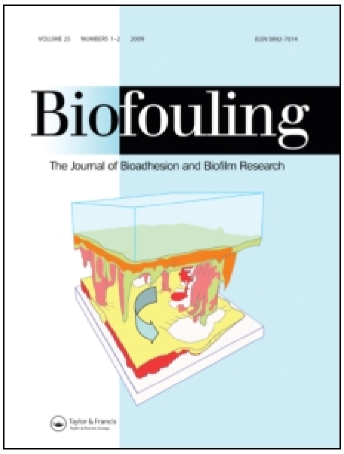

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Structure-Property Relationships of Silicone Biofouling-Release Coatings: Effect of Silicone Network Architecture on Pseudobarnacle Attachment Strengths

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Structure–Property Relationships of Silicone Biofouling-Release Coatings: Effect of Silicone Network Architecture on Pseudobarnacle Attachment Strengths

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Model silicone foul-release coatings with controlled molecular architecture were evaluated to determine the effect of compositional variables such as filler loading and crosslink density on pseudobarnacle attachment strength. Pseudobarnacle adhesion values correlated with filler loadings in both condensation and hydrosilylation-cured silicones. Variation of crosslink density of hydrosilylation-cured silicones had an insignificant effect on attachment strength. X-ray photoelectron spectroscopy (XPS) indicated that the mode of failure upon detachment of the pseudobarnacle was dependent upon the crosslink density; samples with high crosslink density failed cohesively within the silicone.

Keywords: silicone foul-release coatings; pseudobarnacle adhesion; condensation cure; hydrosilylation cure

INTRODUCTION

Biofouling is ubiquitous in the marine environment and compromises the performance of seafaring vessels by decreasing the maximum attainable speed and increasing fuel consumption (Haslbeck & Bohlander, 1997). Application of an antifouling coating to the exposed surfaces of vessels is the most common method to combat fouling (Bleile & Rodgers, 1989). Current coatings comprise heavy metals such as tin or copper and may also contain an organic biocide booster. These coatings function by deterring organismal settlement. The use of tin will be banned in 2008, and copper usage is regulated in some European countries (Walker, 1998). Silicone foul-release coatings are currently under evaluation as an alternative nontoxic technology (Callow & Fletcher, 1994; Brady, 2000; Darkangelo Wood *et al.*, 2000; Truby *et al.*, 2000). Although organisms can attach to silicones, they can be removed either by brushing or by hydrodynamic self-cleaning (Callow *et al.*, 1988; Meyer *et al.*, 1994; Swain & Schultz, 1996). Fouling coverage on silicone coatings is generally less than on other nontoxic surfaces (Swain *et al.*, 1997; Watermann *et al.*, 1997).

The superior properties of silicones have been attributed to their being within an optimum range of critical surface tension (Goupil *et al.*, 1973; Meyer *et al.*, 1995). It has been suggested that the low glass transition temperature (T_g) of silicones as reflected in their molecular mobility may also contribute to their superior fouling-release characteristics (Bausch & Tonge, 1996; Brady, 1997). The modulus of silicones (and by implication, their rheological properties) may also contribute to their efficacy as fouling release surfaces (Kohl & Singer, 1999; Brady & Singer, 2000). Interfacial slippage and friction also play a role in enhancement of release properties of silicones compared with other nonstick surfaces such as fluoropolymers (Newby *et al.*, 1995; Newby & Chaudhury, 1997).

There are many reports on the utility of silicones as foul-release coatings; however, there are few reports

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of the effect of compositional variables of the coating on bioadhesion strength. Truby *et al.* (2000) showed that oil incorporation may prove beneficial in decreasing the adhesion of barnacles and certain species of oysters. Bacterial settlement patterns on silicone coatings amended with oils of various compositions were dependent upon the hydrophilicity of the oil that was incorporated into a silicone matrix (Dalton *et al.*, 2000). Wynne *et al.* (2000) compared the fouling-release performance of a filled condensation-cured RTV (RTV11) with that of an unfilled hydrosilylation system. The attachment strength of barnacles (*Balanus eburneus*) was lower on the *unfilled* hydrosilylation cured coating than the *filled* condensation cured system (RTV11). However, in a separate study Swain *et al.* (1998) compared the fouling release properties of RTV11 with silica filled system (DC3140) and found that the calcium carbonate filled system outperformed the silica filled system. Wynne *et al.* (2000) suggested that the better performance of the calcium carbonate filled coating relative to the silica coating could be attributed to a reduction in the surface modulus of the calcium carbonate filled coating resulting from depletion of the calcium carbonate at the surface upon water exposure. Wynne *et al.* (2000) concluded that a systematic determination of structure property relationships was necessary to fully understand the foul release performance of the coatings.

In order to address the above issues, model systems have been employed in which the molecular architecture of both condensation-cured and hydrosilylation-cured silicone coatings have been controlled and the relationship between coating composition (crosslink density and filler loading) and pseudobarnacle attachment strengths examined.

MATERIALS AND METHODS

Materials and Panel Preparation

Silicone polymers, Karstedt's catalyst, dibutyltinbis (acetylacetonate), fumed silica, tetraethylorthosilicate, calcium carbonate, and SS4155 were obtained from GE Silicones. Aluminum panels were obtained from the Q Panel Company.

Model silicone foul release coatings were prepared as in the following examples. A condensation-curable coating with 0% filler was prepared by combining 100 g of dimethoxymethylsiloxy terminated polydimethylsiloxane (MW = 3100, 0.032 moles) with 3.56 g tetraethylorthosilicate (0.017 moles) and 0.65 g dibutyltin bis (acetylacetonate)(1.5 mmoles). As an example of a filled system, a coating with 13% filler was prepared by combining 87 g of dimethoxymethylsiloxy terminated polymer (0.028 moles), 13 g calcium carbonate (0.129 moles), 3.0 g tetraethylorthosilicate (0.014 moles) and 0.65 g dibutyltinbis(acetylacetonate)(1.5 mmoles). Samples were dispensed onto aluminum panels primed with SS4155 using a doctor blade. Samples were allowed to cure for 7 d under ambient conditions prior to testing.

A masterbatch for hydrosilylation-curable model systems was prepared by combining 200 g of hexamethydisilazane treated fumed silica and 800 g of vinylterminated polydimethylsiloxane (equivalent weight = 4111). The masterbatch was combined with additional vinyl polymer if necessary, mixtures of crosslinkable hydride polymer (equivalent weight = 102) and linear hydride (equivalent weight = 1257) so that the ratio of total hydride to vinyl was maintained at 1.2/1.0. To the mixture was added 10 mg of tetravinyltetramethylcyclotetrasiloxane (0.000023 moles) followed by 10 μl of Karstedt's catalyst (10.9% Pt, 4.8 μmol Pt). The amounts of masterbatch, linear vinyl, linear hydride, and crosslinkable hydride polymers for the different coating systems are given in Table I.

Aluminum panels were coated using the procedure described above for the condensation-curable systems.

Laboratory Testing

The tensile properties of the model foul-release coatings were obtained in accordance with ASTM Method D412, using 1–1.5 mm thick sheets of the cured coating. Contact angle measurements were performed according to literature methods using a Rame-Hart NRL100 goniometer. Critical surface tensions were calculated using Zisman plots (Baier & Meyer, 1992; Meyer *et al.*, 1994; 1997). Surface roughness was determined using a Park Universal Scanning Probe operating in the contact mode at a 1 Hz line scan rate. The rheological properties

TABLE I Composition of hydrosilylation cured model systems

Coating type	Masterbatch (g)	Vinyl polymer (g)	Linear hydride (g)	Crosslinking hydride (g)
16% filler 50/50 hydride ratio	80	5.0	13.5	1.1
16% filler 25/75 hydride ratio	80	10.6	7.28	1.78
16% filler 0/100 hydride ratio	80	17.4		2.56
10% filler 50/50 hydride ratio	50	34	14.5	1.12
5% filler 50/50 hydride ratio	25	58	15.3	1.24

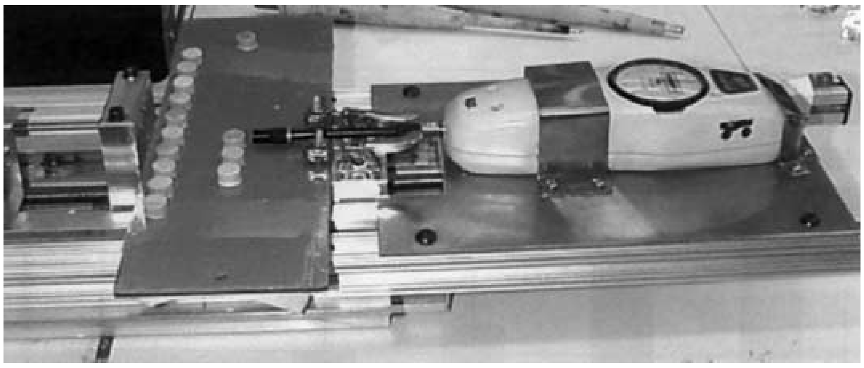


FIGURE 1 Pseudobarnacle adhesion tester.

were obtained on a Rheometrics System IV spectrometer over a frequency range of 1×10^{-1} to $1 \times 10^{2}\,\mathrm{rad\,s^{-1}}$.

Pseudobarnacle Adhesion Tests

Pseudobarnacle adhesion measurements were performed on calcium carbonate filled coatings using ASTM D5618 (Swain *et al.*, 1997). For hydrosilylation cured samples, the tests were modified as follows. Wooden studs of known diameter were glued to the silicone surface using Epoxi-Patch obtained from the Dexter Corporation. The adhesive was allowed to harden for 5 d under ambient conditions before testing. In this case, the force gauge was mounted on a traveling rack that moved at $0.63\,\mathrm{cm\,s^{-1}}$ or $0.08\,\mathrm{cm\,s^{-1}}$ parallel to the coating surface (see Figure 1). From an analysis of variance (ANOVA), the velocity of the traveling rack had no effect on pseudobarnacle adhesion values (probability value $(P) = 0.174$, degrees of freedom $(\mathrm{df}) = 59$).

X-ray Photoelectron Spectroscopy (XPS)

The XPS measurements were conducted in a Surface Science Instruments SSX-100 system, employing a monochromatic Al kα source (600μ spot). A fixed pass energy of 150 eV was used for survey scans, and 50 eV for high resolution scans of individual core levels. The surface charging that occurred due to the nonconductive nature of the samples was neutralized with 1–2 eV low energy electrons from an electron flood gun. Atomic compositions were computed from XPS peaks using empirically determined sensitivity factors derived from measurements on standard materials. The C1s signal was curve fitted using mixed Gaussian/Lorentzian line shapes. The binding energy of the C1s signal from the hydrocarbon at 284.6 eV was used as an internal calibration of the absolute binding energy scale.

RESULTS AND DISCUSSION

Condensation Curable Silicone Coatings

In order to quantify the effect of filler loading on organismal detachment strengths, moisture-curable silicone networks containing 0% to 29% calcium carbonate were prepared by the reaction of dimethylmethylsiloxy endcapped-polydimethylsiloxane with tetraethylorthosilicate and the appropriate filler amount using dibutyltinbis(acetylacetonate) as the catalyst. Pseudobarnacle adhesion values were obtained rather than barnacle adhesion values in order to decrease the standard error in measurement as well as to decrease the experimental time and serendipity of barnacle settlement. Swain *et al.* (1997) showed that over large ranges in organismal adhesion, an excellent correlation existed between pseudobarnacle adhesion strength and barnacle adhesion strength for silicone coatings.

Pseudobarnacle adhesion values were shown to increase as the filler loading increased (see Figure 2, $\mathrm{df} = 99$, $p = 0.000$). As the filler loading increased, the tensile strength of the coating also increased; thus, the higher the tensile strength of the coating, the greater the pseudobarnacle adhesion (see Figure 3). Note that in order to reduce the pseudobarnacle adhesion strength to 1/2 of the highest value, the tensile strength of the coating must be reduced to 1/4. Therefore, coatings with the greatest durability and strength will be the least effective in terms of easy removal of fouling organisms.

Kendall (1971) reported that the release performance of elastomers depended on both the surface energy and elastic properties. He developed the equation below to relate the reversible pull-off force of a stud bonded to thin elastomeric glue:

$$\mathrm{P_c} = \pi \mathrm{a}^2(2\omega_\mathrm{a}\mathrm{K}/\mathrm{t})^{1/2}$$

where $\mathrm{P_c}$, t, ω_a, K and a are respectively, the critical pull off force, thickness of the coating, work of adhesion, elastomer bulk modulus, and contact radius. In his experiments, the detachment rate was

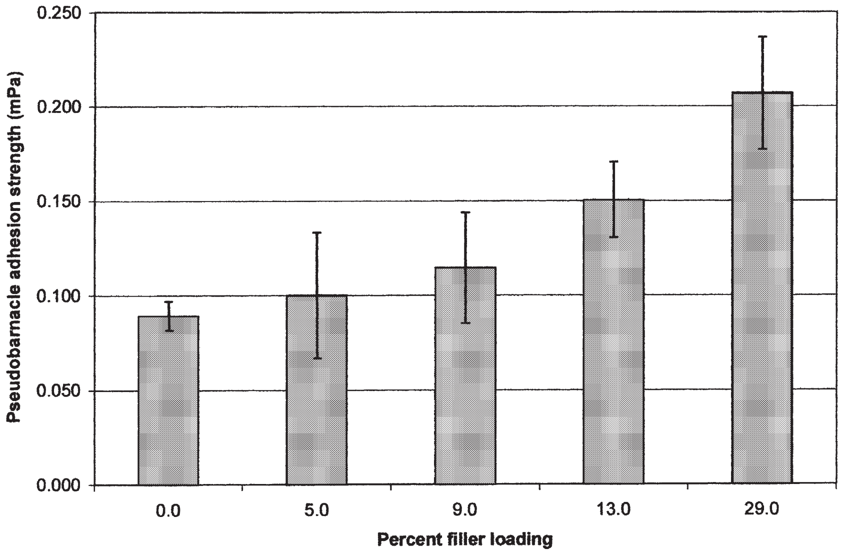


FIGURE 2 Effect of filler loading on pseudobarnacle adhesion strength in condensation-cured systems (df = 99, $p = 0.000$). Error bars = one SD.

essentially zero and therefore, dissipative processes could be ignored. Kohl and Singer (1999) have successfully applied the Kendall equation to silicone duplex coatings, where they demonstrated the thickness dependence of the pull off force.

The present authors have derived an equation to relate the shear pull-off stress with the shear modulus and fracture energy as shown below. In this case, the fracture energy is comprised of reversible (surface energy) and irreversible (dissipative) terms because the tests were not performed at infinitely slow speeds.

$$\sigma_f = (2G_aG'/t)^{1/2}$$

where σ_f is the critical pull-off stress, G_a is the fracture energy, G' is the shear storage modulus at low frequency and t is the thickness of the coating. This equation is analogous to that obtained from the fracture energy analysis of lap shear joints (Wu, 1982). The applicability of this equation is restricted to cases where the radius of the stud was much greater than the thickness of the coating.

The storage moduli (G') were determined independently allowing for the determination of the ratio G_a/t at each filler loading. The storage modulus of the coatings increased with increasing filler loadings; since the thicknesses were essentially the same for all coatings and all surfaces have

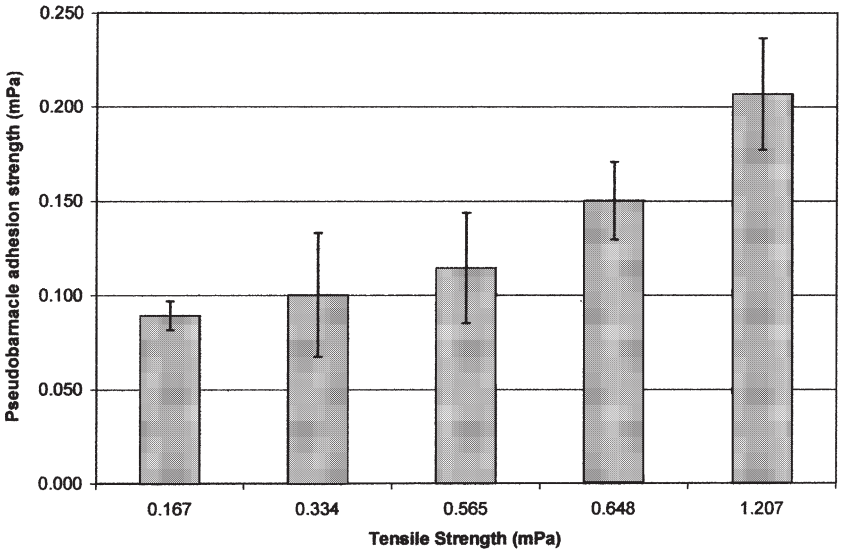


FIGURE 3 Correlation of pseudobarnacle adhesion strength with tensile strength of condensation-cured silicones (df = 99, $p = 0.000$). Error bars = one SD.

TABLE II Model condensation cured coating properties

Filler loading	Storage modulus (G'; mPa)	Tan δ	Psuedobarnacle adhesion strength (σ_f; mPa)	Fracture Energy/thickness (G_a/t; mPa)
0% filler	0.298	0.036	0.09	0.013
5% filler	0.320	0.034	0.10	0.015
9% filler	0.333	0.036	0.11	0.016
13% filler	0.338	0.045	0.15	0.033
29% filler	0.544	0.050	0.21	0.039

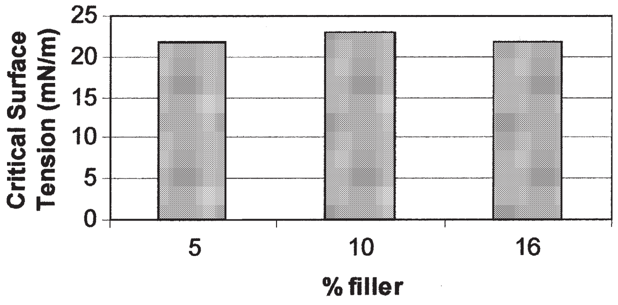
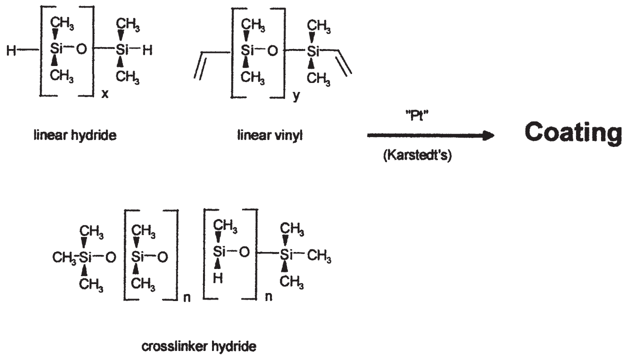


FIGURE 4 Negligible effect of filler loading on critical surface tension of hydrosilylation cured silicone coating.

the same critical surface tension, then any difference in G_a among the samples must be due to dissipative processes. As the filler loading increased there was a corresponding increase in fracture energy. As verification of an increase in dissipative processes as the filler loading increased, a strong positive correlation between the G_a/t and tan δ of the coating was observed ($R_{\text{pearson}} = 0.984$, $p = 0.002$) (Table II). Thus, both the shear modulus of the coating and the dissipative component of the fracture energy increased with increasing filler loading, resulting in higher stresses for pseudobarnacle removal from coatings with higher filler loadings.

Hydrosilylation-Cured Silicone Coatings

Hydrosilylation-cured silicones have the advantage that both the filler loading and crosslink density can be controlled, allowing for a complete description of the molecular architecture. Coatings were prepared according to the scheme below. In this scheme the ratio of crosslinkable poly (dimethyl)(methylhydride)siloxane with multiple hydride groups on the polymer chain and hydride termination was varied between 50/50 and 100/0, while the overall ratio of hydride to vinyl groups was maintained at a ratio of 1.2/1. Filler loadings were also varied from 5 to 16% for the composition that contained a 50/50 ratio of crosslinkable to linear hydride.



Meyer *et al.* (1995) suggested that fouling–release ability is related to the critical surface tension of the coating. Critical surface tension measurements were performed to confirm that the surface energy of the coating did not change upon variation of filler loading in hydrosilylation-cured coatings. No change was observed as the filler level was increased from 5 to 16% (see Figure 4). Surface profiles were

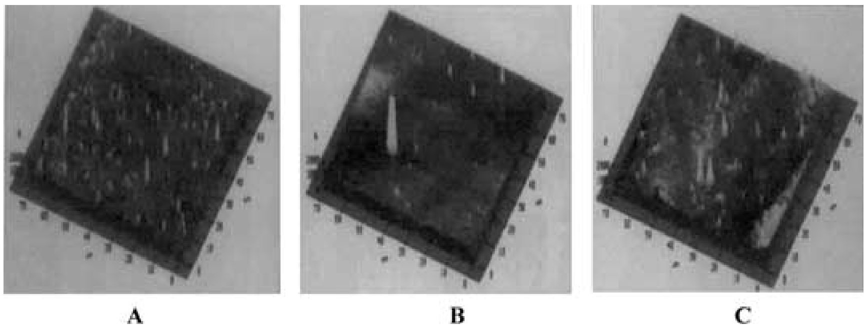


FIGURE 5 Effect of filler loading on surface roughness of hydrosilylation cured silicone coatings. A = 5% filler, rms roughness = 14 nanometers; B = 10% filler, rms roughness = 17 nanometers; C = 16% filler, rms roughness = 19 nanometers.

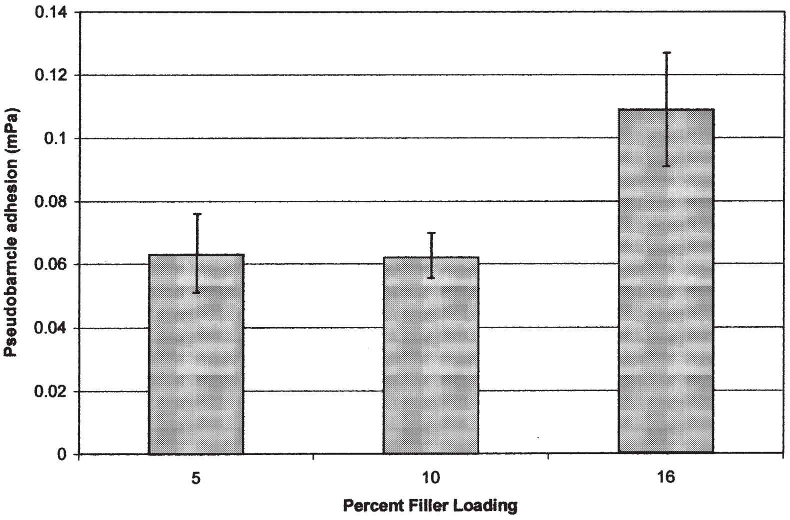


FIGURE 6 Effect of filler loading of hydrosilylation cured silicone coating on pseudobarnacle adhesion (df = 35, $p = 0.000$). Error bars = one SD.

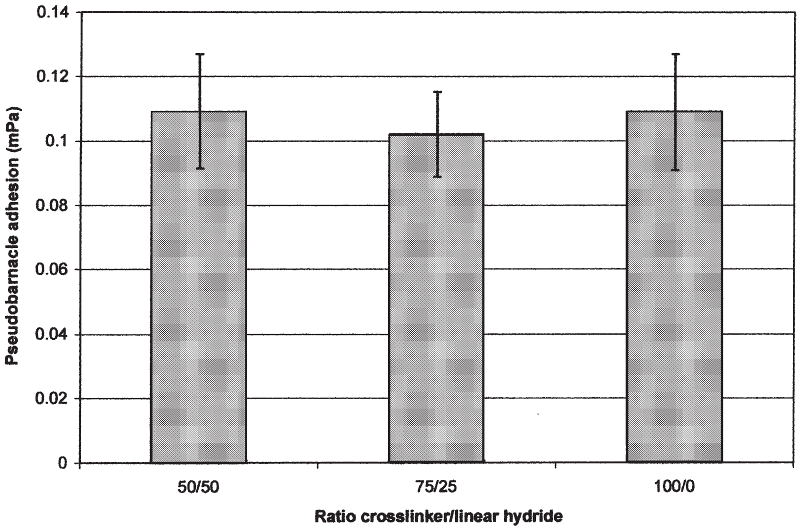


FIGURE 7 Effect of crosslink of hydrosilylation-cured silicone coatings on pseudobarnacle adhesion (df = 35, $p = 0.447$). Error bars = one SD.

also obtained, indicating that filler level had no appreciable effect on surface roughness (see Figure 5).

Variation of the filler loading from 5 to 16% led to a corresponding increase in the pseudobarnacle attachment strength (see Figure 6, df = 35, $p = 0.000$). This result is consistent with the result obtained on condensation cured silicones. The fact that these surfaces have identical critical surface tensions yet exhibit different release properties again implies that other factors beside surface energy are important in defining performance.

The ratio of crosslinker hydride to linear hydride had no effect on pseudobarnacle adhesion values (Figure 7, df = 35, $p = 0.447$). However, this may be explained by the inverse relationship between tan δ and G′ for these coatings (Table III). As the crosslink density is increased, G′ increases whereas tan δ decreases. These opposing forces result in negligible differences in pseudobarnacle adhesion strengths as the crosslink density of the coating is varied.

TABLE III Physical properties of model hydrosilylation cured systems

Filler loading	Crosslinker/linear hydride ratio	G′ (mPa)	Tan δ
5	50/50	0.306	0.005
10	50/50	0.349	0.0100
16	50/50	0.386	0.0200
16	75/25	0.504	0.011
16	100/0	0.592	0.0096

TABLE IV Effect of silicone architecture of hydrosilylation-cured coatings on the failure mode in pseudobarnacle adhesion tests

Filler loading	Crosslinker/linear hydride ratio	Pseudobarnacle adhesion strength (mPa)	% Si (XPS)
5	50/50	0.063 + /− 0.013	6.7
10	50/50	0.062 + /− 0.008	4.8
16	50/50	0.109 + /− 0.018	8.6
16	75/25	0.102 + /− 0.013	12.4
16	100/0	0.109 + /− 0.017	21.8

Berglin and Gatenholm (1999) reported that small amounts of uncrosslinked silicone from both hydrosilylation-cured and condensation-cured silicones are transferred to the pseudobarnacles upon detachment from the surfaces. The failure mode in the present hydrosilylation-cured systems was examined using XPS (Table II). Transfer of silicone to the pseudobarnacles was small at all filler loadings at a constant crosslinker hydride to linear hydride ratio of 50/50. However, the amount of silicone on the pseudobarnacle increased as the crosslinker hydride to linear hydride ratio increased at constant filler loading. At 100% crosslinker hydride, the failure mode is certainly cohesive within the silicone since the amount of silicon present on the pseudobarnacle surface is equivalent to the atomic composition of the silicone (21%). This implies a change in fracture mechanism as a function of crosslink density. Thus, although the adhesion strength is not dependent on crosslink density of the coating, the fracture mechanism becomes cohesive within the silicone as the coating becomes more brittle (Table IV).

CONCLUSION

ANOVA analysis of the attachment strength of psuedobarnacles to model silicone coatings have provided data that suggest that coatings with lower filler loadings will have better fouling-release properties than those with higher filler levels. This result is independent of filler type (silica or calcium carbonate). The most durable coatings contain high filler loadings. Crosslink density had an insignificant effect on attachment strengths of pseudobarnacles but changed the failure mechanism, suggesting that lower crosslink densities are preferred for durable coatings. These results suggest a trade-off between mechanical integrity of the coatings and foul release performance. Research is underway to enhance the fouling-release ability of silicone coatings without compromising durability.

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