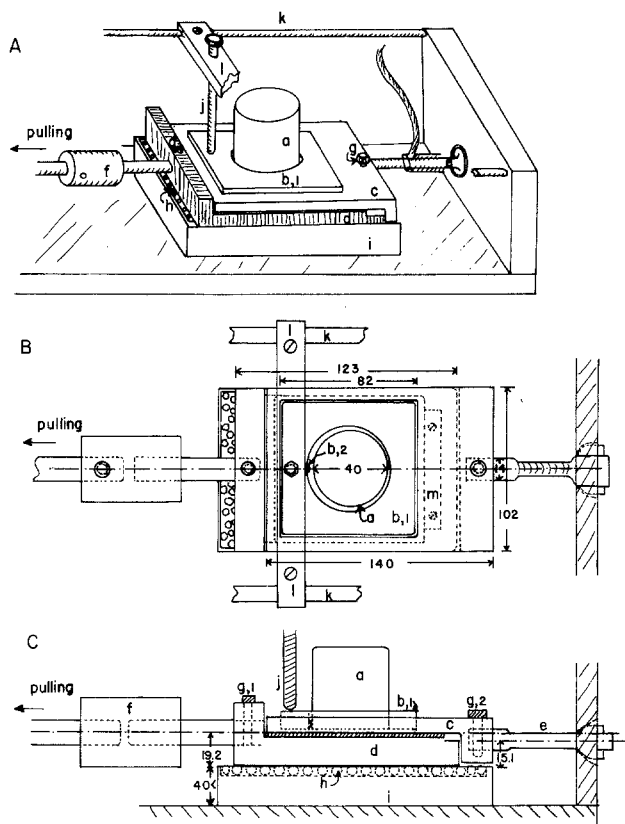

Fig. 1. Abhesion Shear Apparatus. (A) Side View, (B) Top View, (C) Cross section of Side View. (a) Al-sleeve for freezing water; (b) 1-cover, 2-stopper for sleeve and ice abhesion plate; (c) frame for cover and connector of the strain gauge; (d) movable plate support connected to piston (f); (e) strain gauge; (f) connection for piston; (g) 1-pin for connecting (d) to (f), 2-pin for connecting (c) to (e); (h) ball bearings; (i) base carrying ball bearings (h) for easy movement of (d); (j) screw to hold (b) in position; (k) guide rod; (l) holder for (j); (m) metal strip.

Polymer films and substrates

Aluminium (bright polish) and concrete plates (7.5 cm × 7.5 cm × 0.6 cm) were used as substrates. The concrete plates were cut from a block by a diamond saw polished, and glued with epoxy to glass plates. The aluminium plates were cleaned by soaking them in methylene dichloride for about half a day. The plates were then wiped dry with tissue paper and placed into a medium sized desiccator which contained about 100 ml of CH_2Cl_2. After one minute a small amount of polymer solution (10% by weight of polymer in CH_2Cl_2) was poured onto the surface of a plate. Immediately the rolling coater (fig. 2) was drawn across the surface of the plate producing a coated plate which was transferred to another desiccator not containing CH_2Cl_2; it was left there for at least fifteen minutes before applying a second coat. The plate was then air dried for about 24 hours before testing.
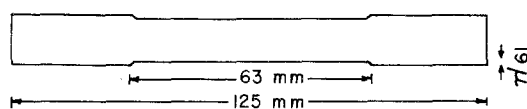
Fig. 2. Film coater

In some cases toluene was used as solvent; a desiccator was then not needed. The concrete surfaces (slabs were 3.5 mm thick) were cleaned first with detergent (Alconox) and subsequently rinsed under tap water for at least thirty minutes. They were dried in ambient atmosphere overnight. These plates have rather large stone particles embedded in cement. It was observed that the stone surfaces were well covered by the polymer film. However, a number of gas bubbles (blisters) were formed on the cement areas and a continuous coating was not produced with methylene dichloride as solvent. Toluene as solvent gave satisfactory films due to its volatility (three coats).

Methylene dichloride and toluene were ACS reagents obtained from Eastman Kodak; silicone fluid (oil) No. 6407 came from Thomas Co. Spraying for producing polymer films gave as good results as coating. The block copolymers were supplied by General Electric Company as well as liquid-1 (dimethylsiloxane prepolymer, oil) 50 c.s. and liquid-2 (dimethylsiloxane prepolymer, oil) 100 c.s. Table 1 contains the characteristics of the various block-copolymers.

Experimental results

Blank tests with Al/ice and concrete/ice gave mean adhesive strength values at −10 °C of 5.56 ± 1.08* kg/cm² and 7.56 ± 0.72* kg/cm², respectively.

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* The ± values are standard deviations.

The most satisfactory coating (65 wt. % of polysiloxane, 35 wt. % of ploycarbonate, siloxane chain length 20, T_g − 66 °C) on aluminium gave mean adhesive strength values at −10 °C (a) with methylene-dichloride as solvent 0.18 ± 0.07 kg/cm²; (b) with toluene as solvent 0.16 kg/cm²; (c) with 10 wt. % of Thomas silicone oil added 0.054 ± 0.03 kg/cm² with methylene-dichloride as solvent, (d) with toluene plus 10 wt. % silicone oil 0.04 kg/cm². The mean values for concrete as substrate are as follows (−10 °C): (a) toluene as solvent 0.57 kg/cm², (b) plus 10 wt. % of silicone oil 0.033 kg/cm² (if the coating was renewed after each adhesion test an adhesive strength of 0.031 kg/cm² was achieved).

The films with 65 wt. % polysiloxane and chain lengths 40 and 100 gave adhesive strength values at −10 °C with methylene-dichloride as solvent and Al as substrate of 0.12 kg/cm² and 0.19 kg/cm², respectively, i.e. these values are practically as good as that for the sample of 65 wt. % of polysiloxane, chain length of 20 and $T_g = -66$ °C. However, addition of 10 wt. % of silicone oil gives values of 0.20 kg/cm² and 0.21 kg/cm², respectively. These values are very little different from those without silicone oil while
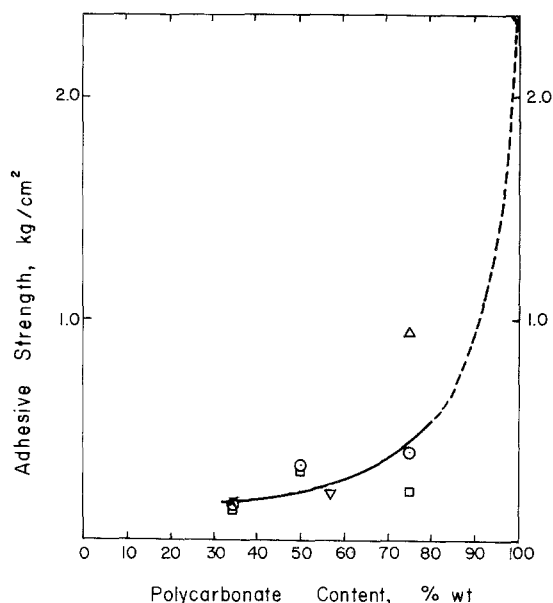
Fig. 3. Adhesive strength (kg/cm²) as function of polycarbonate wt. % (− 10 °C); (Al-substrate); Siloxane block chain length DP: △ 5, ▽ 10, ⊙ 20, □ 40, × 100; ○ Lexane 100% (see table 1)

Table 1. Poly(dimethylsiloxane) bisphenol-A polycarbonate block copolymers (G. E.)

No.	Polymer	Polysiloxane Wt. %	Polycarbonate Wt. %	$\overline{DP}$ (Siloxane)	$\overline{DP}$ (Carbonate)	T_g*) (°C)
1	Lexan 100–111	0	100	100	—	—
2	228–1218	25	75	5	5	30–35
3	XD–11	25	75	20	20	100
4	131–848	25	75	40	40	130–135
5	LR–3320	43	57	10	4[1])	−20
6	Si-50-20	50	50	20	6[1])	—
7	Si–50–40	50	50	40	(12)[1])	—
8	LR–5630	65	35	20	3[1])	−66
9	Si–65–40	65	35	40	6[1])	—
10	Si–65–100	65	35	100	(16)[1])	—

[1]) Calculated values
*) Glass temperature

the value for 65 wt. % and chain length 20 decreased to 0.05 kg/cm².

The figures described below all refer to adhesive strength at −10 °C, aluminium substrates (unless otherwise indicated) and methylene-dichloride as solvent.

Figure 3 gives the adhesive strength for films with Al-substrates in kg/cm² as a function of the weight percentage of polycarbonate (or weight percentage of polysiloxane). It is apparent that these values decrease with decreasing polycarbonate content (or with increase in polysiloxane) and generally with increasing polysiloxane block-chain length (see table 1).

Figure 4 shows the adhesive strength as function of polycarbonate (or polysiloxane) content for polymer films with additions of various weight percentages of various silicone oils. Here again, the adhesive strength decreases with decreasing polycarbonate content. The values are affected to different degrees by the silicone oils. The longer chain silicone oils (i.e. those with higher viscosities) affect the adhesive strength adversely. (See (1) and (2) G. E. higher viscosity silicone oils with DP 20 $T_g = 100$ °C; the same coating without oil gives lower abhesion values ○; (see table 1).

Figure 5 depicts adhesive strength as a function of polysiloxane block chain length. The adhesive strength is independent of this length in the range of 20 to 100 for 65 weight % of polysiloxane samples. It increases with block length for 43 to 50 weight % polymers until it apparently reaches a plateau for a length of 40 which is higher than that for the
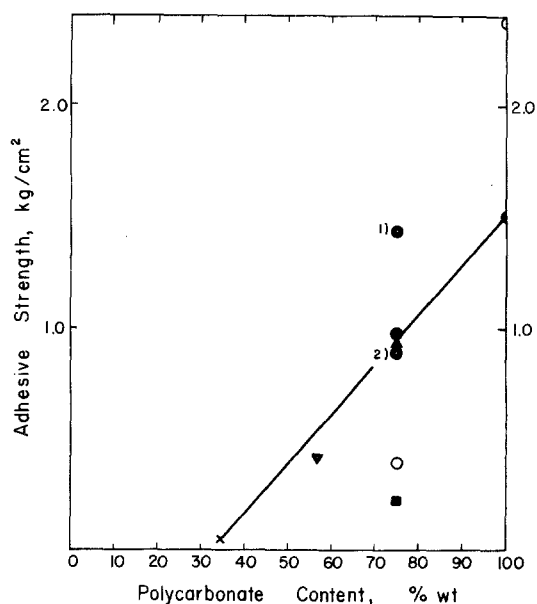

Fig. 4. Same as figure 3 with addition of 10 wt. % of silicone oils: ● Lexane 100% polycarbonate (Thomas Oil), ○ no oil; ● DP = 20 $T_g = 100$ °C (Thomas Oil); ●[1]) ditto plus 50 s.c. oil (G. E.), ●[2]) ditto plus 100 c.s. oil (G. E.), ▲ DP = 5 $T_g = 30$ °C to 35 °C (Thomas Oil), ■ DP = 40 $T_g = 130$ °C to 135 °C (Thomas Oil), ▼ DP = 10 $T_g = −20$ °C (Thomas Oil), × DP = 20 $T_g = −66$ °C (Thomas Oil), ○ DP = 20 $T_g = 100$ °C without oil (see table 1)

65 weight % polysiloxane samples and decreases rapidly for 25 weight % of siloxane with increasing block length and appears to reach a lower plateau than for 40 weight % of siloxane practically coinciding with the 65 weight % values (see table 1).

Figure 6 shows the same plot as that in figure 5 with the difference that 10 weight % of silicone oil (Thomas) was added to the
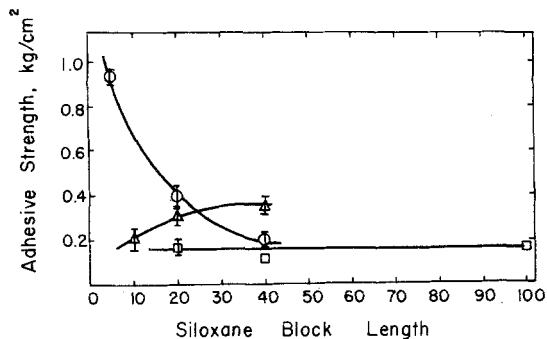
Fig. 5. Adhesive strength (kg/cm²) as function of siloxane block chain length ($-10\,°C$, Al-substrates): ○ 25 wt. % siloxane, △ 43 to 50 wt. % siloxane, □ 65 wt. % siloxane (see table 1)
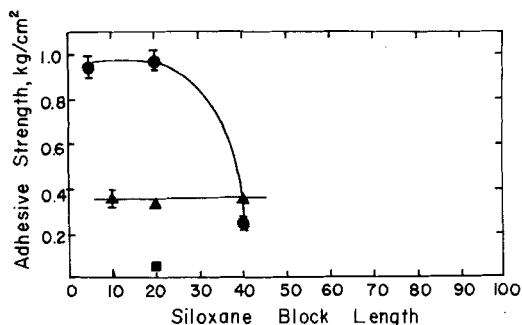

Fig. 6. Same as figure 5 but with 10 wt. % of (Thomas) silicone oil: ● 25 wt. % solixane, ▲ 43 to 50 wt. % siloxane, ■ 65 wt. % siloxane (see table 1)

block-copolymers. Here 65 weight % of polysiloxane with length 20 and glass temperature $T_g = -66\,°C$ shows by far the lowest adhesive strength of all films. Films with 43 to 50 weight % of polysiloxane seem to be independent of block chain length. It is expected that silicone oil will generally alter abhesive strength in either direction due to increased hydrophobicity, plasticiser and lubricating action. The 25 weight % curve is now concave towards the block length axis (see table 1).

Figure 7 indicates the effect on polysiloxane block chain length on adhesive strength with additions of 10 weight % of different silicone oils. The Thomas No. 6407 oil decreases adhesive strength most. The polymer samples have a polysiloxane weight % of 25 and block chain-lengths of 5, 20 and 40. The trend of the samples with G. E. Oils is indicated in the figure (see table 1).

Adhesive strength as a function of temperature for the sample of 43 weight % of polysiloxane, block chain length 10 and $T_g = -20$

is shown in figure 8; the adhesive strength increases at an accelerating rate with decreasing temperature. The adhesive strength values with 10 weight % of Thomas Oil are for this sample actually higher than those without oil.

Figure 9 illustrates adhesive strength-temperature for the sample with 65 weight % of polysiloxane, block length 20 and $T_g = -66\,°C$ with and without 10 weight% of Thomas silicone oil. The strength values actually pass through a pronounced maximum at about $-10\,°C$. Those for the films plus 10 weight % of oil are much smaller than those without the oil.

Adhesive strength as function of strain rate is shown in Fig. 10 for the sample with 65 weight % of polysiloxane block chain length 20 and $T_g = -66\,°C$. The adhesive strength is practically constant in a range of ca. 0.2

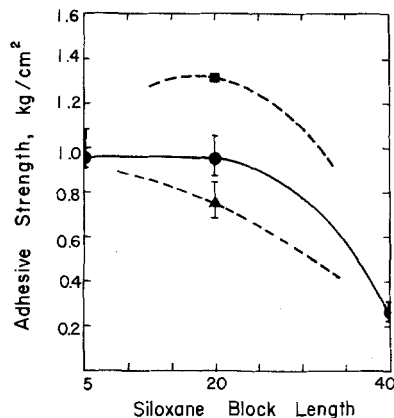Fig. 7. Same as figure 5 but with addition of various silicone oils: ■ 10 wt. % c.s. 50 G. E., ▲ 10 wt. % c.s. 100 G. E., ● 10 wt. % 6407 J. Thomas. The trend for the abhesion values for the polymer with G. E. oils are indicated (see table 1)

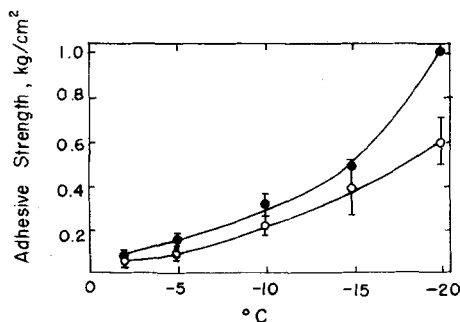Fig. 8. Adhesive strength (kg/cm²) as function of temperatuie (Al-substrates). Sample: DP (siloxane) = 10, polycarbonate 57 wt. %, $T_g = -20\,°C$; ○ without silicone oil, ● 10 wt. % silicone oil (Thomas)
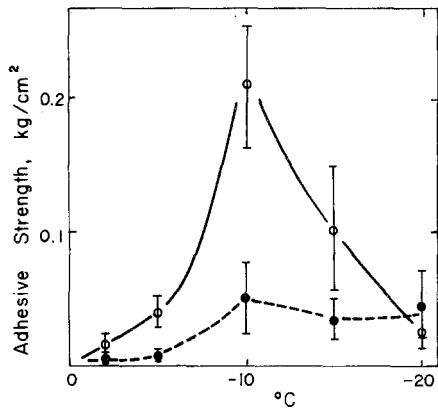
Fig. 9. Same as figure 8. Sample: DP (siloxane) = 20, polycarbonate 35 wt. %, $T_g = -66\,°C$; ○ without silicone oil, ● 10 wt. % silicone oil (Thomas)
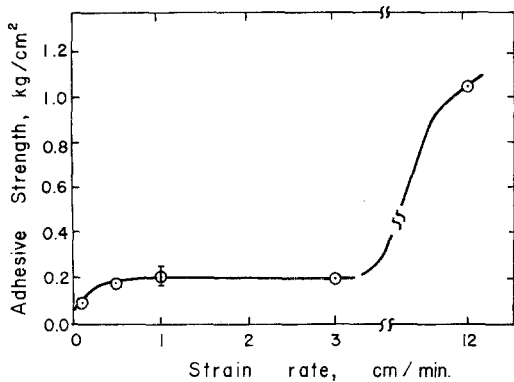

Fig. 10. Adhesive strength (kg/cm²) as function of strain rate (cm/min; −10 °C, Al-substrate). Sample same as in figure 9 (without silicone oil)

cm/min to 3 cm/min. However, beyond this range the adhesive strength values increase quite rapidly with strain rate and appear to become constant near 12 cm/min.

(b) Concrete as substrate

The concrete plates had rather large stone particles to which the polymers adhered very well, but they tended to come off the cement areas using methylene-dichloride as solvent for the block-copolymer. Toluene, however, due to its low volatility gave satisfactory coatings. These coatings were applied to concrete surfaces giving results similar to those with aluminium as substrate. The adhesive values appear to scatter somewhat more for concrete than for aluminium substrates probably due to the porosity of the concrete surfaces.

Figure 11 shows results for adhesive strength as a function of temperature for the sample of 65 weight % polysiloxane, chain length 20 and $T_g = -66\,°C$. The coats were not removed between tests at different temperatures. Adhesive strength passes again through a maximum at about −10 °C. However, the maximum decreases if the coats are removed and renewed after each adhesion test.

(c) I. R. Attenuated Total Reflectance measurements (ATR)

An attempt was made of ascertaining whether the siloxane blocks lie preferentially in the surface of the polymer films. The measurements were carried out on a Beckman I. R. 12 spectrophotometer using an ATR accessory with a multiple internal reflection crystal having a face angle of 45° and a thickness of 2 mm. The polymer films were approximately 25 μ thick.

The ratios of the respective absorbancies are taken for transmission and reflectance measurements, respectively; these absorbance ratios are plotted versus the polysiloxane weight % of the samples as shown in figure 12 (the samples are numbered according to table 1). The ratios b/a correspond to the absorb-
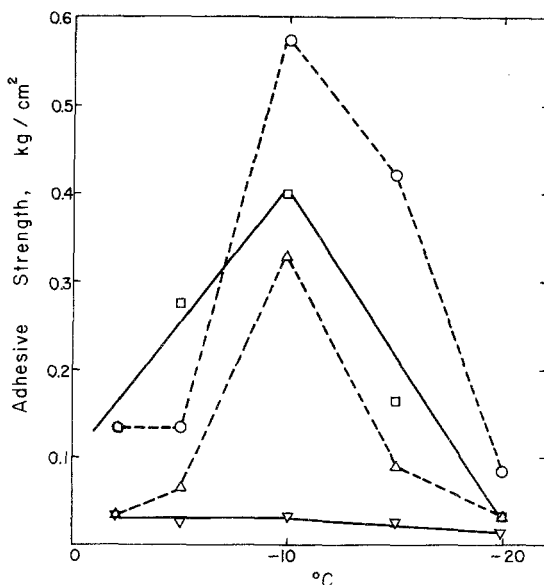

Fig. 11. Adhesive strength (kg/cm²) as function of temperature (concrete substrates). Sample: DP siloxane) = 20, polycarbonate 35 wt. %, $T_g = -66\,°C$. ○ without recoating after each abhesion; □ with recoating; △, ▽ ditto with silicone oil
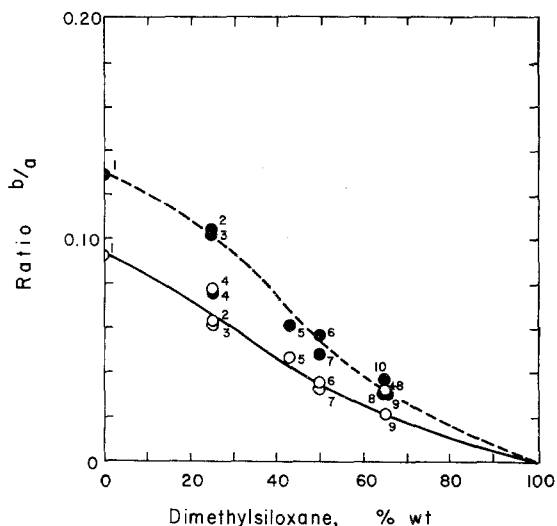
Fig. 12. I. R. Results: Ratios b/a (see text) as function of siloxane wt. %: ○ ATR (I. R. attenuated total reflectance measurements), ● I. R. Transmittance (for numbers see table 1)

ances for 'a' at 2960 cm^{-1} for C–H stretching in CH$_3$ groups for either block component (i.e. polysiloxane and polycarbonate, respectively) and for 'b' to C–H stretching at 3060 cm^{-1} for phenyl groups in polycarbonate. Hence

$$\frac{b}{a} = \frac{\text{C–H stretching in phenyl groups (polycarbonate)}}{\text{C–H stretching in CH}_3 \text{ groups (polycarbonate and polysiloxane)}}$$

If polysiloxane is preferentially situated in the surface then (b/a))Reflectance $<(b/a)$Transmission. This is actually the case as figure 12 shows.

(d) Miscellaneous experiments

A few experiments were carried out with polyethylene. Aluminium plates were dipped in a solution of polyethylene in p-xylene at a temperature somewhat higher than 100 °C. In some cases mineral oil was also dissolved in p-xylene, so that the final coating contained about 10 weight % of mineral oil. The plate was air dried after dipping and further dried under vacuum at 70 °C to 80 °C. Polyethylene consisted of polymer pellets; mineral oil was extra heavy (Rexall). Silanox, a hydrophobic fumed silicon dioxide 101 came from Cabot Co. Polyethylene gave an adhesive strength value of 2.4 kg/cm^2, with 10 weight % of mineral oil the value dropped only to

1.9 kg/cm^2; Autolube from G. E. gave a strength value of 0.04 kg/cm^2 but the ice was sliding indefinitely on the coating. Lexane plus 10 weight % of silanox gave a value of 1.7 kg/cm^2, the block copolymer with 65 weight % of polysiloxane chain length 20 and $T_g = -66$ °C gave with 10% of silanox 0.9 kg/cm^2.

All the coatings tested here are inferior to the polycarbonate-polydimethyl siloxane block copolymers.

In addition the following were tested (see table 2): coatings of penta-decafluoro octyl alcohol, plus 99 weight % of Lexane (polycarbonate) PC 8; Fluorolube S 30 plus 98.7 weight % Lexane PC9; dodecyl sodium sulfonate plus 99 weight % Lexane PC13; oleylamine plus 99 weight % Lexane PC14; Vydack 550 (DuPont) plus 99 weight % of Lexane PC15; 100 weight % Lexane saturated with silicone oil (ca. 20 parts) PC17; Formvar 15/95 E grade, Monsanto: 100 weight % FO; 90 weight % plus 10 weight % CaCl$_2$Fl; 95 weight % plus 5 weight % CaCl$_2$ F2; 99 weight % plus 1 weight % dodecyl sodium sulfonate F4; 99 weight % plus 1 weight % penta-decafluoro-octyl alcohol F5; 99 weight % plus 1 weight % CaCl$_2$ F6; 99 weight % plus 1% Th(NO$_3$)$_4$ · H$_2$O F7; 99 weight % plus 1 weight % oleylamine F8.

The films with electrolyte are so-called self-healing films (table 2, F1, F2, F4, F6, F7). This means that after abhesion the electrolyte

Table 2. Miscellaneous Abhesion Experiments (Al – Substrates, −10 °C)

Coating	Adhesive Strength kg/cm^2 (Mean Values)	Type of Break A-Adhesive, C–Cohesive M–Mixed
PC–8	0.51	A
PC–9	0.77	A
PC–13	0.95	M
PC–14	0.69	M, A
PC–15	0.79	M, A
PC–17	0.55	M, A
F–0	1.18	M
F–1	0.23	A
F–2	0.37	A
F–4	0.72	M
F–5	0.61	M
F–6	0.95	M
F–7	1.67	M
F–8	1.13	M

diffuses again into the polymer/ice interface forming a saturated liquid solution as long as the temperature is above the eutectic point (3).

Discussion

An essential condition for a good abhesive coating is its hydrophobic surface. The ATR experiments definitely indicate that the polysiloxane blocks are preferentially situated in the surface. The above finding is confirmed by experiments carried out by *LeGrand* and *Gaines* (4). These workers prepared films of blends of polycarbonate polymers with small amounts (0.1% to 10%) of dimethylsilicone-polycarbonate block copolymers. The surface properties (e.g. contact angles, frictional coefficients) were those of silicone surfaces at the air/polymer interface and those of polycarbonate at the glass substrate/polymer interface. If the coating substrate was either Teflon (polytetrafluoroethylene) or glass pretreated with silicone, then this interface (e.g. stripping of the film) showed also the properties of a dimethyl-silicone surface.

Very recently *O'Malley* (5) investigated the surface properties of polyhexamethylene sebacate-polydimethylsiloxane block copolymers and blends of the blockcopolymers with the pure polyester hexamethylene sebacate. The surfaces showed in all cases the properties of dimethylsiloxane (i.e. polyblends and pure block-cepolymers). The critical surface tensions according to *Zisman*'s (6) technique were always 22 dyne/cm. The polysiloxane content in the polyblends ranged from 0.01% to 10%; in the block copolymers this content was 19% to 70%. A polydimethylsiloxane film had a critical surface tension of 21 ± 1.0 dyne/cm. According to *Zisman* (6) a critical surface tension of 22 to 24 dyne/cm is characteristic of methyl groups lying in the surface. $-CF_3$ groups in the surface give a much lower critical surface tension, i.e. 6.0 dyne/cm. Polyhexafluorene would be such a polymer. The situation for the siloxane-carbonate block polymer is indicated below.

The experiments indicate that a good hydrophobic surface is not sufficient to give good abhesion. The dimethylsiloxane content must lie in a certain range of weight percent and chain length and the glass temperature must be low. This glass transition temperature is a measure of segment mobility. If the weight content, T_g and chain length are outside the favorable range, then apparently the rheological-mechanical properties of the film become somewhat similar to those of ice and abhesion is decreased. For best results the rheological properties of ice and polymer must be sufficiently different. Addition of silicone oil not only acts as lubricant but also as plasticizer (see figs. 4, 6, 7, 8, 9, 11). Here again the polymer must be in the optimum range of dimethylsiloxane content and chain length, otherwise such addition proves detrimental. These conclusions are supported by the fact that the block copolymer having 65 wt. % of polydimethylsiloxane, chain length 20, plus silicone oil and $T_g = -66\,°C$ is the best for abhesion. The maximum in the adhesive strength-temperature plot must be due to a corresponding change in rheological properties. There may be a secondary transition point close to this maximum; however, this is not known yet.

The sharp increase in adhesion with strain rate beyond a certain value is due to relaxation phenomena, i.e. the time is too short for the materials to give during the available abhesion time. Porosity usually also plays a role in abhesion; however the block-copolymers give films with very smooth surfaces. It is surprising that not even the fluorinated compounds give lower adhesion values than the best block-copolymer with silicone oil (see table 2).

The lowering of adhesion by electrolytes (see table 2) is due to a saturated electrolyte solution layer in the interface as long as the temperature is above that for the eutectic one for the electrolyte (3).

Film Surface
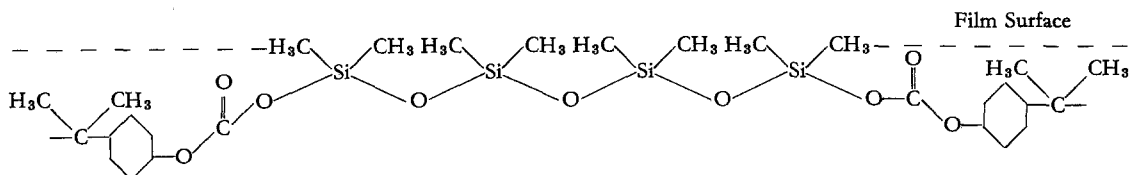
kindly supplying the block-copolymers and information about their characteristics.

Summary

The ice releasing characteristics of a series of polydimethylsiloxane-polycarbonate block-copolymers films have been investigated. The abhesion is not only a function of the hydrophobic nature of the surface of the films but is also dpendent of the polysiloxane content, its block chain length and the glass temperature of the polymer, i.e. it is dependent on the rheological properties of the films relative to ice. Addition of some silicone oil to the films only improves the abhesion of the optimum block-copolymers which have a suitable polydimethylsiloxane composition. The oil acts as plasticizer and lubricant. Attenuated infrared reflectance measurements show that the polydimethylsiloxane blocks lie preferentially in the polymer/air interface, i.e. the methyl groups are located uppermost.

Zusammenfassung

Die eislösenden Eigenschaften einer Serie von Polydimethylsiloxanen-Polycarbonaten Block-Copolymer Filmen wurde studiert. Die Abhäsion ist nicht nur eine Funktion der hydrophobischen Eigenschaften der Filme sondern ist auch abhängig von dem Polysiloxan-Anteil, ihrer Block-Länge und Glas-Temperatur, das heißt sie hängt auch von den rheologischen Eigenschaften der Filme relativ zum Eise ab. Zugabe von etwas Silicon-Öl zu den Filmen verbessert nur die Abhäsion der optimalen Block-Copolymeren, die einen günstigen Polydimethylsiloxane-Gehalt haben. Das Öl wirkt als „Plasticizer" und Schmiermittel. Messungen der Infrarot-Reflektionen zeigen, daß das Polydimethylsiloxan hauptsächlich in der Polymer/Luft-Grenzfläche liegt und im besonderen, daß die Methyl-Gruppen zuoberst liegen.

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