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Adhesive strength of silica filled polyacrylic acid coatings

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ADHESIVE STRENGTH OF SILICA FILLED POLYACRYLIC ACID COATINGS

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

by

Louis Ou

May 2001

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APPROVED FOR THE DEPARTMENT
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ABSTRACT

ADHESIVE STRENGTH OF SILICA FILLED POLYACRYLIC ACID COATINGS

by Louis Ou

The adhesive strength of silica filled polyacrylic acid coatings was determined as a function of the silica content. Tape adhesion test and Sebastian V were used to measure the adhesive strength. The coating adhesive strength was found to be good and rather insensitive to silica content up to 60 weight % silica, after which it degrades quickly toward zero. The results also showed the adhesive strength to be lower than the cohesive strength from 0 to 70 weight % silica. Beyond 80 weight % silica, the adhesive strength was found to be greater than the cohesive strength. These results were significant since no adhesive strength data or model on silica filled polymer coatings was previously available. They may also enable mechanical integrity optimization of pressure sensitive paint, which is a very high silica content polymer coating used to measure air pressure in wind tunnel tests.

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Chapter I

Introduction

A polymer composite is a combined material created by the assembly of two or more components - a selected filler and a compatible polymer matrix binder - in order to obtain specific characteristics and properties. The filler acts as a reinforcing agent while the polymer binder holds the filler together and protects it from adverse environmental effects. The filler material can be fibers, particles, or whiskers. The components of the composite do not dissolve in each other but act in concert. The resulting property of the composite is synergistic^[1].

The simplest technique to fabricate a composite is called lay-up molding, or contact laminating. This application involves laying the dry reinforcement, which is the chosen filler, into the mold and then applying the polymer matrix. The wet composite is rolled to distribute the polymer matrix uniformly and to remove air pockets. The composite hardens as the solvent evaporates from the polymer matrix. Another layer of reinforcement is then laid on the top, after which more polymer matrix is spread over the reinforcement^[2]. In other words, the filler is saturated with the liquid binder and the lay-up is made by building sequential layers to obtain the desired final thickness.

In addition, the polymer binder can also be fused, mixed with the filler, and then applied to a mold. Alternatively, the polymer binder can be dissolved in a solvent and mixed with the filler that remains insoluble, but well distributed in the polymer solution. The composite is then formed by extrusion or applying the mixture to a mold. In both

cases, the composite solidifies and hardens as the solvent evaporates from the polymer binder.

Pressure sensitive paint (PSP) is a very high silica content polymer composite coating used to measure air pressure in wind tunnel tests. Pressure is one of the fundamental physical quantities of aerodynamics, and is frequently monitored in wind tunnel tests. The traditional pressure measuring technique uses a series of pressure sensing taps, or pressure orifices, which are tedious, time consuming, and expensive to mount, plus provide a poor representation of the pressure distribution map of the target surface. It often takes up to 30% of the total cost of an aircraft wind tunnel model, which amounts to the order of \$150,000 to \$300,000^[3].

PSP phosphorescent upon ultra violet light radiation and the phosphorescence is oxygen sensitive. In this application, luminophor such as octaethylporphyrin (PtOEP) is often contained in a uniform thin coating of silica filled polymer composite that is spray painted onto the target object^[4]. Since the phosphorescence responds to oxygen partial pressure, the surface pressure can be obtained by video monitoring the emission intensity from the surface^[5]. PSP thus allows real-time pressure monitoring of the target. In contrast to pressure orifices, PSP is inexpensive and easier to apply. In addition, PSP gives continuous pressure mapping on the object surface.

This project is derived from a previous effort by Dr. Art Diaz in the Department of Chemical and Materials Engineering to develop silica filled polymer composite coatings with adequate mechanical properties for PSP use. The effort focused on finding the best composition and formulation for the coating. The coatings with the best

performance used silica of 40 μ m in diameter with polyacrylic acid (PAA) as the binder. The coating contained approximately 95 weight % silica. With such high silica content, the adhesion and mechanical integrity of the coating was an issue^[6].

One can calculate the minimum amount of polymer needed to completely coat the silica particles with a mono-layer coating. This calculation in Appendix A considered monodispersed silica particles of 40 μ m diameter and a mono-layer PAA thickness of 10 nm covering all the silica particles. The calculation indicated that only 0.3 weight % of polymer is needed, which yields 99.7 weight % of silica. Therefore the PSP formulation using 95 weight % silica and 5 weight % polymer had theoretically enough polymer to completely coat all the silica particles.

The objective of this project is to characterize the adhesive strength of silica filled polymer coatings on aluminum substrate. The adhesive strength will be determined for the complete range of silica content. The focus of this project is not the optimization of PSP. The coating materials and processing will be based on the previous study of PSP composition and formulation. The results from this study may enable future optimization of the coating composition and formulation for the best mechanical integrity. The research hypothesis is: the adhesive strength of silica filled polymer coatings on aluminum has a monotonic response to the silica content.

Chapter II

Literature Review

A literature review was conducted to find information on the relationship between composition and properties of particle filled polymer composites. CD Access Network and On-Line Catalog at SJSU library were used to survey for literatures. Twelve relevant articles were found, but none was on the adhesion of polymer composites. In addition, the studies addressed composition only up to 70 volume % (84 weight %) silica. The articles on composite mechanical properties such as shear and elastic modulus, tensile strength, and microhardness were reviewed and are summarized below. These articles may provide insights on correlating the response of the adhesion to silica content.

In a report by Sheldon, some equations for predicting shear modulus in particle filled polymer composites were compiled^[7]. For composites with concentrated elastomeric polymer binder, Equation 2-1 was used by Mooney to describe the influence of filler on shear modulus. Mooney extended Einstein's viscosity equation for an infinitely dilute suspension of spheres to a suspension of finite concentrations. The space-crowding effect of the suspended spheres on each other was taken into consideration. The approach is partly empirical where the interaction parameters are left for experimental determination. No effort was made to obtain their values from hydrodynamic theory^[8]. In Equation 2-1, G and G_1 are the shear moduli of the filled and unfilled polymer, respectively. K_E is Einstein's coefficient and it assumes different values depending on the shape of the filler. The value 2.5 is for spherical particles. The

volume fraction of the filler is v_2 . The maximum packing fraction is v_m and the value 0.74 is for hexagonal close packing and 0.524 is for simple cubic packing, etc.

$$\ln G/G_1 = K_E v_2 / (1 - v_2/v_m) \quad (2-1)$$

Figure 2-1 compares Equation 2-1 with monodisperse experimental data by V. Vand and polydisperse experimental data by H. Eilers^[8]. The predictions are in very good agreement with experimental data for spherical particles. Equation 2-1 appears to be useful in predicting shear modulus.

Figure 2-1. Mooney theoretical prediction comparing to experimental data by Vand (x) and by Eilers (o). (Modified from reference 8)

Van Der Poel simplified Equation 2-1 to Equation 2-2 for the special case of the filler and polymer respectively taking on values of Poisson's ratios 0.25 and 0.5^[9].

$$G/G_1 = 1 + [1.25v_2/(1 - 1.28v_2)]^2 \quad (2-2)$$

For composites with rigid polymer binders, where the polymer is plastic rather than elastomer (Poisson ratio less than 0.5), and where the moduli of polymer and filler are closer in value, Kerner's Equation by Nielsen *et al.* is proposed as stated in Equation 2-3^[9]. Equation 2-3 was derived from analyzing the effect of a uniform hydrostatic compression and of a uniform tension on an average filler grain. The bulk coefficients of linear expansion of the composite are found by an analysis of the dilatation and bulk stress for average spherical grains^[10]. In Equation 2-3, $A=K_E-1$, where K_E is Einstein's coefficient. $B=(G_2/G_1 - 1)/(G_2/G_1 + A)$, where G_2 is the filler modulus. $X = 1 + v_2(1/v_m^2 - 1/v_m)$.

$$G/G_1 = (1 + ABv_2) / (1 - BXv_2) \quad (2-3)$$

Sheldon's compilation was a useful compilation of theoretical equations for shear modulus of particle filled polymer composites. However, parameters used in the equations, such as v_m , maximum packing fraction, may be difficult to determine exactly.

It is also not clear how well these equations would apply to adhesive strength. More study is thus needed.

Shang *et al.* reported the effects of filler size and surface treatment on the elastic modulus and tensile strength of silica filled polymer composites were studied^[11]. Spherical silica particles of 0.6 and 0.014 μm in diameters were blended with ethylene-vinyl acetate (EVA) copolymer (72 weight % ethylene and 28 weight % vinyl acetate). Silica surface treatments included heat and a combination of heat and exposure to trimethylchlorosilane (TMCS). Figure 2-2 shows the elastic modulus as a function of silica volume percentage for silica particle size of 0.6 and 0.014 μm ^[10]. Composites with both sizes of silica showed higher elastic moduli than the unfilled EVA and the effect was twice as big with 0.014 μm than 0.6 μm silica. In a particle filled polymer matrix, the bonded and adsorbed polymer chains became stiff due to loss of their flexibility and resulted in the higher elastic modulus. The heat-treated silica composites had higher moduli than the heat/TMCS treated silica composites. With identical silica content, the composites with finer silica had higher moduli. This was likely due to the additional surface area provided by finer silica, which results in better bonding with the polymer binder.

Figure 2-2. Effect of silica volume fraction on elastic modulus. (Modified from reference

11)

Figure 2-3 shows the tensile strength as a function of silica volume percentage for silica particle size of 0.6 and 0.014 μm ^[11]. The composites with 0.6 μm silica had lower and decreased tensile strength than the unfilled EVA polymer. This indicates that silica with this size weakened the polymer. In contrast, the composites with the finer 0.014 μm silica showed improved tensile strength, at least for silica volume fractions of 15 volume % or less. At lower silica fractions, the tensile strength improved with increased silica

volume %, to a maximum at approximately 4 volume %. The tensile strength then declined but stayed higher than unfilled EVA polymer at least till 15 volume %. Composites containing heat treated silica had higher tensile strength than those containing heat/TMCS treated silica.

Figure 2-3. Effect of silica volume fraction on tensile strength. (Modified from reference 11)

Guth-Smallwood Equation, stated in Equation 2-4, was used to predict the elastic modulus of the composite. The equation assumes the modulus behavior as a linear function of filler content at low concentration and as a power series at higher

concentration^[12]. E is the elastic modulus of the composite. E_p is the elastic modulus of the unfilled EVA. V_f is the volume fraction of silica.

$$E = E_p (1 + 2.5V_f + 14.1V_f^2) \quad (2-4)$$

The study by Shang *et al.* on elastic modulus and tensile strength with different silica sizes and content were plausible. Elastic modulus increased with higher filler loading. Tensile strength behaved differently depending on the filler size. Heat/TMCS treated silica was less effective than silica with only heat treatment. The study did not extend beyond 20 volume % silica. In addition, how well adhesive strength tracks elastic modulus and tensile strength with various silica contents is unknown.

Pope *et al.* studied the elastic modulus of transparent silica polymer composites. Transparent silica polymethylmethacrylate (PMMA) composites were prepared by the impregnation of porous silica gels with organic monomer and polymerization in situ^[13]. The silica gel is formed by hydrolysis and polymerization reactions in liquid solution at temperature near ambient. After gelation, the gel is dried and heat-treated, rendering a porous solid or a dense glass or ceramic. The porous silica gel is then impregnated with organic monomer, methyl methacrylate, followed by in situ polymerization. The resulting composite is transparent since the phase dimension between the silica and polymer is on the order of 100 angstroms, much smaller than the wavelengths of visible light (3700 to 7000 angstroms). As shown in Figure 2-4, elastic modulus increases with higher silica content^[13].

Figure 2-4. Elastic modulus versus silica volume fraction. (Modified from reference 13)

For composites with a significant disparity in the moduli between filler and binder, Pope proposed that the composite elastic modulus approaches an inverse exponential relationship and the relationship is approximated by Equation 2-5^[13]. In Equation 2-5, E_c and E_s are the elastic moduli of the composite and silica respectively. V_p is the volume fraction of PMMA, and b is an empirical factor equals 2.45.

$$E_c = E_s \exp (-bV_p) \quad (2-5)$$

Pope's proposed relationship for elastic modulus is incomplete since it does not account for the polymer modulus. In addition, few experimental data points were collected and they are primarily in the 50 silica volume % region. Most of all, the silica used in this study was treated such that it became a porous ceramic. Since porous ceramic would have different mechanical properties than particle silica, composites

formed with porous silica ceramic would behave differently from ones formed with particle silica.

Farquhar *et al.* studied the elastic properties and microhardness of silica filled epoxy^[14]. Anhydride cured cycloaliphatic epoxy was blended with 25 μ m sized silica particles. The silica content varied from 0 to 60 volume %. Acoustic wave speed measurements were used to obtain elastic module and Vickers microhardness measurements were used to attain microhardness. Both elastic modulus and microhardness increase with higher filler content. Elastic modulus was found to be as high as 17 GPa. The experimental results were correlated with an analytical model by Christensen and Lo which approximated the structure of a composite with filler particles having an aspect ratio of about one. The model assumed the particles well dispersed, well bonded to the matrix, and randomly oriented. Figures 2-5 shows the elastic module and microhardness results^[14]. The dashed lines are the predicted responses from Christensen and Lo's model.

The study by Farquhar *et al.* clearly points out that both elastic modulus and microhardness increase with higher silica content. However, data points were only provided up to 60 volume % silica and concentrated around 25 and 55 volume %. No details were provided on the calculations based on Christian and Lo's model.

Figure 2-5. Elastic modulus and microhardness for a range of filled epoxy encapsulants.

(Modified from reference 14)

One report on adhesive strength was found. Avery presented a nondestructive paint adhesion prediction meter (APM) for metal surfaces^[15]. The device works by reading the surface roughness of metal surface. A proprietary synthetic elastomer pad, acting like Velcro, is pressed against the metal surface. The elastomer is very sensitive to microscopic changes in the porosity of the surface. The force required to pull the pad off the metal surface is then compared to the readings from metal surfaces with known good adhesion.

Masking tape paint pull test and epoxy stud paint pull test were used to validate the result from APM. For masking tape paint pull test, painted aluminum is scribed to form cut squares. Masking tape is then adhered to the painted surface and pulled off. The amount of paint remaining indicates the adhesive strength. For epoxy stud paint pull test, an aluminum pull stud with epoxy is adhered to the paint surface. The force needed to pull the paint off the aluminum surface is measured.

Results from APM compared favorably with outcome from masking tape paint pull test and epoxy stud paint pull test. This report shows the importance of surface roughness' effect on paint adhesion. Moreover, it brought up two common paint adhesion test used in the industry, masking tape paint pull test and epoxy stud paint pull test. Both methods would be useful in testing the adhesive strength of silica filled polymer composite coatings.

Summary

The survey of the literature revealed some studies on mechanical properties of silica filled polymer composites such as elastic modulus, tensile strength, and hardness. Equations were presented to predict the elastic modulus with particle fillers. Generally elastic modulus increases with higher silica content. The effect of silica filler on tensile strength varies depending on the silica size. Finer silica is better reinforcing fillers. However, the studies are far from complete or comprehensive. Most studies emphasized the low silica content region since the silica was generally used to reinforce the composites. Few studies addressed silica content region beyond 70 volume % (84 weight %) and very limited experimental data was available beyond 60 volume % (77 weight %). The relationship between adhesive strength and mechanical properties is unknown. Table 2-1 summarizes the studies.

No significant work has been reported on the adhesive strength of silica filled polymer coatings. Avery's report on paint adhesion gave insights on the two common adhesion test used in the industry, masking tape pull test and epoxy stud pull test. To

better understand the adhesive strength of silica filled polymer composite coatings with high silica content, more research is needed.

Table 2-1. Literature review summary.

Author	Materials	Range Studied, silica vol % (wt %)	Response to Increased Silica Content
Sheldon	N/A	0 – 70 % (0 – 84 wt %)	Shear modulus increased
Shang <i>et al.</i>	silica 0.6 μ m / EVA	0 – 20 % (0 – 35 wt %)	Elastic modulus increased Tensile strength decreased
	silica 0.014 μ m / EVA		Elastic modulus increased Tensile strength increased, peaked at 4 % (8 wt %)
Pope <i>et al.</i>	silica gel / PMMA	25 – 70 % (43 – 84 wt %)	Elastic modulus increased
Farquhar <i>et al.</i>	silica 25 μ m / epoxy	0 – 60 % (0 – 77 wt %)	Elastic modulus increased Microhardness increased

Chapter III

Experimental Procedure

The coating materials and processing used in this project were based on the previous study of PSP composition and formulation in the Department of Chemical and Materials Engineering. Zero to 95 weight % of silica filled polymer coatings on aluminum plates were prepared. Adhesive strength of the coatings were determined with tape adhesion test and Sebastian V strength testing system and analyzed with respect to silica content.

1. Materials

Silica 7 from J. T. Baker was used for the silica filler. It is a nominally spherical silica powder with particles sized 40 μ m. PAA was used for the polymer binder. Carbopol 678 (PAA) from BFGoodrich Co. was selected. It was available in powder form and was used as received. Kaolin (china clay) from J. T. Baker was used to increase the bonding between silica and PAA^[6]. It was also in powder form and used as received. Aluminum plates were used as the substrate for the coatings. Aluminum was chosen since it is often the surface of interest in wind tunnel tests.

2. Processing of Silica/PAA Coatings

2.1 PAA Gel Formulation Carbopol 678 was slowly added to de-ionized water in a ratio of 1:20 (PAA:water) while stirring. The mixture was then stirred for an additional 2 hours with an air driven stirrer at high speed. Air drive stirrer was used instead of

magnetic stirrer because the latter is not effective for viscous gels. The resulting mixture was a clear viscous gel. The pH of the gel was measured using Insta-Chek 0-13 (pH paper) and the gel was acidic with pH 4. Ten percent NaOH (wt/vol.) solution was added drop wise until the pH was 7. The neutralization strengthens the gel's binding capability to form a good coating^[6]. The gel thickened but remains clear.

2.2 Silica Slurry Preparation Silica 7 was mixed with de-ionized water in a ratio of 1:4 (silica:water) to make a slurry. The mixture was stirred with a glass rod until a smooth slurry was formed. Kaolin was prepared in similar fashion and ratio (1:4 Kaolin:water) to form a Kaolin slurry.

2.3 Silica/PAA Composite Formulation The silica slurry was mixed with the PAA gel and the mixture was stirred with an air driven stirrer at high speed for 1 hour. The Kaolin slurry (1/10 the amount of silica slurry) was then added to the mixture. The silica/PAA/Kaolin mixture was stirred for another hour. The final mixture was a white, smooth, viscous slurry. Table 3-1 lists the experimental sample compositions. The samples had silica contents ranging from 0 to 95 weight % (0 to 90 volume %). The relevant calculation of the sample composition can be found in Appendix B.

Table 3-1. Composition of silica/PAA coating samples.

Silica Wt. %	Silica Vol. %	Silica Wt., g	PAA Wt., g	PAA : Silica
0	0	0.000	0.500	pure PAA
5	2	0.026	0.500	19.000
10	5	0.056	0.500	9.000
15	7	0.088	0.500	5.667
20	10	0.125	0.500	4.000
25	13	0.167	0.500	3.000
30	16	0.214	0.500	2.333
35	20	0.269	0.500	1.857
40	23	0.333	0.500	1.500
45	27	0.409	0.500	1.222
50	31	0.500	0.500	1.000
55	36	0.611	0.500	0.818
60	40	0.750	0.500	0.667
65	46	0.929	0.500	0.538
70	51	1.167	0.500	0.429
75	58	1.500	0.500	0.333
80	64	2.000	0.500	0.250
85	72	2.833	0.500	0.176
90	80	4.500	0.500	0.111
95	90	9.500	0.500	0.053

2.4 Silica/PAA Coating Preparation

Aluminum plates were cut into rectangles of 1½ by 2½ inch. They were washed with soapy water, and then rinsed with acetone.

Acetone was effective in rinsing off grease from human handling and other contamination sources. The silica/PAA/Kaolin mixture was then poured onto the aluminum plates. A glass rod was used to spread the mixture evenly across the plates. The mixture was left to air dry and cure for approximately 8 hours.

The silica/PAA/Kaolin mixture was stored to determine its shelf life. No settling of the mixture was observed after 8 days and after a total of 3 weeks. At the end of the third week, the mixture was stirred and poured on aluminum plates to test the coating. The resulting coatings appeared as good as with freshly prepared ones. Thus the silica/PAA mixture has a good shelf life. The use of drinking water in the preparation, instead of de-ionized water, also appeared to have no effect on the resulting coating.

3. Adhesive Strength Measurements

To obtain qualitative readings of the adhesive strength, tape adhesion test was applied on coatings with silica weight % range from 0 to 95 in increments of 10 percent. Tape adhesion test is similar to the masking tape pull test reported by Avery^[15]. It is ideal for conducting adhesion test on coatings applied to a flat, uniform surface.

To quantitatively measure the adhesive strength, a Sebastian V tester from Quad Group was used. Sebastian V is an automated, non-hydraulic electro-mechanical strength testing system, similar to the epoxy stud pull test reported by Avery^[15].

3.1 Tape Adhesion Test Tape Adhesion Test Kit from Paul N. Gardner Company, Inc. was used. It complies with ASTM Test Method D3359 and DIN Standard No.

53151^[16]. The main components of the kit include a blade holder with nylon guide, multiple tip cutter, and tape – Permacel #99. Figure 3-1(a) illustrates the kit and Figure 3-1(b) shows a close up illustration of the tip cutter. A tip cutter with a tip spacing of 1.5 mm was used.

Figure 3-1. (a) Tape Adhesion Test Kit from Paul N. Gardner Company, Inc. (b) Close up illustration of a 1.5 mm tip cutter. (Modified from reference 16)

For this test, the coating sample was placed on a smooth flat base to insure adequate support. The tip cutter was mounted on the handle where the maximum tooth extension was near the nylon guide. The handle assembly was first placed on a coating sample so that it rested on the nylon guide and the rear (narrow end) of the handle. The handle was then raised so that the tip cutter contacts the test surface. The top of the handle was about 15 degree with respect to the test surface as shown in Figure 3-2.

Figure 3-2. Illustration of the relative position of handle assembly to the sample coating.

With enough pressure on the handle to insure that the tip cutter penetrates the coating, the handle assembly was pulled along the test surface for a distance from 0.75 to 1.00 inch. The same procedure was repeated with a second cut intersecting the first pattern at 90-degree angle. A pattern of 49 squares forming one large square was produced on the coating.

Tape was then applied firmly on the diced coating, covering all the squares, and then peeled off slowly. The remaining number of squares of coating on the aluminum substrate was compared to the classification scale for tape adhesion test, as shown in Table 3-2, to obtain a score.

Coatings with weak adhesive strength had a greater number of the squares lifted off by the tape than coatings with higher adhesive strength. A score of 0 is assigned for the case when more than 32 squares were lifted off. A score of 5 is assigned for the case when the coating stayed completely intact. This indicates that the coating adhesive strength to the substrate was at least 200 pounds per square inch (psi)^[16].

Table 3-2. Classification scale for tape adhesion test. (Modified from reference 16)

surface of cross-cut area	none					greater than 32 squares lifted off
classification	5	4	3	2	1	0

3.2 Sebastian V Adhesive Strength Measurement Aluminum pull studs with stud diameter 7/24 inch were used for Sebastian measurements. Commercial Super Glue was used to bond the pull stud to the target coating. A mounting spring clip was used to secure the stud while the glue cured, as shown in Figure 3-3.

Figure 3-3. A mounting spring clip securing the stud bonding to the sample coating.

After the glue cured and the mounting spring clip was removed, the sample coating-pull stud assembly was placed on the pull stack of the Sebastian. The coating sample was placed on the platen on top of the pull stack while the stud was lowered into

the pulling grip chamber. After the grip was tightened, measurement proceeded automatically after pressing the start button. Figure 3-4 is a photograph of the Sebastian strength testing system that was used.

Figure 3-4. Photograph of Sebastian V strength testing system.

Figure 3-5 shows the relative position of the coating sample-pull stud assembly and the applied force. Force was applied on the stud at a constant rate of 0.5 lb/sec.

The force measurement output was displayed in volts. As the adhesive strength of the coating fails, the corresponding maximum voltage was recorded. The maximum voltage was converted to force unit by the factor 55 lb/V^[17]. A voltage chart recorder was connected to the Sebastian to trace the voltage output. The chart recorder was set at an upper limit voltage of 1 V and a tracing speed of 1 inch/minute.

Figure 3-5. Illustration of the coating sample-pull stud assembly and the applied force.

The adhesive strength of the coating in pounds per square inch (psi) was obtained using the following expression.

$$\text{Adhesive Strength (psi)} = \text{maximum force output (lb)} / \text{stud head surface area (in}^2\text{)}$$

The used studs can be recycled for additional measurements by the following steps.

1. Soak the stud in water for an hour to soften the bonding coating then wash away the coating with water.
2. Scrub the remaining glue with sand paper. Avoid sanding excessively and decrease the surface area of the stud head.
3. Clean the studs with soapy water and acetone. Acetone dissolves any remaining glue and grease.

Chapter IV

Results and Discussion

The coatings made with low silica content appeared transparent, smooth and continuous. As the silica content increased, the coating became increasingly white, grainy, and discontinuous. Coatings with 80 weight % silica or higher appeared white and powdery. Nonetheless, coatings with various silica contents exhibited good cohesive and adhesive strength. Good cohesive strength means the coating did not crack when the solvent evaporated, or the bonding between the silica particles and the polymer binder was good. Good adhesive strength means the coating adhered to the substrate upon drying, or the bonding between the coating and the aluminum substrate was good. Even the coatings with up to 95 weight % silica showed no cracks and adhered to the substrate well. The coating thicknesses were approximately 0.1 mm. In this report the composition of the coatings will be designated as follows, unless noted otherwise. X% = X weight % silica.

1. Tape Adhesion Test

The quality of the coating adhesive strength was first tested using tape adhesion test. The results are summarized in Table 4-1. The untreated scores are the raw data and the average scores are the arithmetic means of the untreated scores. The filtered scores are the arithmetic means of the untreated scores with abnormal scores screened out. Coatings up to 50% achieved scores of 4 or 5. A score of 5 indicates that the coating

adhesive strength was at least 200 pounds per square inch (psi)^[16]. As the silica content increases, the scores dropped toward 0.

The abnormally lower scores of 2 and 3 were observed on coatings with 20 and 40%, respectively, and were probably due to contaminated aluminum surface. Repeating the test with clean aluminum substrate gave more reasonable results. Thorough aluminum surface treatment with soap water and acetone therefore is critical for accurate tape adhesion test.

The tip cutter easily damaged the coatings with greater than 70 weight % silica. As the tip cutter slid across these coatings, cracks and crumbles were observed along the cut edges. However, all the cut squares stayed in place and adhere to the substrate. This indicates that cohesive strength degrades with high silica content.

The photograph in Figure 4-1 shows the 70% coating after the tape adhesion test. The squarely cut coating can clearly be observed on the top. Some bare aluminum areas are exposed after the tape lifted the cut coating. Coating lifting's are especially apparent along cut edges. The bottom tape shows the peeled off coating bits.

The photograph in Figure 4-1 also reveals that at 70%, the coating broke cleanly from the aluminum substrate, as illustrated in Figure 4-2(a). The cohesive strength of the coating withstood the lifting force of the tape. The coating broke when the adhesive strength failed and was lifted off from the substrate. This indicates that with 70% adhesive strength fails before cohesive strength.

Table 4-1. Tape Adhesion Test scores for coatings with 0 to 95 weight % silica.

Silica Wt.%	Silica Vol.%	Untreated Score	Average Score	Filtered Score	Comment on Coating
0	0	5, 5	5	5	Completely transparent, smooth, continuous.
10	5	5, 5	5	5	Transparent, smooth, continuous.
20	10	3, 5, 5	4.3	5	Transparent, smooth, continuous. Score of 3 caused by Al substrate contamination (coating corner lifting before test).
30	16	5, 5	5	5	Transparent, smooth, continuous. Some cut coating square edge lift off.
40	23	4, 2, 4	3.3	4	Semitransparent, smooth, continuous. Score of 2 caused by Al substrate contamination (coating corner lifting before test).
50	31	4, 4, 4	4	4	Semitransparent, smooth, continuous.
60	40	3, 3	3	3	White, discontinuous.
70	51	1, 2, 2	1.7	1.7	White, grainy, discontinuous. Coating easily damaged by tip cutter. Cracks and crumbles along cut edges. Lift off in chunks.
80	64	2, 1, 2	1.7	1.7	White, powdery, discontinuous. Coating easily damaged by cutter tip. Crack and crumbles along cut edges. Lift off in chunks, but bottom surface left on substrate.
90	80	1, 0	0.5	0.5	
95	90	0, 0	0	0

Figure 4-1. Photograph of a coating with 70 weight % silica after the tape adhesion test.

With some of the squares, only part of the area was lifted off by the tape, as illustrated in Figure 4-2(b). This suggests that cohesive strength failed along with adhesive strength. However, this may be due to the nature of the tape adhesion test since the tape was pulled up at an angle. The partial area lift off may be a result of the additional bending stress placed on the cohesive strength of the coating. Figure 4-2(c) illustrates the bending stress during the tape pull up. Hence it was concluded that for 70% coating, the cohesive strength is greater than the adhesive strength.

(a) clean break, coatings with ≤ 70 weight % silica.

(b) clean break, coatings with ≤ 70 weight % silica.

(c) bending stress.

(d) unclean break, coatings with ≥ 80 weight % silica.

Figure 4-2. Illustrations of different breaks and bending stress in tape adhesion test.

Figure 4-3 shows the photograph of 80% coating after tape adhesion test. The result is very different than that of 70% coating. The lifted coating bits contained no whole square, only coating bits along cut edges. In addition, few bare aluminum areas were exposed around the cut squares. As the tape was pulled, the cohesive strength failed and the coating delaminated between the top and bottom surface. The bottom surface remained on the substrate while the top surface was lifted off by the tape. This unclean break is illustrated in Figure 4-2(d). The cohesive strength did not withstand the lifting force of the tape. It was concluded that for 80% coating, the cohesive strength is weaker than the adhesive strength. Table 4-2 summarizes the relative strength of cohesive and adhesive properties.

Figure 4-3. Photograph of a coating with 80 weight % silica after the tape adhesion test.

Table 4-2. Summary of relative adhesive and cohesive strengths.

Silica Content, Wt. %	Relative Strength
0 - 70 %	Adhesive < Cohesive
70 - 80 %	Adhesive = Cohesive
80 - 100%	Adhesive > Cohesive

The filtered tape adhesion test scores from Table 3 were plotted in Figure 4-4. The two abnormal scores from 20 and 40% were not included since they were caused by contaminated aluminum substrates. The curve stays at 5 between 0 and 30%. This indicates that the adhesive strength was at a minimum of 200 psi up till 30% since a score of 5 signifies adhesive strength of at least 200 psi^[16]. The curve shows a general downward slope after 40%, indicating the loss of adhesive strength as silica content increases. After an initial decrease at around 40%, the curve quickly drops toward zero after 50%. The adhesive strength was very sensitive to silica content after 50%. The change was effectively linear. This suggests that the interface between the coating and substrate did not change with the coatings of less than 50%. Table 4-3 summarizes the tape adhesion test score curve in Figure 23. The scores between 50 and 100% were fit with a linear equation. The X in the equation stands for silica weight percentage.

Figure 4-4. Tape adhesion test score vs. silica content.

Table 4-3. Tape adhesion test score summary.

Silica Content, Wt. %	Tape Adhesion Test Score
0 – 50 %	4 – 5
50 - 100 %	$8.44 - 0.09X$

The major disadvantage of the tape adhesion test is evident in Figure 4-4. Since the tape adhesion test results are given in discrete scores from 0 to 5, the results are discontinuous. Performing more tests on coatings with smaller weight % increments probably would not yield much more information.

2. Sebastian V Adhesive Strength Measurement

A total of 100 data points were collected on coatings with 0 to 95% using Sebastian. Measurements were taken in 5% increments. Additional measurements were made for those coatings showing poor reproducibility. The raw result is placed in Appendix C for reference.

The voltage trace for a 50% coating is shown in Figure 4-5(a) as an example. As the Sebastian started applying load to the adhered coating, the trace moved to higher voltage readings and recorded the output voltage. As the load gradually increased, the trace formed a slope on the chart. The Sebastian ceased applying load when the coating finally broke from the substrate. The trace recorded the maximum voltage and remained constant until the instrument was reset. With reset, the voltage output dropped to 0 and so did the trace.

A close inspection of the 50% coating after Sebastian measurement revealed silica particles on the circular bare aluminum region left by the stud. This can be seen in the photograph of the 50% coating Figure 4-5(b). This coincides with the finding from tape adhesion test that the interface between the coating and substrate changed at 50%.

(a)

(b)

Figure 4-5. (a) Voltage trace from the Sebastian measurement of a coating with 50 weight % silica. (b) Photograph of a coating with 50 weight % silica after the Sebastian measurement.

Five specimens, each with 10, 20, 30, 50, and 70 weight % silica, showed that there was no clear breakage of the coating from aluminum substrate after the Sebastian stopped applying load at the maximum voltage. The coating on the stud detached from the substrate. However, it was still connected to the surrounding coating, which still adhered to the substrate. Figure 4-6 illustrates this behavior. Continuing the test by manually engaging the 'continue' button on the Sebastian initiated the applied load. At this point the load was applied to the coating at the circumference of the stud. The

voltage trace formed a second slope. When the load finally forced the coating to break completely from the substrate, a second maximum voltage was recorded. The voltage trace for the 70% coating in Figure 4-7 shows the two voltage plateaus.

Figure 4-6. Illustration of stud pull on coating with no clear break after first maximum voltage in Sebastian measurement.

Figure 4-7. Voltage trace with 2 plateaus from the Sebastian measurement of the coating with 70 weight % silica.

Therefore the first voltage maximum in Figure 4-7 corresponds to the detachment of the coating from substrate, or the adhesive strength of the coating. The second voltage maximum corresponds to the breaking of the coating on the stud from the coating on the substrate, or the cohesive strength of the coating. Consequently the two-plateau phenomenon shows that adhesive strength fails before cohesive strength. Accordingly at 70%, adhesive strength fails before cohesive strength, or the adhesive strength is less than the cohesive strength.

Since the cohesive strength was also under stress during the initial load of the first voltage maximum, the difference between the first and second voltage maximum is an estimate of the cohesive strength. For the 70% coating shown in Figure 4-7, this difference gives the value of 0.235V.

It should be noted that the area of adhesive stress and cohesive stress were not the same in the Sebastian measurement, as illustrated in Figure 4-6. Adhesive stress occurred on the interface of coating and aluminum substrate. Cohesive stress took place between the coating on the stud and the coating on the substrate. The voltage values corresponding to adhesive strength and cohesive strength therefore cannot be compared directly.

Figure 4-8 is a photograph of the 20% coating that had two voltage plateaus. Three circular bare aluminum regions are shown since three measurements were made on the same coating. The two-plateau result was from measurement B in the figure. The cohesive stress area of the coating is visible surrounding the stud mark.

Figure 4-8. Photograph of a coating with 20 weight % silica after three Sebastian measurements.

The two-plateau results present the possibility of using the Sebastian for measuring the cohesive strength of the coatings. However, the approach is not feasible with the current instrument set up. The two-plateau results were not always repeatable. Out of the 80 adhesive strength measurements made with coatings having 70 weight % silica or less, only 5 measurements showed the two-plateau phenomenon. The two-plateau phenomenon was not observed on coatings above 70%. Since adhesive strength is the focus of this research, no further investigation was done on measuring cohesive strength with the Sebastian.

Figure 4-9 is a close up photograph of the stud marks on the 80% coating after two Sebastian measurements. The stud marks reveal no bare aluminum substrate but contain coating flakes still adhering to the substrate. The cohesive strength of the coating

was unable to withstand the pulling load. The coating delaminated between the top and bottom surface as illustrated in Figure 4-10. The top surface remained on the substrate while the bottom surface was pulled off by the stud. This indicates that for 80% coating, the cohesion failed before the adhesion, or the cohesive strength is less than the adhesive strength.

Figure 4-9. Close up photograph of stud marks on a coating with 80 weight % silica after the Sebastian measurement.

Figure 4-10. Coating cohesion failure in Sebastian measurement.

The relative strengths of cohesion and adhesion of the coatings revealed by the Sebastian measurement agrees with the tape adhesion test results. Table 4-2 summarizes these relative strengths.

Of the data points collected with the Sebastian, 12 data points were discarded because the coatings had defects. Four data points were discarded because the coating detached from the aluminum substrate during curing, probably due to the presence of residual contamination on the substrate. Another 4 data points were abandoned due to abnormal discoloration of the coating, where the coating appeared yellowish instead of white. Contaminated PAA or silica probably caused the color change. Three data points were rejected due to suspected poor bonding between the stud and coating. After the Sebastian measurement, the specimens had irregular instead of circular stud marks and some glue was observed on the coating surface. The defect was likely rooted in flawed sample preparation or faulty glue. One data point was discounted because the coating texture was coarse and had bubble-like troughs. This may have resulted from air being trapped in the silica/PAA mixture during stirring. The trapped air moved up to the surface as the solvent evaporated. The resulting coating surface hence was uneven.

Table 4-4 shows the Sebastian adhesive strength measurement results, in both volt (V) and pounds per square inch (psi). Data points outside of 1 standard deviation were not included. The average is the arithmetic mean of 3 to 10 data points collected for each silica weight %. For the data points with two voltage plateaus, the estimated cohesive strength is shown. The silica/PAA coatings could attain adhesive strengths above 200 psi.

Table 4-4. Sebastian adhesive strength measurement results.

Silica weight %	Silica volume %	Average Adhesive Strength		Cohesive Strength (V)
		(V)	(PSI)	
0	0	0.334	275	
5	2	0.284	234	
10	5	0.292	240	0.041
15	7	0.277	228	
20	10	0.261	215	0.093
25	13	0.263	217	
30	16	0.270	222	0.414
35	20	0.249	205	
40	23	0.265	218	
45	27	0.247	203	
50	31	0.239	196	0.258
55	36	0.235	193	
60	40	0.245	202	
65	46	0.215	177	
70	51	0.186	153	0.235
75	58	0.137	113	
80	64	0.116	95	
85	72	0.091	75	
90	80	0.031	26	
95	90	0.020	16	

For comparison, the adhesive strengths of some common adhesives are listed in Table 4-5. Super Glue and epoxy are on the high end and can achieve adhesive strengths of 4,000 psi. The silica/PAA coatings, with values in the range of 200 to 300 psi, are close to Elmer's glue, 400 psi in strength.

Table 4-5. Adhesive strength of common adhesives.

Adhesive	Adhesive Strength Range (psi)	Note / Source
Epoxy	4000	Miller-Stephenson Chemical Co. ^[18]
Optical adhesives	1000-3000	Non silicone / AI Technology ^[19]
Acrylics	870-2900	Shear load / Kirk Othmer Encyclopedia of Chemical Technology ^[20]
Polyurethanes	870-2465	Shear load / Kirk Othmer Encyclopedia of Chemical Technology ^[20]
Super Glue	4000	Tensile / Elmer's Products Inc. ^[21]
Elmer's glue	400	Tension shear / Elmer's Products Inc. ^[21]
Silica/PAA coatings	200-300	Tensile, 0 to 60 weight % silica

The adhesive strength results were plotted against silica content in Figure 4-11. The data was fitted with a sixth power polynomial equation with least square method. An artificial data point of 0 adhesive strength at 100% was used in addition to the experimentally data points for the curve fitting. The resulting R^2 value was 0.9905. The error bars represent the standard deviations for each silica weight %. The varying standard deviation reflects the difficulty in achieving good measurements since numerous factors can affect the measurement outcome. Environmental conditions such as moisture

and temperature could affect the measurement results. Other factors such as contamination, material quality, and human error also influence the outcome.

Figure 4-11. Adhesive strength versus silica content using Sebastian measurement.

Figure 4-11 shows that the adhesive strength decreased as the silica content increased. The unfilled PAA coating had noticeably higher adhesive strength. The adhesive strength dropped as soon as silica was present with the initial amount, and the effect was bigger than with subsequent additions. Although the adhesive strength decreased as the silica content increased, it did stay above 200 psi up till 60%. Between 5 and 60%, the adhesive strength declined from 234 to 202 psi, a 14% decrease, then dropped dramatically beyond 60%. Between 60 and 80%, the adhesive strength declined

59%, from 234 to 95 psi. The 60% composition thus represents a threshold for the dramatic loss of adhesive strength of the silica/PAA coatings.

Beyond 80%, the curve in Figure 4-11 decreases toward 0, but at a more gradual rate. This coincides with the finding on the relative cohesive and adhesive strengths of the coating, as summarized in Table 4-2. Above 80%, the cohesive strength fails before the adhesive strength. Hence the measurements above 80% actually depict the cohesive strength instead of the adhesive strength.

Although there were limited data points for the cohesive strength, they reveal that the cohesive strength initially increased with the silica content up to 30%, then decreased with higher silica contents. The relationship between the adhesive strength and cohesive strength can be seen in Figure 4-12.

In region A of Figure 4-12, the silica content increases from 0 to 30% and the cohesion is greater than adhesion. The adhesive strength decreases while the cohesive strength increases. The cohesive strength peaks at 30 %.

In region B, between 30 and 60%, the cohesion is still greater than adhesion. The adhesive strength continues to decrease gradually while the cohesive strength starts to decline, at a much faster rate than the adhesive strength.

In region C, between 60 and 80%, the cohesive and adhesive strengths both decline rapidly. The cohesive and adhesive strengths became equal at around 80%.

In region D, from 80 to 100 %, both the adhesive and cohesive strength decline toward 0. However, the adhesive strength is higher than the cohesive strength.

Figure 4-12. Adhesive strength versus cohesive strength.

3. Comparison of Tape Adhesion Test And Sebastian V Measurement

Both tape adhesion test and Sebastian test were used to measure the adhesive strength of the silica filled polymer coatings. However, they have a number of differences. The tape adhesion test measured adhesive strength on the area defined by the squares cut out with the cutter tip. Though each individual square was 0.0225cm^2 , the test score was based on the all of the 49 squares, which was 1.1025cm^2 . The Sebastian test measured the area defined by the stud, which was $0.067\text{in}^2 (=0.4311\text{cm}^2)$. Thus the area measured with tape adhesion test was over 2.5 times larger than the area with the Sebastian test. The larger measuring area gave more consistent results. The tape adhesion test results were thus less scattered than the Sebastian test results. Additionally, for the tape adhesion test, the target coating was cut before the tape was applied. The

cutting process damaged the coating. In contrast, the Sebastian test allowed the measurements to be made without damaging the coating until the measurement was taken. The Sebastian test therefore provided better and more accurate measurements. Moreover, tape adhesion test results were given in scores ranging from 0 to 5. The highest score of 5 indicates adhesive strength of at least 200 psi. The tape adhesion test gave qualitative, discrete results and could not distinguish adhesive strengths above 200 psi. Consequently tape adhesion test could not detect the adhesive strength decrease from 275 to 222 psi in region A of Figure 4-12. In contrast, the Sebastian test gave quantitative and continuous adhesive strength measurement results.

Despite the differences between the tape adhesion test and Sebastian test, their adhesive strength results showed the similar decline as the silica content increased. The tape adhesion test results showed the major decline around 50% while the Sebastian test results had the dramatic decrease around 60%. The relative strengths of the coating cohesion and adhesion shown by the two tests were in good agreement, as summarized in Table 4-2. Between 0 and 70%, the cohesive strength was greater than the adhesive strength. Between 70 and 80%, the cohesive and adhesive strengths were approximately equal. Beyond 80%, the adhesive strength was greater than the cohesive strength.

4. Comparison of Experimental Results with Literature Findings

Since no model was available for the adhesive strength of silica filled polymer coatings, the available models on mechanical properties such as shear and elastic modulus, tensile strength and microhardness were reviewed for possible relationship with

the adhesive strength. No relationship was found. The adhesive strength of silica filled polymer coatings on aluminum declined monotonically as the silica content increased while the mechanical properties generally increased as the silica content increased, as summarized in Table 2-1. The only exception was the tensile strength of 0.6 μ m silica/EVA composite reported by Shang *et al*, which decreased rapidly as the silica content increased, as shown in Figure 2-3. Hence the mechanical properties and adhesive strength are not comparable.

The composite shear and elastic modulus equations found in the literature were applied to adhesive strength. Two packing fractions, hexagonal = 0.74 and simple cubic = 0.524, were used for Mooney's equation (Equation 2-1). Kerner's equation (Equation 2-3) and Pope's equation (Equation 2-5) were not applicable to adhesive strength since they contain the parameters, G_2 and E_s , which are the adhesive strength of pure silica powder. The details of the calculations can be found in Appendix D and the results are shown in Figure 4-13. The equations are not appropriate for adhesive strength since they predicted the increase of adhesive strength as the silica content increased which is contrary to the experimental results.

Figure 4-13. Adhesive strength predictions with various mechanical property equations.

Chapter V

Conclusion and Suggestion for Future Work

This study showed that the adhesive strength of silica filled polyacrylic acid coatings on aluminum declined monotonically as the silica content increased. The adhesive strength decreased gradually and stayed above 200 psi up till 60 weight % silica, then degrades toward 0 beyond 60 weight % silica. Between 0 and 70 weight % silica, the cohesive strength was greater than the adhesive strength. Between 70 and 80 weight % silica, the cohesive and adhesive strengths were approximately equal. Beyond 80 weight % silica, the adhesive strength was greater than the cohesive strength.

The coating materials and processing used in this study were based on the previous study of PSP composition and formulation. The coatings with the best performance contained approximately 95 weight % silica. This study showed that there were still adequate cohesive and adhesive strength at 95 weight % silica.

The literature search revealed no data or model on the adhesive strength of silica filled polymer coatings. While models were found on mechanical properties, no connection was found between the mechanical property models and the adhesive strength. Attempt to treat the adhesive strength with the models revealed that the mechanical property models were not applicable to the adhesive strength.

For future study, the following is recommended to further investigate the adhesive strength of silica filled polymer coatings for PSP use. The recommendations are to improve the bonding between the silica and polymer, thus leading to better coating cohesion and adhesion.

1. Studying the effect of degassing during the coating curing process. Better control of the degassing may minimize moisture trapping in the coating and lead to better bonding between the silica and polymer
2. Improving the silica/PAA mixing process. Better mixing process may avoid trapping air in the coating and give better bonding between the silica and polymer.
3. Studying the effect of silica particle size on the adhesive strength. Smaller sized silica can fill voids better and provide more surface area, resulting in better bonding with the polymer binder.
4. Using different solvents for coating preparation. Different solvents may improve the bonding ability of the polymer.

References

- [1] Lubin, George, ed. Handbook of Composites. New York: Van Nostrand Reinhold, 1982. 2.
- [2] Strong, A. Brent. Fundamental of Composites Manufacturing: Materials, Methods, and Applications. Dearborn, MI: Society of Manufacturing Engineers, 1989. 108.
- [3] McLachlan B. G., and J. H. Bell. "Pressure-Sensitive Paint in Aerodynamic Testing." Experimental Thermal and Fluid Science 10 (1995): 470.
- [4] Wan, Jiang. "Fast Response Luminescent Pressure Sensitive Coating and Derivative of Tetra(pentafluorophenyl)porpholactone." Diss. University of Washington, 1993. 1.
- [5] Kavandi, Janet. "Luminescence Imaging for Aerodynamic Pressure Measurements." Diss. University of Washington, 1990. 1.
- [6] Diaz, Arthur. Private Communication. Dec. 1996
- [7] Sheldon, R. P. Composite Polymeric Materials. London: Applied Scientific, 1982. 64-67.
- [8] Mooney, M. "The Viscosity of a Concentrated Suspension of Spherical particles." Journal of Colloid Science 6 (1951): 162-167.
- [9] Sheldon, R. P. Composite Polymeric Materials. London: Applied Scientific, 1982. 65.
- [10] Kerner, E. H. "The Elastic and Thermo-elastic Properties of Composite Media." Proceedings of the Physical Society B69 (1956): 808-812.
- [11] Shang, S. W., J. W. Williams, and K-J. M. Soderholm. "How the Work of Adhesion Affects the Mechanical Properties of Silica-Filled Polymer Composites." Journal of Materials Science 29 (1994): 2406-2416.
- [12] Guth, Eugene. "Theory of Filler Reinforcement." Journal of Applied Physics 16 (1945): 20.
- [13] Pope, E. J. A., M. Asami, and J. D. Mackenzie. "Transparent Silica Gel-PMMA Composites." Journal of Materials Research 4, 4 (1989): 1018-1025.

- [14] Farquhar, Donald S., and James E. Steinwall. "Elastic Properties of Filled Epoxy Encapsulants." Proceedings of the International Intersociety Electronic Packaging Conference-INTERpack'95 Part 2 (of 2): 707-711.
- [15] Avery, Jim Van. "Nondestructive Pain and Bonding Adhesion Prediction Meter for Metal Surfaces." Proceedings of the 1996 41st International SAMPE Symposium and Exhibition Part 2 (of 2): 1023-1211.
- [16] Paint Adhesion Test Kit User Guide. Pompano Beach, FL: Paul N. Gardner Company, Inc., 1986. 1-4.
- [17] The Sebastian Five Operation Manual. Spokane, WA: Quad Group. 5.
- [18] Miller-Stephenson Chemical Co. Retrieved Jan. 15, 2001 from <http://www.miller-stephenson.com/907.htm>.
- [19] AI Technology. Retrieved Jan. 15, 2001 from <http://www.aitechnology.com/optical.html>.
- [20] Kroschwitz, Jacqueline I., Mary Howe-Grant, ed. Kirk Othmer Encyclopedia of Chemical Technology 4th ed., vol. 1. New York: Wiley, 1991. 453.
- [21] Elmer's Products Inc. Private communication. 24 Jan. 2001.

Appendix A

Theoretical Calculation of Silica Weight % for Mono-Layer Polymer Coverage of Silica Particles in Silica/PAA Composites

The following calculates the minimum amount of polymer (PAA) needed to completely coat the silica particles with a mono-layer coating. The calculation assumes monodispersed spherical silica particles of 40 μ m diameter and a mono-layer thickness of 10 nm.

r = silica particle radius = 20 μ m = 2×10^{-4} cm assume 40 μ m diameter silica particles

ρ_s = silica density = 2.32g/cm³

V_s = volume of a silica particle = $\frac{4}{3} \pi r^3$

M_s = mass of a silica particle = $V_s \rho_s$

ρ_p = polymer (poly acrylic acid, PAA) density = 1.051g/cm³

δ = thickness of mono-layer polymer coverage = 1×10^{-6} cm assume 10 nm mono-layer thickness

V_p = volume of mono-layer PAA covering a silica particle

= ~ surface area of a silica particle x thickness of mono-layer polymer coverage

= $4\pi r^2 \delta$

M_p = mass of mono-layer PAA covering a silica particle = $V_p \rho_p$

$$V_s / V_p = (4/3 \pi r^3) / (4\pi r^2 \delta)$$

$$= r / 3\delta$$

$$= 2 \times 10^{-4} \text{cm} / 3 \times 1 \times 10^{-6} \text{cm}$$

$$= 1.5 \times 10^2$$

$$V_s = 1.5 \times 10^2 V_p$$

$$\text{silica vol\% for mono-layer polymer coverage} = V_s / (V_s + V_p)$$

$$= 1.5 \times 10^2 V_p / (1.5 \times 10^2 V_p + V_p)$$

$$= 99.3\%$$

$$\text{silica wt\% for mono-layer polymer coverage} = M_s / (M_s + M_p)$$

$$= V_s \rho_s / (V_s \rho_s + V_p \rho_p)$$

$$= (1.5 \times 10^2 V_p \times 2.32 \text{g/cm}^3) / (1.5 \times 10^2 V_p \times 2.32 \text{g/cm}^3 + V_p \times 1.051 \text{g/cm}^3)$$

$$= 99.7\%$$

Appendix B. Silica/PAA Coating Composition Calculation

Formulation

PAA:H₂O= 1:20= 0.050
 Silica:H₂O= 1:4= 0.250
 Kaolin:H₂O= 1:4= 0.250
 Kaolin:Silica= 1:10= 0.100

Density

PAA= 1.051 g/cm³
 Silica= 2.320 g/cm³

Silica wt %	Silica vol %	PAA wt, g	PAA gel vol	Silica wt, g	Silica slurry vol	Kaolin wt, g	Kaolin slurry vol	Total H ₂ O wt, g	Solids: H ₂ O	Solid wt %	PAA: Silica pure PAA
0	0	0.500	10.000	0.000	0.000	0.000	0.000	10.000	0.050	0.048	19.000
5	2	0.500	10.000	0.026	0.105	0.003	0.011	10.116	0.052	0.050	9.000
10	5	0.500	10.000	0.056	0.222	0.006	0.022	10.244	0.055	0.052	5.667
15	7	0.500	10.000	0.088	0.353	0.009	0.035	10.388	0.057	0.054	4.000
20	10	0.500	10.000	0.125	0.500	0.013	0.050	10.550	0.060	0.057	3.000
25	13	0.500	10.000	0.167	0.667	0.017	0.067	10.733	0.064	0.060	2.333
30	16	0.500	10.000	0.214	0.857	0.021	0.086	10.943	0.067	0.063	1.857
35	20	0.500	10.000	0.269	1.077	0.027	0.108	11.185	0.071	0.066	1.500
40	23	0.500	10.000	0.333	1.333	0.033	0.133	11.467	0.076	0.070	1.222
45	27	0.500	10.000	0.409	1.636	0.041	0.164	11.800	0.081	0.075	1.000
50	31	0.500	10.000	0.500	2.000	0.050	0.200	12.200	0.086	0.078	0.818
55	36	0.500	10.000	0.611	2.444	0.061	0.244	12.689	0.092	0.085	0.667
60	40	0.500	10.000	0.750	3.000	0.075	0.300	13.300	0.100	0.091	0.538
65	46	0.500	10.000	0.929	3.714	0.093	0.371	14.086	0.108	0.097	0.429
70	51	0.500	10.000	1.167	4.667	0.117	0.467	15.133	0.118	0.105	0.333
75	58	0.500	10.000	1.500	6.000	0.150	0.600	16.600	0.130	0.115	0.250
80	64	0.500	10.000	2.000	8.000	0.200	0.800	18.800	0.144	0.126	0.176
85	72	0.500	10.000	2.833	11.333	0.283	1.133	22.467	0.161	0.139	0.111
90	80	0.500	10.000	4.500	18.000	0.450	1.800	29.800	0.183	0.155	0.053
95	90	0.500	10.000	9.500	38.000	0.950	3.800	51.800	0.211	0.175	

Appendix C: Sebastian V Measurement Data

stud diameter = 0.291666 in = 0.74083316 cm
radius = 0.1458333 in = 0.37041658 cm
area = 0.06681335 in² = 0.43105304 cm²
conversion factor 55 lb/V

Silica wt %	Silica vol %	Adhesive Strength (V)		Adhesive Strength(psi)		Result (V)									
		avg	std dev	avg	std dev	1	2	3	4	5	6	7	8	9	10
0	0	0.334	0.030	275	25	0.335	0.308	0.314	0.384	0.331					
5	2	0.284	0.025	234	21	0.309	0.285	0.259							
10	5	0.292	0.022	240	18	0.298	0.306	0.253	0.294	0.316	0.284				
15	7	0.277	0.033	228	27	0.329	0.26	0.24	0.276	0.279					
20	10	0.261	0.026	215	21	0.294	0.269	0.259	0.214	0.258	0.25	0.282			
25	13	0.263	0.040	217	33	0.278	0.158	0.246	0.281	0.291	0.298	0.274	0.279	0.263	0.263
30	16	0.270	0.037	222	31	0.28	0.26	0.259	0.331	0.294	0.198	0.27	0.269		
35	20	0.249	0.026	205	21	0.259	0.239	0.279	0.219						
40	23	0.265	0.031	218	26	0.265	0.248	0.291	0.29	0.301	0.245	0.214			
45	27	0.247	0.026	203	22	0.258	0.235	0.277	0.217						
50	31	0.239	0.018	196	15	0.263	0.24	0.231	0.22						
55	36	0.235	0.022	193	18	0.257	0.213	0.235							
60	40	0.245	0.029	202	24	0.207	0.249	0.296	0.25	0.24	0.23				
65	46	0.215	0.016	177	13	0.199	0.231	0.215							
70	51	0.186	0.029	153	24	0.15	0.18	0.184	0.231	0.186					
75	58	0.137	0.019	113	16	0.113	0.141	0.135	0.16						
80	64	0.116	0.018	95	15	0.104	0.092	0.123	0.128	0.125	0.135	0.117	0.084	0.134	
85	72	0.091	0.019	75	16	0.105	0.08	0.11	0.07						
90	80	0.031	0.010	26	8	0.051	0.025	0.023	0.034	0.017	0.037	0.03	0.032		
95	90	0.020	0.010	16	8	0.02	0.03	0.01							

Appendix D: Adhesive Strength Prediction Calculation

Adhesive Strength, pure PAA = 303 psi
 Density
 PAA = 1.051 g/cm³
 Silica = 2.320 g/cm³

Guth Smallwood Equation

$E = E_p (1 + 2.5V_f + 14.1V_f^2)$
 E = composite adhesive strength
 V_f = silica volume fraction
 E_p = pure PAA adhesive strength

Mooney's Equation

$\ln G/G_1 = K_e v_2 / (1 - v_2/v_m)$
 $G = G_1 \exp(K_e v_2 / (1 - v_2/v_m))$
 G = composite adhesive strength
 G_1 = pure PAA adhesive strength
 K_e = Einstein's coefficient (spherical particle) = 2.5
 v_2 = silica volume fraction
 v_m = maximum packing fraction = 0.52 simple cubic packing
 = 0.74 hexagonal packing

Van Der Poel

$G/G_1 = 1 + \{1.25v_2/(1 - 1.28v_2)\}^2$
 $G = G_1(1 + \{1.25v_2/(1 - 1.28v_2)\}^2)$
 G = composite adhesive strength
 G_1 = pure PAA adhesive strength
 v_2 = silica volume fraction

Silica Wt%	Silica Vol %	Guth	Mooney		Van Der Poel	
			simple cubic	hexagonal		
0	0	303	303	303		303
5	2	320	319	319		303
10	5	352	348	346		304
15	7	377	371	368		306
20	10	421	413	405		309
25	13	474	467	449		315
30	16	534	539	505		322
35	20	625	680	601		337
40	23	703	844	698		353
45	27	819	1220	877		384
50	31	948	2021	1150		428
55	36	1129	5374	1748		514
60	40	1280		2671		621
65	46	1555		6330		895
70	51	1801				1325
75	58	2180				2703
80	64	2538				6235
85	72	3063				
90	80	3643				
95	90	4445				

March 30, 2001

Darsh T. Wasan
Editor-in-Chief, Journal of Colloid and Interface Science
Illinois Institute of Technology
3300 South Federal Street
Chicago, IL 60616-3793

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provided that:

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question is original to our text and appears
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another source; proper credit is given to
our publication(s).

Christine Smith
Date 4-19-2001
ACADEMIC PRESS,
Orlando, Florida 32887-6777

APR 16 2001

Dear Sir:

I would appreciate permission to include a portion of Figure 2, Theoretical curves fitted to experimental data by Vand and Eilers, which appears in "The Viscosity of a Concentrated Suspension of Spherical Particles," by M. Mooney, Journal of Colloid Science, 6, 1951, pp. 167, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Public Domain Material

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou
Louis Ou

We grant permission for the use of the figure requested above.

Editor

Date

April 5, 2001

Mr. Carl W. Harris
Journal of Materials Science
Kluwer Academic Publishers
101 Philip Drive
Norwell, MA 02061

Dear Mr. Harris:

I would appreciate permission to include portions of the following figures that appear in "How the Work of Adhesion Affects the Mechanical Properties of Silica-Filled Polymer Composites," by S. W. Shang, J. W. Williams, and K-J. M. Soderholm, Journal of Materials Science, 29, 1994, pp. 2408-2409, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Figure 1. Effect of volume fraction and surface properties of Stober silica filler on Young's modulus of polymer composites.

Figure 2. Effect of volume fraction and surface properties of Cab-O-Sil silica filler on Young's modulus of polymer composites.

Figure 3. Effect of volume fraction and surface properties of Stober silica filler on the tensile strength of polymer composites.

Figure 4. Effect of volume fraction and surface properties of Cab-O-Sil MS-7 silica filler on the tensile strength of polymer composites.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou
Louis Ou

PERMISSION GRANTED, PROVIDED THAT
COMPLETE ACKNOWLEDGEMENT IS GIVEN TO
THE ORIGINAL SOURCE OF PUBLICATION.

DATE

CARL W. HARRIS, PUBLISHER
KLUWER ACADEMIC PUBLISHERS

We grant permission for the use of the figures requested above.

Signature

Title

Date

April 1, 2001

Dr. Robert P. Frankenthal
Editor-in-Chief
Journal of Materials Research
506 Keystone Drive
Warrendale, PA 15086-7573

Dear Sir:

I would appreciate permission to include a portion of Figure 9, Natural log of elastic modulus versus volume fraction PMMA, which appears in "Transparent Silica Gel-PMMA Composites," by E. J. Pope, M. Asami, and J. D. Mackenzie, Journal of Materials Research, Vol. 4, No. 4, Jul/Aug 1989, pp. 1024, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou
Louis Ou

We grant permission for the use of the figure requested above. *PROVIDED PERMISSION IS GRANTED BY THE AUTHORS. YOU MAY ALSO WISH TO INQUIRE TO THE AUTHORS ABOUT OBTAINING AN ORIGINAL FIGURE.*

[Signature]

Editor

4/6/01

Date

PUBLICATION ASSISTANT

April 10, 2001

Dr. John D. Mackenzie
Department of Materials Science and Engineering,
University of California, Los Angeles
405 Hilgard Avenue, Room 6531 Boelter Hall
Los Angeles, CA 90095-1595

Dear Sir:

I would appreciate permission to include a portion of Figure 9, Natural log of elastic modulus versus volume fraction PMMA, which appears in "Transparent Silica Gel-PMMA Composites," by E. J. Pope, M. Asami, and J. D. Mackenzie, Journal of Materials Research, Vol. 4, No. 4, Jul/Aug 1989, pp. 1024, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou

We grant permission for the use of the figure requested above.

Signature

Date

April 5, 2001

Dr. Tai Ran Hsu
Program Committee Chair
International Intersociety Electronic Packaging Conference-INTERpack'95
Department of Mechanical and Aerospace Engineering
San Jose State University
One Washington Square
San Jose, CA 95192-0087

Dear Sir:

I would appreciate permission to include portions of Figure 3, Young's modulus of a range of filled epoxy encapsulants and Figure 5, Vickers hardness of a range of filled epoxy encapsulants, which appear in "Elastic Properties of Filled Epoxy Encapsulants," by D. Farquhar and J. Steinwall. Proceedings of the International Intersociety Electronic Packaging Conference-INTERpack'95, Part 2, pp 710-711, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou

We grant permission for the use of the figures requested above.

Committee Chair

Date

March 30, 2001

Gary Landon
Paul N. Gardner Company, Inc.
316 N. E. First Street
Pompano Beach, FL 33060

Dear Sir:

I would appreciate permission to include portions of the Paint Adhesion Test Kit figure, 1.5mm Tip Cutter figure, and test score classification table, which appear in the Paint Adhesion Test Kit Operation pamphlet, 9/86, in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou

We grant permission for the use of the figures requested above.

Signature

PAUL N. GARDNER, JR.
Title **President**
PAUL N. GARDNER CO. INC.
316 Northeast First Street
Pompano Beach, Florida 33060
(954) 946-9454 Fax (954) 946-9309
gardner@pncdo.com

4/3/01
Date

March 30, 2001

Richard Riegert
Technical Director
Quad Group, Inc.
1815 South Lewis Street
Spokane, WA 99224

Dear Sir:

I would appreciate permission to include a portion of the Sebastian Five photograph, which appears on the Multi-Purpose Physical Tester Sebastian Five Force Applicator product description (MRC 3/88), in my master thesis with the title "Adhesive Strength of Silica Filled Polymer Coatings" in the Department of Chemical and Materials Engineering at San Jose State University.

Your consideration of this request is deeply appreciated. A copy of this letter is included for your records.

Sincerely,

Louis Ou
Louis Ou

*P.S. In reply
I hope it was to reply.
This was submitted with my
to the pile and just put
for a couple of weeks
Richard*

We grant permission for the use of the figure requested above.

Richard Riegert
Technical Director

April 3, 01
Date

Dear Louis -

I would be very happy to have you use the Sebastian photo and do any reasonable thing to help you in your master thesis. I would be happy to read your thesis before it is submitted if you wish. I have worked in the coatings area for many years. Best to you, Richard