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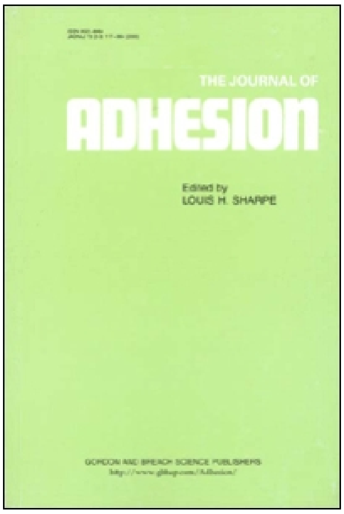

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ESCA Studies of Silicone Release Coatings

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ESCA Studies of Silicone Release Coatings

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X-ray photoelectron spectroscopy (XPS or ESCA) has been used to examine the surfaces of silicone release coatings to shed light on phenomena not adequately addressed by our previous contact angle studies. In most cases, the surface composition of the coatings corresponds to pure polydimethylsiloxane. Other components of the coatings, *e.g.* the emulsifier in the emulsion-based material, are not detected by ESCA. The differences in surface tension between the coatings must be due to other factors, possibly different surface morphologies or low molecular weight constituents that are removed in the high vacuum environment of the ESCA experiment. Delamination has little effect on the surface composition of the silicone coatings but some transfer of silicone to the adhesive occurs in all cases during the release process. The amount transferred increases as the crosslink density of the coating decreases. However, the release force also increases suggesting that bulk effects are more important than surface effects.

INTRODUCTION

We recently published some surface tension values for cured polydimethylsiloxane (PDMS) coatings using the Kaelble contact angle approach based on the use of the Owens–Wendt equation.[1] The average value obtained was 20.3 $\mathrm{mNm^{-1}}$ with a polar component of 1.0 $\mathrm{mNm^{-1}}$ and a dispersion force component of 19.3$\mathrm{mNm^{-1}}$. This value agrees well with other PDMS studies in the literature.

The same approach enabled us to calculate interfacial properties, such

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as the contact angle, between these coatings and pressure sensitive adhesives.[2] This is relevant to the familiar use of such coatings as release liners for adhesive labels. We found that only in certain limited cases was any correlation observed between the surface properties and the measured release force. In general the release process was not simple adhesive failure but was complicated by other phenomena such as transfer of material across the interface. There were also a few inexplicable aspects of the contact angle study, particularly the lowering of the silicone release paper surface tension after delamination from the adhesives in some instances.

Remaining questions and concerns that were not adequately addressed by our contact angle studies fell into two main areas as follows:

A) Are the differences in surface tension between various silicone release coatings significant? *e.g.*, does the high polar component of the emulsion-based material imply presence of emulsifier molecules (PVA) in the surface? Do the most highly crosslinked solventless systems have different surface compositions to the more open solvent-based systems?

B) Can the transfer of material across the interface on delamination, that is evident in some cases, be quantified? Is transfer or interpenetration related to the low silicone surface tensions encountered on delamination with the solvent-based materials?

A more chemically discriminating technique than contact angle for examining these surfaces was required to make further progress. We chose X-ray photoelectron spectroscopy (XPS or ESCA) because of its surface sensitivity, providing data from *ca.* the top 5 nm of the materials, and its ability to quantify surface atomic composition. In particular, the element Si would be diagnostic of silicone transfer to the adhesive.

Six of the coatings studied in our earlier publication[1] were characterized by ESCA to answer questions in category A above. For the effect of delamination study, category B concerns, we chose one example each of the three systems used to produce these silicone release coatings: solventless, emulsion and solvent application. This choice also spans the range of crosslink densities available in the coatings. This is valuable as the best known correlation between release force and coating structure is with crosslink density.[3] One standard adhesive was selected for this study and the surface composition of both the adhesive and the silicone release coating determined before and after lamination together. Other specific systems were examined to address particular issues; these are described later.

EXPERIMENTAL

We favor the use of the Owens–Wendt equation with five contact angle test liquids: water, glycerol, methylene iodide, α-bromonaphthalene and *n*-hexadecane. Our reasons for these choices are given in an earlier publication.[1] Two of these liquids affect the coatings. Methylene iodide marks some of the coatings although its contact angle does not change with time. Hexadecane swells all the coatings giving a contact angle that diminishes with time. The value extrapolated to zero time was used in this case.

The following commercially available Dow Corning® brand paper coatings were used:

Syl-off® 7044 paper coating
Syl-off® 1171 paper coating
Syl-off® 291 paper coating
Syl-off® 292 paper coating
Syl-off® 294 paper coating
Syl-off® 23 paper coating

All are based on polydimethylsiloxane. The first material is a solventless product, the next is applied as an emulsion and the rest are solvent-based materials. The coatings were applied to James River Paper Company super-calendered 40 lb kraft. Coating technique, adhesive lamination and release testing were done in a standard manner similar to that described by Gordon and Colquhoun[4] except a peel rate of 30.5 cm per minute was chosen. A Scott horizontal release tester using a 180° peel configuration was used. These procedures are Dow Corning Corporate Test Methods and are available on request. Curing the silicone solvent based coating involves drying in a forced air oven for 30 seconds at 150°C so very little solvent should remain. The solvent used is a mixture of toluene and heptane. An acrylic adhesive, GELVA® GMS-263 from Monsanto Co. was used as the adhesive in these studies. The toluene–heptane mixture is used as the solvent for the adhesive also. The crosslink densities given in Table III were not directly measured; they are calculated from coating composition.

ESCA data were collected on a cryopumped Perkin Elmer Physical

Electronics Model 550 ESCA/AES instrument with double-pass cylindrical mirror analyzer and a Mg anode X-ray source. Pass energies of 100 eV were used for both the survey and atomic composition multiplex spectra. Raw spectral data were manipulated using Physical Electronics version V MACS software system. Only atomic composition data are reported here; however peak position and shape were also occasionally useful, *e.g.*, the oxidized acrylic carbons in the adhesive gave a distinctive broadening of the carbon multiplex peak on the high binding energy side.

RESULTS AND DISCUSSION

Table I contains the previously reported surface tensions of the silicone coatings and their atomic composition. In every case inspection of the survey spectrum revealed no elements other than C, O or Si. Other elements were occasionally seen in trace quantities when a multiplex spectrum of that particular region was taken, *e.g.*, *ca.* 0.1% Sn, from the catalyst, was seen in the surface of Syl-off® 1171, the emulsion-based material.

Repeatability of the ESCA surface composition on same and different batches of material is ±0.5%. This is similar to the variations observed between the different silicone coatings. From the ESCA standpoint they are all very pure PDMS surfaces with no significant variations that might account for the surface tension differences.

Other studies[5] have shown correlation of contact angle and ESCA

TABLE I

Surface tension and composition of silicone coatings

	Surface tension mNm^{-1}			Atomic composition %		
	σ^d	σ^p	σ Total	C	O	Si
Syl-off® 7044	20.3	1.7	22.0	49.9	25.8	24.3
Syl-off® 1171	17.6	2.5	20.1	50.5	25.2	24.3
Syl-off® 291	17.1	0.6	17.7	50.2	25.4	24.4
Syl-off® 292	20.9	0.7	21.6	50.0	25.2	24.7
Syl-off® 294	16.6	1.5	18.1	49.3	26.0	24.7
Syl-off® 23	19.9	0.7	20.6	49.9	25.2	24.9
Syl-off® 7044 + 20% VR additive	24.9	0.7	25.6	46.0	29.0	25.0
PDMS theory				50	25	25
VR additive theory				37	33	30

data, particularly when receding contact angles were considered. Such receding angles are not determined in the Owens–Wendt approach. Moreover the other studies covered a wider range of contact angle than the present study and were on fluoropolymers not silicones. There are several possibilities that could account for the observed lack of correlation in the present case:

i) The surface tension values derived from the contact angles are not significantly different.

ii) The contact angle technique is detecting differences in the outermost surface layers that are obscured by the *ca.* 5 nm sampling depth of the ESCA technique.

iii) Low molecular weight components, *e.g.* the solvent, in the surface affect the contact angle but are volatilized in the high vacuum ESCA environment and are not detected.

iv) There are morphological differences between the various surfaces that cause the contact angle variations.

The variability of the contact angle data is further examined in Table II. This contains values for two liquids, water and methylene iodide, for those coatings which gave the most divergent results. Also included

TABLE II

Contact angle/surface composition comparison

	Contact angle			Atomic composition %		
	θ_{H_2O}	$\theta_{CH_2I_2}$	σ^a Total mNm^{-1}	C	O	Si
Syl-off® 7044	102	77	19.3	49.9	25.8	24.3
Syl-off® 1171	95	76	20.5	50.5	25.2	24.3
Syl-off® 291	103	75	20.1	50.2	25.4	24.4
Syl-off® 23	98	67	24.5	49.9	25.2	24.9
Unfilled PDMS elastomer[b]	102	69	25.8	50.8	26.2	23.0
Filled PDMS elastomer (Dow Corning® 3110 rubber)	105	67	24.9	52.0	24.7	23.3
Filled PDMS elastomer (Silastic® L rubber) + 40% Dow Corning® 200 fluid, 350 cs.	113	66	27.0	50.2	25.5	24.1

[a] Calculated using Owens–Wendt equation, these 2 liquids only.

[b] Contact angle data from ref. 6, ESCA data from ref. 7. (Samples of different origin).

are other silicone substrates which further extend the observed contact angle range but which would also be expected to provide a PDMS surface. Two of these elastomer samples contain silica filler but contact angle studies indicate that the filler is not present in the surface.[6] The ESCA data in Table II also confirm this point.

Repeatability of contact angles on the same batch of material is ±2°. Different batches of material can sometimes differ by 8–10°. Table II has values that differ by twice this, *e.g.* Syl-off® 1171 (θ_{H_2O} 95°) and the fluid-filled elastomer (θ_{H_2O} 113°) have surface compositions within 0.3% of each other for all three elements, so we do not favor the first reason above as the explanation of the lack of correlation.

The consistent good agreement with the PDMS composition suggests that the second and third possibilities are not the case, particularly as, apart from one solvent heptane, none of the components (catalysts, PVA emulsifier in the emulsion-based material, toluene) are as surface active as PDMS. Curing at 150°C should remove the heptane.

We favor the fourth reason. Increasing roughness would make angles greater than 90° larger and angles less than 90° smaller. To a certain extent this is so, the higher values of the water contact angle tend to be associated with the lower values of the methylene iodide contact angle. Moreover, from electron microscopy studies[8] we know that different silicone paper coatings have different morphologies. The underlying fibrous structure of the paper is very evident with non-uniform silicone distribution in some instances and even holes created by trapped water during cure of an emulsion-based coating. Elastomers will replicate the roughness of the mold material so any generalization is impossible. All that can presently be said is that the surface morphology of the elastomers is very different to that of the paper coatings and the contact angle differences may well originate in the morphological differences. Controlled roughness studies have yet to be attempted.

The emulsion-based material, Syl-off® 1171, contains PVA emulsifier and we had wondered if its high polar component of surface tension was because some PVA was in the surface. The ESCA data do not support this hypothesis. We have found very few materials that will share the surface with PDMS. One such material is listed in Table I. This proprietary variable release (VR) additive is included because it is one of the few instances we have noted where a correlation is seen between surface properties and release force.[2]

Table III contains the results of the delamination study for three of the coatings chosen to cover the three types of coating application and

TABLE III

Effect of delamination on surface properties and composition

	Atomic composition %				Surface tension mNm^{-1}			
Delaminated pairs	C	O	Si	Δ Si change on delamination	σ Total	Change on delamination	Release Force Nm^{-1}	Calculated crosslink density (units per crosslink)
Syl-off® 7044	50.3	24.8	24.9	0.6	20.8	1.2	11	30
adhesive	79.0	20.4	0.7	0.6	27.2	7.7		
Syl-off® 1171	51.1	25.4	23.3	1.0	19.8	0.3	14	200
adhesive	78.1	20.4	1.5	1.4	30.8	4.1		
Syl-off® 23	49.9	25.1	25.0	0.1	14.1	6.5	32	1700
adhesive	77.1	19.8	3.0	2.9	28.0	6.9		
Syl-off® 7044 + VR additive	47.5	27.9	24.6	0.4	Not measured		60	—
adhesive	65.5	26.6	8.0	7.9	Not measured			
Unlaminated adhesive	80.5	19.4	0.1					

to span the available range of crosslink densities, as calculated from the coating composition. The delaminated surfaces of the solventless and solvent-based silicone coatings are insignificantly different from the PDMS composition. The emulsion material is significantly changed. The laminating process involves conditioning at 70°C for 20 hours and this may have allowed sufficient mobility for PVA molecules to diffuse into the 5 nm surface region.

The most notable feature of Table III is the Si levels on the delaminated adhesive, good evidence of silicone transfer across the interface. This is barely significant with the most highly crosslinked coating but increases as crosslink density decreases. Reduction in the number of crosslinks increases the chance of unreacted chains not bound to the network so this trend is in the expected direction. However, it is not so easy to reconcile this observation with the increase in release force with reduced crosslink density.

Unreacted PDMS might be expected to form a weak boundary layer and contribute to a reduction in release force. Some other factor must thus be affecting the release process. One likely possibility is the Lake–Thomas effect.[9] This has been used to account for differences in adhesive strength of elastomers[10] and may be relevant to the release situation also. In less crosslinked systems a greater number of bonds must be stressed in order to cause chain rupture and subsequent adhesive failure. We suggest this effect might operate in the physical release situation where more bonds must be stressed in order to cause separation between chains in the less highly crosslinked systems and consequently more work has to be put into the process of separation.

The large differences between measured release force and the thermodynamic work of adhesion[2] also may imply that bulk effects such as viscoelastic deformation of the coating, that would be expected to be a function of its crosslink density, are more important than the surface effect. This seems to be the case in the mechanism of adhesive failure of polydimethylsiloxane elastomers.[6,11]

To put these degrees of silicone transfer in perspective it should be remembered that the ESCA technique samples a depth of *ca.* 5 nm. This is ten times the thickness of a monolayer of extended chains of PDMS.[12] Thus a transfer of one such monolayer would contribute a Si level of 2.5% (1/10th of 25%) similar to the amount transferred in the lowest crosslink density case, the solvent-based coating. In reality a partial coverage of a more coiled PDMS structure is more likely than this idealized extended monolayer configuration.

Table III also contains surface tension data for the delaminated surfaces. Reductions in surface tension of the adhesive are consistent with silicone transfer to the adhesive. However, the smallest amount of transferred silicone is associated with the greatest change in adhesive surface tension. These delamination results cannot be readily explained, particularly the low surface tension value for the solvent-based coating after delamination. No component of the PDMS coating, adhesive, or either solvent if retained in the laminate, could account for such a low value. The ESCA study shows it to have as pure a PDMS surface region as any coating we have examined.

The VR additive data in Table III are interesting. Surface tensions on delamination were not measured but the ESCA data show considerable transfer of silicone to the adhesive. The shift in composition of the silicone coating surface towards a more PDMS-like composition implies that it is the additive that is transferred. Thus, although the surface properties and release force correlate when this additive is used, we were wrong earlier[2] when we ascribed this agreement to true adhesive failure. Such is clearly not the case in the light of the new ESCA data.

Another way of varying crosslink density is to deliberately undercure, *e.g.* by lowering cure temperature, and then examining the coating over a period of time as room temperature curing slowly proceeds. This was done for a solventless coating by curing for 20 hours at 70°C. The material was then laminated against the acrylic adhesive as before, the

TABLE IV

Effect of aging prior to lamination on undercured coating

	Atomic composition %				Days elapsed after cure before lamination	Release force Nm^{-1}
	C	O	Si	Δ Si		
Delaminated pairs						
Silicone coating	50.1	25.8	24.0	0.2	0	120
Adhesive	69.2	21.9	9.0	9.0		
Silicone coating	49.8	25.7	24.4	0.1	3	40
Adhesive	77.6	20.1	2.3	2.3		
Silicone coating	50.4	24.8	24.7	0.1	5	16
Adhesive	80.0	18.9	1.0	1.0		
Unlaminated substrates						
Silicone coating	50.0	25.8	24.2		0	
Silicone coating	49.4	26.1	24.5		3	
Silicone coating	49.8	25.5	24.6		5	
Adhesive	80.8	19.2	0			

only variable being the post-cure time elapsed before laminating. These results are shown in Table IV. As the post-cure time increases the crosslink density should also increase. As with the other studies reported here this causes a reduction in the amount of silicone transferred across the interface during the release process and a reduction in the force required to effect that release.

CONCLUSIONS

Some of the questions raised by the contact angle study have been answered by ESCA. Transfer of silicone to the adhesive on delamination does occur and can be readily quantified with ESCA by monitoring the element Si. The degree of transfer increases as the crosslink density decreases. This is associated with an increase in release force and implies that in this case surface effects are less important than bulk effects. No significant differences in ESCA composition are seen between the various silicone release coatings; they are all essentially pure PDMS surfaces. Other possible components such as catalysts, the PVA emulsifier in the emulsion-based coating, or retained solvent in the solvent-based coating, are not detected in the surface region. Only in rare instances, such as with the VR additive, are surface compositions detected that are different to PDMS. The ESCA study has not explained the differences in surface tension derived from contact angle study of the PDMS coatings. We believe that these differences are most probably related to different surface morphologies rather than low molecular weight components such as solvent retained in the contact angle study but removed in the high vacuum of the ESCA experiment.

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