SERDP TECHNICAL REPORT

PRIMERLESS RTV SILICONE SEALANTS/ADHESIVES PP-1135

APRIL, 2003

U.S. Army Tank-automotive & Armaments Command (TACOM)

Armament Research Development & Engineering Center (ARDEC)

Armament Systems Processing Division
Picatinny Arsenal, New Jersey 07806-5000

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D. Eichinger, B. E., Rigby, D., and Stein, J., "Simulating the cohesive properties of Ultem and related molecules". Annu. Tech. Conf. Soc. Plast. Eng. **59th (Vol. 2**), 1592 (2001). 85

E. Eichinger, B. E., and Stein, J., "The Mechanism of the Pt(0) Catalyzed Hydrosilylation Reaction". Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **42 (1)**, 251 (2001). 90

F. Eichinger, B.E. and Stein J., "A Quantum Mechanical Study of the Bonding of a Silyl Ester to Hydrated Alumina", Surface Science, **492**, 75 (2001). 92

G. Eichinger, B.E., Rigby, D., and Stein, J., "Cohesive Properties of Ultem and Related Molecules from Simulations", Polymer, **43**, 599 (2002). 105

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TEAM MEMBERS

Mr. Dean Martinelli	Principal Investigator	U. S. Army TACOM - ARDEC
Mr. Joseph Brescia	Team Leader	U. S. Army TACOM - ARDEC
Ms. Stacey Kerwien	Team Leader	U. S. Army TACOM - ARDEC
Mr. Donald Rorabaugh		U. S. Army TACOM - ARDEC
Mr. John Osterndorf		U. S. Army TACOM - ARDEC
Mr. Francis Sullivan		U. S. Army TACOM - ARDEC
Mr. David Mao		U. S. Army TACOM - ARDEC
Dr. Brad Forch		U.S. Army Research Laboratory
Mr. Richard Beyer		U.S. Army Research Laboratory
Mr. James Tira		Honeywell/DOE Kansas City
Mr. Karl Davis		Honeywell/DOE Kansas City
Ms. Diane Kleinschmidt		Naval Air Warfare Center
Mr. Alan Fletcher		U. S. Air Force Research Laboratory
Mr. William Anspach		U. S. Air Force Research Laboratory
Dr. Judith Stein		General Electric CRD
Ms. Christina Darkangelo Wood		General Electric CRD
Dr. Rachid Kerboua		General Electric CRD
Ms. Gosia Rubinsztajn		General Electric CRD
Mrs. Eriny Youssef		General Electric CRD
Dr. James Cella		General Electric CRD
Dr. Richard Uriarte		General Electric CRD
Ms. Rebecca DiCola		General Electric CRD
Dr. Bruce Eichinger		Molecular Simulations Inc. (Accelrys Inc.)
Dr. Erich Wimmer		Molecular Simulations Inc (Accelrys Inc.)
Dr. John Dillard		Virginia Polytechnic Institute
David Xu		Virginia Polytechnic Institute
Eric Weber		Virginia Polytechnic Institute

ABSTRACT

This is the final report for the Strategic Environmental Research and Development Program (SERDP) funded project PP1135, *Primerless RTV Silicone Sealants/Adhesives*. The objective of the project, the development of primerless addition curable silicone sealants/adhesives, was met for all three phases of the program. Detailed results for the first four years of effort also were reported in SERDP technical reports *Primerless RTV Silicone Sealants/Adhesives - PP1135* issued in 1999, 2000, 2001, and 2002 (References 1-4). Three Six Sigma green belt projects were completed as part of this project.

The research portion of the program was divided into three phases. In the first phase, primerless, elevated-temperature curing, RTV silicone formulations that adhere to metals and glass were developed, and in the second phase, primerless, room temperature curing, RTV silicone formulations that adhere to metals and glass were developed. In the third phase of the effort primerless RTV silicone formulations that provide adhesion to selected thermoplastic substrates were developed validated.

Computational methods were used to guide the material formulation efforts, and calculations to determine the interaction between adhesion promoters and substrates resulted in the identification of promising adhesion promoter candidates. Lap shear screening tests of formulations modified with these adhesion promoters led to the development of optimized formulations, that provided adhesion to various substrates without the use of environmentally unfriendly silane primers. These formulations consisted of RTV 630 and RTV 866 base resins modified with combinations of adhesion promoters, cross-linking compounds, and inhibitors. The first-generation formulation, PLS100-630, consisting of RTV 630 modified with a bis(trimethoxysilylpropyl)fumarate adhesion promoter and a silicon hydride cross-linking compound, provided primerless adhesion to metals and glass under an elevated curing cycle. Similarly, the second-generation formulation PLS200-866, which consisted of RTV 866 modified with adhesion promoter bis(trimethoxysilylpropyl)succinate (US Patent 6,447,922) and a 2-methyl-3-butyn-2-ol inhibitor, provided primerless adhesion to metals, glass, and thermoset plastics under a room-temperature curing cycle. For the third phase, two primerless formulations, PLS-300-866 and PLS300A-630, that used a new adhesion promoter (dBPA) to provide excellent adhesion to Nylon 6,6 substrates, has been developed (Patent Application 20030049465). Lap shear properties with Nylon 6,6 substrates exhibited high strengths with cohesive failures. A technology assessment also was conducted for the XM 984 Extended Range Mortar. Simulations and actual flight tests were conducted successfully with the PLS200-866 primerless RTV formulation.

The final phases of this effort were focused on additional technology assessment and transitioning of the optimized formulations into DoD and DOE applications. In support of this effort, the Polymer Production Facility (PPF) at the Department of Energy, Kansas City Plant, formulated the adhesion promoters and additives, and packaged and distributed complete primerless RTV kits, (PLS 100-630, PLS200-866, PLS300A-630 and PLS300-866) to the DoD and DOE team members for evaluation. Testing showed these kits to have properties equal to the laboratory-fabricated versions.

INTRODUCTION

This is the final report for the Strategic Environmental Research and Development Program (SERDP) funded project PP1135, Primerless RTV Silicone Sealants/Adhesives. The objective of the project, the development of primerless addition curable silicone sealants/adhesives, was met for all three phases of the program. The information in this report includes an overall review of the technical results and accomplishments made on this program. Detailed results of the efforts completed in the first four years also were reported in the Yearly December SERDP technical reports *Primerless RTV Silicone Sealants/Adhesives - PP1135* issued in 1999, 2000, 2001, and 2002 (References 1-4). Three Six Sigma green belt projects were completed as part of this project.

Because of their unique combination of material characteristics/properties, room temperature vulcanizing (RTV) silicones find use in a wide variety of applications where other materials are often not suitable, because of the limits imposed by operating and environmental conditions. Due to these unique properties, RTV silicones are commonly the "material of choice" for designers who desire to improve the performance of Department of Defense (DoD) materiel and weapon systems. These RTV silicones find extensive uses as sealants, adhesives, coatings, heat insulators, and encapsulating materials. However, in order for RTV silicones to consistently achieve a high level of adhesion to various substrates, current technology requires the use of a silane primer prior to silicone application. These silane primers usually contain between 90 and 98 percent volatile organic compound (VOC) solvents that evaporate into the air when the primer is applied. High VOC solvents pose a significant environmental concern and are hazardous to the health and safety of the workers using them; as a result, these solvents are regulated by a variety of local, state, and federal laws, as well as by executive orders in the Department of Defense. In addition, the waste primer and its associated applicators are classified as hazardous waste and must be discarded using highly regulated, laborious, and costly procedures. For these and other reasons, it is apparent that the development of primerless silicone technology will have a tremendous and lasting impact on pollution prevention in manufacturing processes that utilize these materials. The purpose of this project therefore was to develop, evaluate, and transition self-bonding, addition cured silicones capable of providing excellent adhesion to a variety of substrates without requiring the use of a primer or compromising the durability, compatibility, thermal resistance, and long-term stability of the material, as compare to currently available RTV materials requiring silane primers for bonding.

In order to accomplish this effort, the Armament Materials Team of the Armaments Research, Development, and Engineering Center (ARDEC), in a collective effort with the Department of Energy (DOE), General Electric Global Research Center (GE-GRC), Air Force Research Laboratory (AFRL), and Naval Air Warfare Center (NAVAIR), prepared a comprehensive proposal to address the Strategic Environmental Research Development Program (SERDP) Statement of Need, PPSON-99-04, "Elimination of High VOC Primers with RTV Sealants" in the 1998 fiscal year. The proposed approach necessitated the development, evaluation, and transition of self-bonding, addition curable RTV silicone adhesives/sealants capable of providing adhesion to various substrates

without using environmentally hazardous primers. The proposal was approved by the SERDP Science Advisory Board (SAB) in September 1998; funding was received at the end of December 1998. An initial contract package supporting a 3-year effort then was prepared, coordinated with all concurring ARDEC Offices, and submitted to the ARDEC Procurement Directorate, who approved and submitted the package to the Small Business Administration; contract number DAAE30-99-C-1042 was issued to GE-GRC on 27 January 1999. This was later extended to a 4 - year contract ending 31 January 2003.

The Army at ARDEC was responsible for overall program management of the effort and GE was responsible for the design of new adhesion promotion systems. To aid this development, GE subcontracted Molecular Simulations Inc. (MSI) to provide molecular modeling of adhesion promoter-platinum interactions and adhesion promoter-surface interactions. GE also subcontracted Virginia Polytechnic Institute (VPI) to perform surface analysis and failure mode analysis of samples fabricated with the amended RTV silicone sealant/adhesive systems. In addition to providing management for the effort, the ARDEC Armament Materials Team also was responsible for conducting physical testing and adhesion evaluations with the amended RTV silicone systems. The DOE/Kansas City Plant, managed by Honeywell, performed various laboratory tests including physical property testing and electrical property testing of the candidate primerless systems as well as developing and fabricating "commercial" quality test kits of the finalized RTV formulations. The Air Force Research Laboratory and the Naval Air Warfare Center also tested candidate formulations to verify the performance of the material at the environmental conditions required for their specific applications. In addition, all of the three DoD organizations tested the kits fabricated by the DOE KCP to insure the kits had strength and performance properties equivalent to the laboratory fabricated versions.

The research and development effort was divided into three main phases, which focused on a methodological development of primerless adhesion promoting technology using a risk reduction strategy. In these phases, primerless formulations, that were amended with adhesion promoters, specifically synthesized to provide excellent adhesion to substrates for which known DoD applications for these materials exist, were developed. The rest of the effort focused on primerless RTV kit preparations and on identifying specific military applications with the aim of transitioning this technology to DoD production items.

The aim of the first phase of the effort, which was completed in the 1999 fiscal year, was to develop an RTV silicone material capable of achieving adhesion to glass and metal substrates without the use of a primer, when subjected to an elevated temperature curing cycle. To accomplish this, RTV 630, an addition curable silicone system commercially available from General Electric, was amended with a bi-functional adhesion promoter compound. Alclad aluminum and bare aluminum were selected as representative substrates to be used to screen adhesion promoters against, and as a substrate basis for molecular modeling studies during this phase of the effort. Molecular modeling studies were initiated in this phase by Molecular Simulations Inc. (MSI) in an effort to both guide the adhesion promoter synthesizing efforts and to help understand the mechanism through which adhesion was attained. Surface analysis studies were conducted at

Virginia Polytechnic Institute to characterize the surface chemistry of the alclad aluminum and bare aluminum substrates. A first-generation formulation (PLS100-630) was developed in this phase; it provided excellent adhesion to both alclad aluminum and bare aluminum without the use of a primer when cured at an elevated temperature.

The goal of the second phase of the effort, which was completed in the 2000 fiscal year, was to develop an RTV silicone material capable of achieving adhesion to glass, thermoset plastic, and metal substrates without the use of a primer under room-temperature curing conditions. To accomplish this, RTV 866, an addition curable silicone system commercially available from General Electric, was amended with less inhibiting adhesion promoters than the bi-functional adhesion promoters developed in the first phase of the project. Extensive molecular modeling studies were conducted in this phase to predict adhesion promoter interactions with the substrate, as well as with the silicone matrix, and to further guide the adhesion promoter synthesizing efforts. The Department of Defense and the Department of Energy labs continued to perform validation testing with the second-generation amended formulations, as was done with the first-generation formulations, and VPI continued surface and failure analysis studies. Down-selection of four adhesion promoters with promising chemistries was carried out, and a robust, primerless, room temperature curing system (PLS200-866) composed of RTV 866 amended with bis(trimethoxysilylpropyl) succinate was optimized to provide excellent adhesion to epoxy, glass-reinforced phenolic, steel, alclad aluminum, bare aluminum, and anodized aluminum substrates.

The purpose of the third phase of the effort was the development of primerless RTV silicone formulations capable of providing adhesion to specific thermoplastic substrates selected due to their frequency of use in DoD and DOE applications. Due to a required restructuring of the project funding distribution schedule from the SERDP office, this phase of the effort, which was scheduled for completion in the 2001 fiscal year, was extended over a two-year period into the 2002 fiscal year. Work in this phase of the effort was focused on developing and evaluating multiple adhesion promoting functionalities, in a rational fashion, using guidance from molecular modeling predictions in the attempt to develop adhesion promoters capable of enhancing adhesion to selected thermoplastic materials. These materials traditionally prove to be very difficult to adhere to using silicone adhesives, even with primers, making this phase the highest risk phase of the effort. Knowledge gained from molecular modeling studies conducted during this phase and the previous phases provided a strong basis from which to identify potential adhesion promoters. GE, having evaluated a multitude of adhesion promoters, has successfully optimized and demonstrated two primerless formulations (PLS300A-630 and PLS300-866) with a third-generation adhesion promoter diallyl bisphenol A that provided excellent adhesion to Nylon 6,6 substrates. Surface analysis and polymer characterization also continued at VPI in order to help direct this formulation work. DOE fabricated "commercial" quality test kits of the three generations of primerless RTV materials. The DoD and DOE labs have concluded validation testing of the kits which had properties equivalent to the laboratory fabricated versions.

EXPERIMENTAL PROCEDURES

Adhesion promoter synthesis procedures can be found in Appendix A.

Formulations

Formulations PLS100-630, PLS200-866, PLS300A-630, and PLS300-866 were prepared by using a 10 to 1 mixture of either RTV 630A with RTV 630B or RTV866A with RTV866B, amended with appropriate additives as noted in the results and discussion section (also referenced in Appendix B). After thorough mixing, the formulations were degassed for a minimum of fifteen minutes prior to preparation of test samples.

Statistical Methods

Either Minitab® 12 or Design Of Experiment® was utilized for statistical analysis in the formulation optimization work performed by GE.

Preparation of Lap Shear Samples

Lap shear specimens were prepared and tested according to ASTM D1002-99 (Reference 5); however, the government labs selected test temperatures, which were representative of the conditions for which typical applications of silicone adhesives exist within each particular organization. In the evaluation of the first-generation and second-generation formulations, the government labs fabricated samples with bare 2024 T-3 aluminum and alclad 2024 T-3 aluminum substrates for testing of the baseline RTV + silane primer) and the optimized primerless RTV formulations. GE fabricated samples using alclad 2024 T-3 aluminum and bare 2024 T-3 aluminum substrates for use in an optimization design of experiments (DOE) in order to develop a primerless first-generation formulation capable of developing adhesion to these substrates under an elevated-temperature curing cycle. Similarly, alclad 2024 T-3 aluminum, bare 2024 T-3 aluminum, sulfuric acid anodized 2024 T-3 aluminum, and 4340 stainless steel substrates were used by GE in an optimization design of experiments (DOE) in order to develop a second-generation primerless formulation capable of providing excellent adhesion to all four of these substrates. Third generation formulations were developed for thermoplastic substrates; Lexan ®, Nylon 6,6, and Ultem ® were used by GE to evaluate and optimize these formulations.

The compounded adhesive formulations were applied to one inch by four inches lap shear panels that were cleaned with an organic solvent (isopropanol or acetone) and then were bonded with a one-inch overlap. Replicates (four to five) were prepared for each sample formulation and for each substrate. Specimens were cured for seven days at ambient temperature or for one hour at 100°C. GE, ARDEC, and DOE evaluated the lap shear strength of samples at –25°F, RT, and 145°F while the Navy and Air Force testing was conducted at temperatures of –65°F, RT, and (400°F for aluminum or 200°F for Nylon 6,6). The ultimate shear strength and the mode of failure, in terms of percentage of cohesive failure, were recorded for each sample. GE conducted all testing at a loading rate of 2.00 inches per minute while the government laboratories conducted testing at loading rates of both 0.05 inches per minute and 2.00 inches per minute. A schematic

diagram of the lap shear configuration, examining several different bonding arrangements that were evaluated to further characterize the effects of substrate and bond-line thickness, under this type of testing condition, appears in Figure 1.

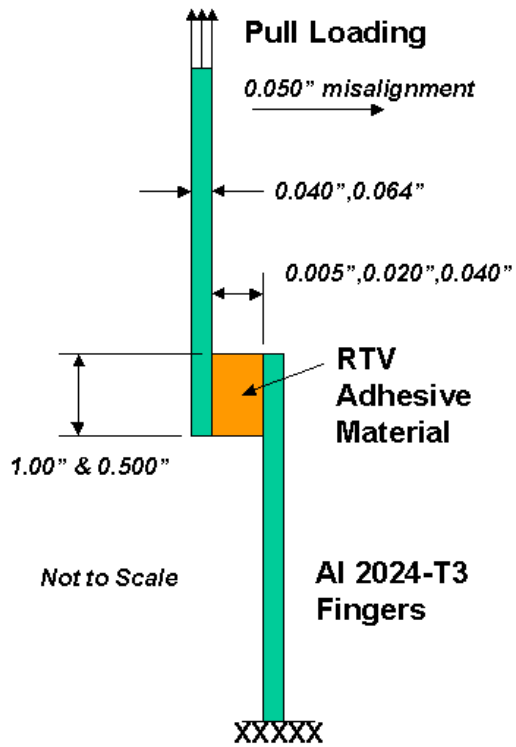


Figure 1: Lap Shear Sample Configuration.

Preparation of Peel Adhesion Samples

GE prepared peel adhesion samples (180° peel) in accordance with ASTM D 903-98 (Reference 6) for testing adhesion to epoxy and glass-filled phenolic substrates. This was necessary because the adhesion obtained in the lap shear configuration was substantial enough that failures occurred in the epoxy and phenolic substrate coupons rather than in the adhesive bond. Stainless steel screens were cleaned by immersion in a 5% alkonox bath at 60-70°C for fifteen minutes, followed by rinsing with distilled water. The screens were primed in a hydrolyzed aminoethylaminopropyltrimethoxy silane/ethanol solution for fifteen minutes. The primer solution for the screens was prepared by mixing 0.01grams of distilled water, 0.95 grams of aminoethylaminopropyltrimethoxy silane, and 0.95 grams of methanol, and allowing the primer solution to stand for three hours. The primer solution then was diluted with 200 milliliters of absolute ethanol. Primed screens were allowed to air dry prior to bonding.

Peel samples were prepared using a mold with four-inch by one-inch spacers with a thickness of 0.125 inches. Epoxy coated coupons or glass-filled phenolic coupons were abraded, cleaned, placed in the mold, and coated with the second-generation adhesive formulations; then screens were placed in the adhesive. Excess adhesive was removed by running a flat blade over the top of the spacers. Replicates (four to five) were prepared for each sample formulation. The samples were cured for seven days at room temperature or for one hour at 100°C. The peel adhesion strength was measured using an Instron 4202 with a crosshead speed of six inches per minute over a distance of 4.5 inches. The first half-inch and last half-inch of data were excluded in the calculation of the average load. A schematic diagram of the peel sample configuration used to conduct design of experiments to develop optimized second-generation formulations that provide adhesion to glass reinforced phenolic substrates and epoxy substrates appears in Figure 2.

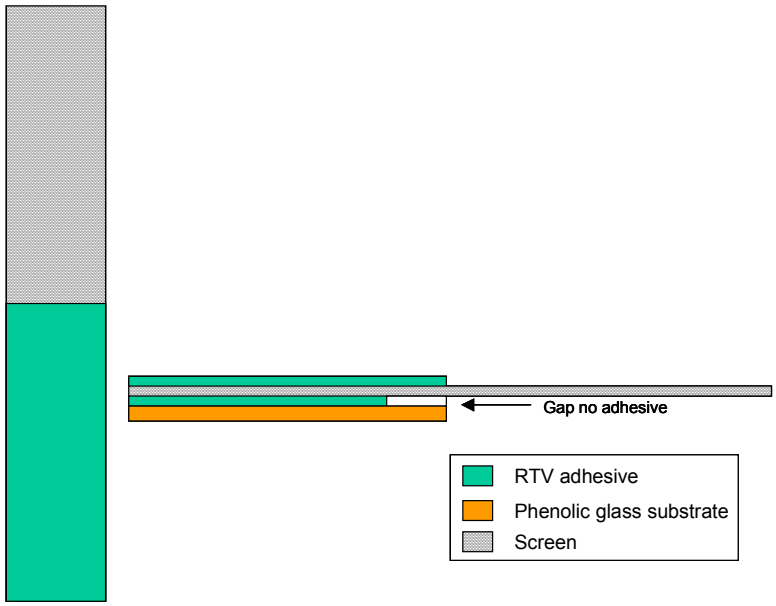


Figure 2: Peel Sample Configuration.

Preparation of Wedge Adhesion Durability Samples

Wedge specimens were fabricated and tested in accordance with ASTM D3762-98 (Reference 7) and durability, as measured by crack growth behavior, was determined for the candidate primerless RTV silicone adhesives. Parameters, including substrate surface preparation and environmental exposure conditions, were evaluated using the wedge – type specimen configuration shown in Figure 3, under Mode I (peel) conditions. The adhesive mixing and curing procedures distributed by GE were followed in the preparation of these bonded specimens (Appendix B).

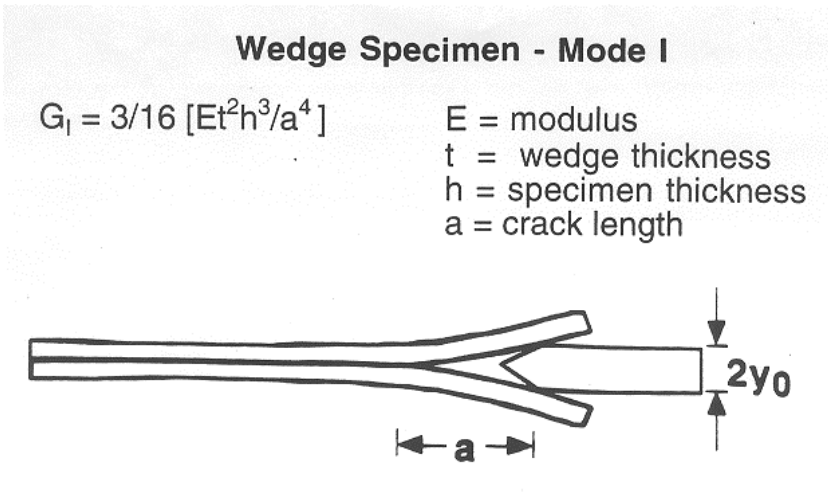


Figure 3: Wedge Specimen Configuration

The fracture behavior was studied by inserting a 3mm wedge into the bonded specimens and measuring the crack growth in samples which were maintained either in air or immersed in water at room temperature. In several instances, the fracture energy for the specimens was sufficiently low that insertion of the wedge, to give an adherend separation of 3 mm by the normal testing procedure, induced de-bonding (crack growth) along the whole length of the sample. In such situations, to obtain controlled crack growth, the wedge was inserted to a depth that resulted in an adherend separation of 1 millimeter. For each test condition, three bonded specimens were studied and the resulting crack data was reported as an average for the results obtained from the three specimens. Crack propagation was followed, and appeared to cease after one hour. Fracture energies were calculated using the measured arrest value for the crack.

Aluminum Wedge – Surface Preparations

Abrade

Abraded, isopropanol cleaned aluminum substrates were prepared by VPI using Al-6061 coupons (1”x 0.25”x10”; W x T x L). The surface of the substrate was initially cleaned with acetone and a Scotch-Brite pad to remove printing and contaminants. The surface then was cleaned with isopropanol (IPA) and dried before applying the silicone adhesive. The IPA-cleaned samples were bonded (0.005 inch bond line thickness) in a wedge-type configuration using first-generation or second-generation primerless RTV silicone adhesives. The mixing and curing procedures distributed by GE were followed in the preparation of these adhesive specimens. Aluminum substrates also were prepared via a base-acid cleaning for bonding with the second-generation adhesive.

Base Acid

For the base-acid treatment, aluminum samples were abraded using Scotch-Brite pads. Subsequently, the surfaces were cleaned using the base-acid procedure. The aluminum substrates were immersed in a 5% (weight) aqueous solution of NaOH at 60°C for three minutes. The specimens then were rinsed in deionized (DI) water and placed in an aqueous dilute HNO_3 (50% volume/volume) solution for two minutes. The samples then were immersed in a beaker of DI water for rinsing. Prior to bonding, the specimens were cleaned with isopropanol and dried.

P2 Etch

P-2 etched aluminum samples were prepared by first cleaning via the base-acid cleaning procedure (as described above) and then by using the P2 etch procedure. The P2 solution is an iron(III) sulfate solution, which oxidizes the aluminum surface. The solution was prepared by combining 122.5 grams of $Fe_2(SO_4)_3$*4 H_2O with 0.l85 liters of concentrated sulfuric acid. These two components were diluted with DI water to a volume of 1 liter. The aluminum panels were submerged in the P2 solution at 70°C for 8 minutes. After removal, the substrates were rinsed under a stream of DI water and then placed in an oven at 115°C for between 30 minutes and one hour to dry.

Coupling Agent

Aluminum specimens were treated with the coupling agents for several time periods using different concentrations of the coupling agent. The optimum treatment conditions were identified as follows: clean aluminum using the base-acid procedure; prepare approximately one liter of a 5% (by volume) solution of the coupling agent in 100% ethanol, immerse the aluminum adherends in the alcohol solution and then add about 30 milliliters of 0.1M hydrochloric acid while stirring; allow the aluminum to remain immersed for approximately 30 minutes; remove the specimens, rinse with deionized water and dry in air. The panels then were stored in a dessicator until they were bonded. In assembling the aluminum wedge specimens, one aluminum panel was placed flat on a surface and metal shims 0.25 mm (0.010”) thick were placed at two locations along the panel to control bond line thickness. One shim was placed at the end of the panel while the other was placed approximately 25 mm (1”) from the other end. The adhesive was then spread evenly between the two shims and another Al panel was placed on the adhesive film. To hold the specimen rigid during curing, the adherends were held together using two metal clips placed at each end. The samples bonded with second-generation adhesive were allowed to cure for seven days at room temperature. Samples bonded with first-generation adhesives were cured at 110°C for 1 hour.

Plastic Surface Preparations

The effect of plastic surface treatments was investigated by preparing surfaces using simple solvent cleaning, a corona treatment, a plasma treatment, or a silane derivatization. These treatments were selected with the idea that alteration (oxidation) of the plastic surface chemistry would enhance the durability of the adhesive bond.

In assembling the plastic wedge specimens, one 6" long x 1" wide x ¼" thick plastic strip was placed flat on a surface and metal shims 0.635mm (0.025") thick were placed at two locations along the panel to control bond line thickness. One shim was placed at one end of the panel while the other shim was placed approximately 25 mm (1") from the other end. The adhesive was then spread evenly between the two shims and another plastic panel was placed on the adhesive film. To keep the specimen rigid during curing, the adherends were held using metal clips placed at each end. For some specimens, aluminum strips were attached to the plastic strips to reduce or eliminate deformation. Specimens bonded with RTV primerless adhesives were cured at 100°C for 1 hour.

Cleaning

Lexan and Nylon 6,6 wedge strips were solvent cleaned in isopropanol (IPA), and air dried before the RTV silicone adhesive was applied. The IPA-cleaned samples were bonded (0.010 inch bond line thickness) in the wedge-type configuration

Surface Activation

After being IPA cleaned, selected Lexan and Nylon 6,6 wedge samples were either corona treated in air (Telsa coil held over the bond surface) for 1 minute, or plasma treated in air (80% argon, 20% oxygen) with a Plasmod RF unit for 5 minutes. Samples then were immediately bonded into wedge specimens to take optimum advantage of the surface activation.

Coupling Agent

Selected specimens were cleaned or cleaned/abraded and then treated with the aminopropyl silane (APS) coupling agent. The two treatments are listed below. After being processed these Lexan and Nylon 6,6 panels then were stored in a dessicator until they were bonded.

1: Pretreatment of the plastic – **solvent cleaning**

a) clean with isopropanol
b) immerse plastic in 0.1M H_2SO_4 for 10 minutes
c) rinse plastic in DI water
d) immerse plastic in silane solution: 5% APS in ethanol (100 mL); add 10 mL 0.1M H_2SO_4
e) allow plastic to remain in the APS – acid solution for 30 min
f) remove from APS solution, rinse in ethanol, and oven dry at 120°C for 30 min.
g) bond with silicone adhesive

2: Pretreatment of the plastic – **abrasion**

a) clean with isopropanol
b) abrade with sand paper (180 grit) or Scotch-Brite to create a moderately rough surface
c) rinse abrasion grit from the surface with alcohol (ethanol or isopropanol)
d) immerse plastic in 0.1M H_2SO_4 for 10 minutes
e) rinse plastic in DI water
f) immerse plastic in silane solution: 5% APS in ethanol (100 mL); add 10 mL 0.1M H_2SO_4
g) allow plastic to remain in the APS – acid solution for 30 min
h) remove from APS solution, rinse in ethanol, and oven dry at 120°C for 30 min.
i) bond with silicone adhesive

Preparation of Tensile Adhesion Samples

In order to evaluate adhesion of the optimized second-generation formulation to epoxy and glass fiber reinforced phenolic substrates, a tensile adhesion test was derived from ASTM D-897 –01 (Reference 8). This was necessary because the peel tests that were utilized to optimize the second-generation primerless RTV formulation were found to yield significant standard deviations due to factors, such as the bond-line thickness of the sample, that were difficult or impractical to tightly control,. To eliminate these high standard deviations for characterization purposes, samples were prepared using 4340 steel "T-Hat" test components (Figure 4) that were blasted on the bonding surfaces with 180-alumina grit, then solvent-wiped with methylethylketone prior to bonding.

Figure 4: Tensile Adhesion Specimen Configuration.

The "T-Hat" components were bonded with the second-generation primerless formulation containing 0.5-millimeter glass beads in order to maintain a bond-line thickness of approximately 20 thousandths of an inch. Pressure was applied to the samples during curing to force the excess adhesive to flow out of the bond-line, and a fixture was utilized to maintain the alignment of the two "T-Hat" components. The samples were allowed to cure for seven days at room temperature prior to testing.

To evaluate adhesion to epoxy, the grit-blasted, solvent-wiped "T-Hats" were coated with an Amerlock 400FD epoxy and then were allowed to cure for 7 days at room temperature prior to grit-blasting, solvent cleaning, and bonding with the primerless second-generation formulation containing 0.5-millimeter glass bead spacers. Pressure was applied to the samples during curing to force the excess adhesive to flow out of the bond-line and a fixture was utilized to maintain the alignment of the two "T-Hat" components. Samples were allowed to cure for seven days at room temperature prior to testing.

Adhesion to glass-reinforced phenolic substrates was evaluated by bonding the grit-blasted, solvent-wiped, "T-Hats" with the second-generation primerless formulation (with the 0.5-millimeter glass bead spacers) to a grit-blasted, solvent cleaned, 1 inch square piece of 1/8 inch thick flat phenolic test specimen that was placed between the two steel "T-Hats" in a "sandwich" configuration. Samples were allowed to cure for seven days at room temperature prior to testing.

Spot Adhesion Tests

Spot adhesion tests were conducted in accordance with ASTM D 3808 – 01 (Reference 9). This is a quick and simple test method to determine whether a candidate primerless RTV adhesive will bond to a particular substrate/ surface preparation test combination.

NMR Imaging

Images were obtained on a GE 33-cm horizontal bore imaging Nuclear Magnetic Resonance (NMR) spectrometer. A standard spin warp imaging sequence was used to obtain a 64 x 64 x 32 mm image with a 1 x 1 x 1 mm voxel (volume element) size. RTV samples were imaged as quickly as possible after being mixed. The starting material was liquid and became solid upon cuing. Tiled, grayscale images, developed from the data were colorized for evaluation.

X-ray Photoelectron Spectroscopy

Data were acquired on a PHI 3500 instrument with an Al K_{α} monochromator. Survey scans were performed with the energy analyzer set at a pass energy of 187 eV. High-resolution scans of individual core levels were obtained with a pass energy of 12 eV.

Secondary Ion Mass Spectrometry

Data were acquired on a PHI 3500 instrument using a 4 kV Xe^{+} source with a one nA beam current. The analyzed area was 4x4 mm. Secondary ions were detected using a quadrupole mass spectrometer.

RESULTS AND DISCUSSION

The aim of this study was to develop RTV silicone sealant/adhesive formulations that were capable of adhering to a variety of metal and non-metal substrates without the use of an environmentally hazardous silane primer. A detailed description of the studies that were conducted and of the accomplishments that were realized in the process of developing the primerless first-generation formulation PLS100-630 (US Patent 6,296,944 - for hydromuconate adhesion promoter) was presented in the technical report *Primerless RTV Silicone Sealants/Adhesives –PP1135* dated December 1999. The second phase of the effort, focused on the development of room-temperature curing formulations that were capable of providing adhesion to metal, glass, and thermoset plastic substrates. A detailed description of the studies that were conducted and of the accomplishments that were realized in the process of developing the primerless second-generation formulation PLS200-866 (US Patent 6,447,922) was presented in the technical report *Primerless RTV Silicone Sealants/Adhesives –PP1135* dated December 2000. However, due to restructuring of the project schedule, much of the validation work that has been conducted with this formulation was discussed in the following year's report *Primerless RTV Silicone Sealants/Adhesives –PP1135* dated December 2001. The results of these studies also have been summarized in four papers co-written by Dr. Bruce Eichinger and Dr. Judith Stein that are included in Appendices C, D, E, and F.

The objective during the third phase of this project was to develop primerless self-bonding RTV silicone sealant/adhesive materials that exhibited good adhesion to selected thermoplastic substrates. To accomplish this task, surface characterization of Lexan ®, Nylon 6,6, and Ultem ® substrates were performed, and molecular modeling studies were conducted utilizing these results in conjunction with quantum mechanical calculations to design chemical structures and critical chemical functionalities to help to guide in the identification and selection of both the second and third-generation candidate adhesion promoters. A detailed description of the studies that were conducted and of the accomplishments that were realized in the process of developing the primerless third - generation formulations (PLS300A-630, and PLS300-866: US Patent Application 20030049465) was presented in *Primerless RTV Silicone Sealants/Adhesives –PP1135* dated December 2002, and a portion of the results of this part of the program study also has been summarized in another paper co-written by Dr. Bruce Eichinger and Dr. Judith Stein and is included as Appendix G.

The adhesion promoters developed for each phase of the study then were synthesized and material performance evaluations were carried out employing predetermined physical property and adhesion strength criteria against which formulations were determined to be acceptable or unacceptable. Formulations that passed this initial screening phase then were further examined using Designs of Experiments and statistical models to establish formulations that provide excellent adhesion to these substrates. The adhesive performances of all of the optimized formulations then were tested in a variety of bonding configurations over temperature ranges required by end-item applications.

The final phases of this effort were focused on additional technology assessment and transitioning of the optimized formulations into DoD and DOE applications, and was completed during the 2003 fiscal year, under the restructured project execution schedule. In support of this effort, the Polymer Production Facility (PPF) at the Department of Energy, Kansas City Plant, has formulated the adhesion promoters and additives, as well as packaged and distributed complete primerless RTV kits, (PLS 100-630, PLS200-866, PLS300A-630 and PLS300-866) to the DoD and DOE team members for evaluation. Testing showed the kits to have properties equal to the laboratory fabricated versions. A technology transfer assessment was conducted with the XM 984 Extended Range Mortar. Several simulations and actual flight tests were conducted successfully with one of the primerless RTV formulation.

Elevated Temperature, Primerless Adhesion to Metals

In the first year of the effort, GE developed a primerless RTV silicone formulation that cured at an elevated temperature and exhibited adhesion to many metal substrates without the need for a silane primer. The design criteria for this system were identified and the adhesive performance and physical properties of this system were compared against a baseline system consisting of RTV 630 with substrates treated with SS-4155 primer for which the process capability was determined (Figure 5). The mean ultimate adhesion value obtained for the baseline system tested in lap shear was found to be 645 +/- 47 pounds per square inch. The two "critical to quality" attributes that were used to select the optimized formulation were "entirely cohesive failure in bonded specimens" and "ultimate lap shear strength values greater than 300 pounds per square inch", while not deviating from the physical properties of the unamended baseline formulation.

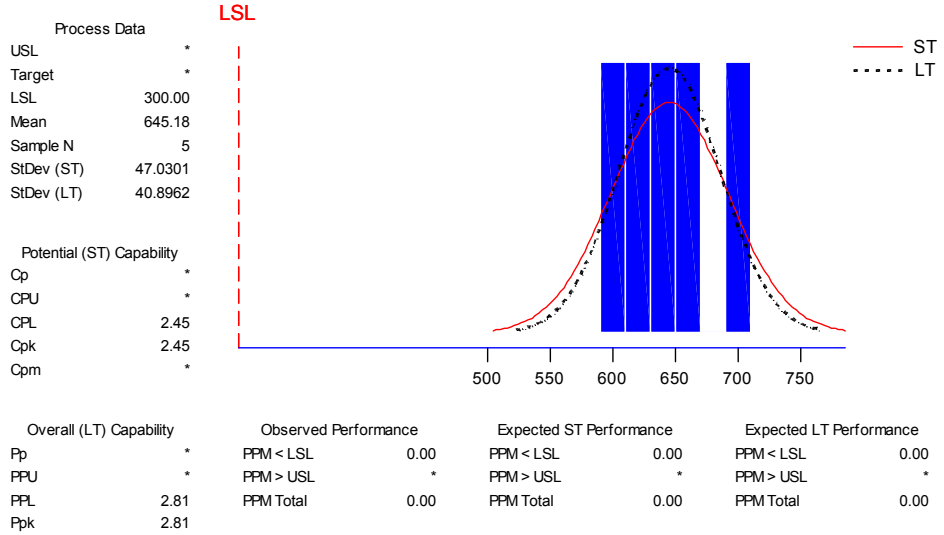


Figure 5: Process Capability of Baseline RTV 630 System with Primer.

This first-generation formulation consisted of the RTV 630 addition curable silicone resin amended with bis(trimethoxysilylpropyl)fumarate adhesion promoter and silicon hydride cross-linker. A screening Design of Experiments was performed by varying the concentrations of adhesion promoter and cross-linker in the first-generation formulation in order to define the experimental design space in which adhesion was attained, then a final central composite Design of Experiments was performed to optimize adhesion, and consequently maximize the performance of the first-generation primerless formulation. The optimized first-generation formulation was determined to consist of 0.67% silicon hydride cross-linker and 0.98% bis(trimethoxysilylpropyl)fumarate adhesion promoter by weight. The mean ultimate lap shear adhesion value obtained for this system was found to be 657.5 +/- 48 pounds per square inch. The process capability for the optimized first-generation formulation is shown in Figure 6.

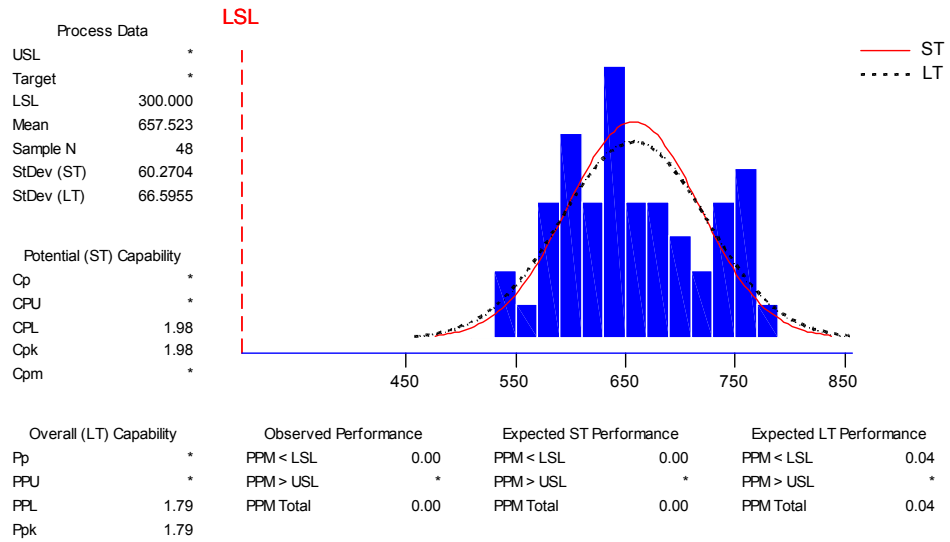


Figure 6: Process Capability of Primerless First-Generation Formulation.

House of Quality Analysis

A list of desired attributes for the new silicone adhesives/sealants was developed by the team and then culled down to the "Critical to Quality" attributes (CTQ's) listed below:

1. Adhere to metals and "plastics" without need for a primer.

2. Adhere to metals and "plastics" with green strength, developing in 24 hours at room temperature or in 4 hours at 165°F.

3. Exhibits cohesive failure after seven days room temperature cure.

4. Attributes such as application rate, shrinkage, and cured physical/mechanical properties comparable to RTV 630.

5. A pourable material with a viscosity range of 150,000 cps to 400,000 cps

6. Cost comparable to that of RTV 630.

7. Shelf life of 1 year @ room temperature.

8. Useful operating temperature range of –75°F to + 400°F.

9. Same DOT shipping code as RTV 630.

10. A two part environmentally friendly system. No health hazard and no VOC by-products more than that produced by RTV 630.

A House of Quality (Figure 7) was constructed using the "Critical to Quality" attributes. It was determined that the three most important CTQ's were:

- environmentally benign
- adhesion to glass, metal, and plastic
- low temperature cure

Product Requirements	*Importance Rating*	Nontoxic	Non polluting low voc's	Raw material quality inputs	Low cost AP package	Pourable	Coefficient of expansion	Adhesion to substrate	Low shrinkage	Non inhibiting AP package	Wide use of temperature	DOT packaging same as RTV630	Dielectric strength	Electrical resistivity	2-part system	Properties of 630 and primer	Green strength	Pot life	Adhesion promoter concentration
CTQ																			
Environmentally benign	5	9	9	6	1	1	1	1	1	1	1	6	1	1	1	1	1	1	1
Adh/glass/metal/plastic	5	1	1	1	1	1	6	9	3	6	6	1	1	1	1	9	9	1	9
Low temp cure	4	1	1	1	1	1	1	6	1	9	1	1	1	1	6	9	9	6	9
Easily applied	3	1	3	1	1	9	1	1	1	3	1	1	1	1	6	9	1	6	3
Dimensional stability	3	1	3	1	1	1	6	3	9	1	1	1	1	1	1	9	1	1	3
Good electrical properties	3	1	1	1	1	1	1	1	1	1	1	1	9	9	1	9	1	1	1
Paintable	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Cool	2	3	3	3	9	3	1	3	1	1	1	1	1	1	3	3	1	3	6
Shelf life	2	1	1	1	1	1	1	1	1	9	1	6	1	1	9	9	3	1	6
Work life	3	1	1	1	1	6	1	1	1	6	1	1	1	1	9	1	6	9	9
Importance Rating		75	87	70	47	74	71	101	65	125	56	66	55	55	170	195	122	94	159
Measurements		**TSCA/OSHA tests, pmn**	**EPA tests**	**Raw material specs, MSDS**		**viscosity**		**Lap Shear**	**Cure Speed**		**adhesion temperature tests**		**ASTM**	**ASTM**		**tensile/hardness/electric properties**	**Tack tests**	**Viscosity**	**Weighing**

Figure 7. House of Quality

Instron Sensitivity Analysis

A Gage Reproducibility and Repeatability (Gage R&R) test was conducted on the Instron tensile machine used to measure the adhesion of amended formulations to substrates and the physical properties of the formulations. A non-destructive test using 3 weights, 2 operators, and 10 different sampling opportunities was performed. The tolerance selected for the gage was ± 10 lb. The percent total gage R & R was 1.33 %, which verified the sensitivity of the Instron to measure improvements as RTV630 was reformulated (Figure 8). The largest variability was attributed to part-to-part differences (changes in the weights). In addition to determination of the Instron measurement capability using a nondestructive test, the measurement capability also was evaluated under experimental conditions. The procedure involved a destructive test using 15 samples, 1 operator, and the baseline formulation on primed bare aluminum. The standard deviation of the test method was 34 psi. From these two evaluations, it was determined that the Instron test method would distinguish differences in adhesion strength among samples as well as differences in physical properties.

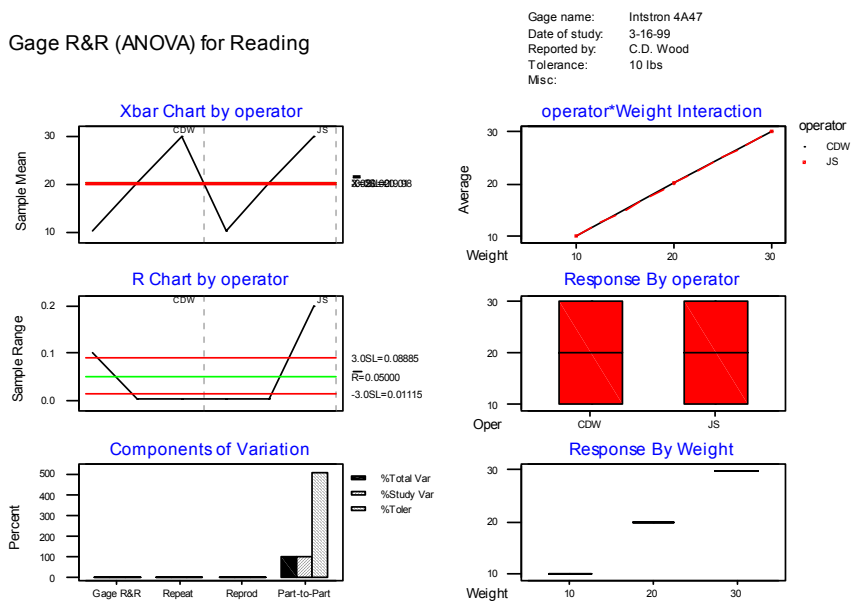


Figure 8. Gage R&R for Nondestructive Testing

Baseline Benchmark Testing of Unamended RTV 630

A benchmarking test of the adhesive properties of unamended RTV630 then was performed using the Instron machine. Al/Al lap shear samples, with and without primer (SS4155), were fabricated and cured for 1 hour at 100°C. Unamended RTV630 displayed an average adhesion value of 645.18 ± 38.4 psi with primer and 362 ± 6.05 psi without primer. A one-way analysis of variance (ANOVA) determined that a statistically significant difference existed between the adhesion strength of RTV630 with and without primer. Process capability was obtained for the primerless system. This process had a Z_{st} score = -95 (Figure 9) using a lower specification limit of 300 psi for adhesion.

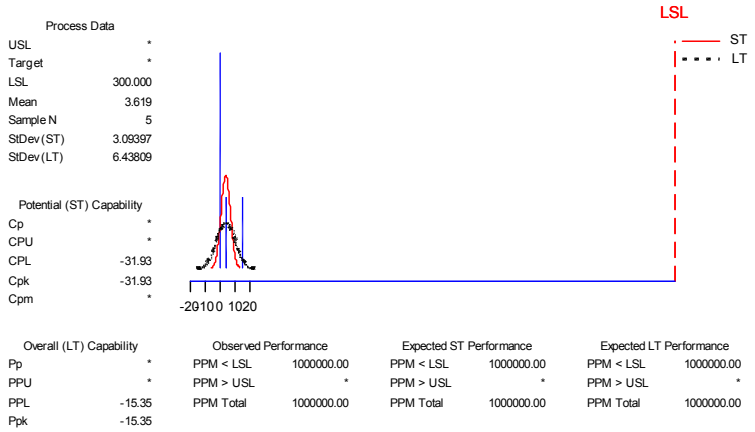


Figure 9. Process Capability Calculation for Unamended RTV630 Without Primer

Using SS4155 primer, the current process had a Z_{st} score = 7.3 (Figure 10).

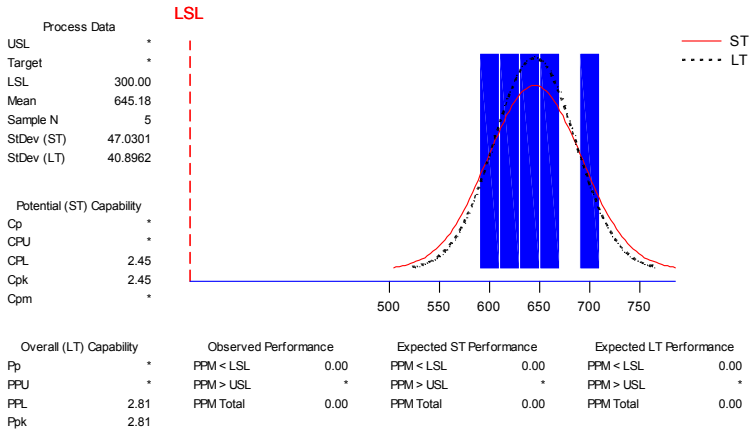


Figure 10 Process Capability of Unamended RTV 630 Baseline System With Primer

Reformulation of RTV630 Using First Generation Adhesion Promoter

RTV630 was reformulated using an adhesion promoter developed as part of this program effort, bis(trimethoxysilylpropyl)fumarate. A screening Design of Experiments (DoE) was performed to define the experimental space in which adhesion can occur. A final central composite DoE was performed to optimize adhesion. Experiments were conducted on samples cured at 100°C/1 hr. The percent of the adhesion promoter bis(trimethoxysilylpropyl)fumarate was varied from 0.5% to 1.5%; the ratio of adhesion promoter to additional silicone hydride was varied from 0.5 and 1.5.

The constraints on the design were found to be:

- The bis(trimethoxysilylpropyl)fumarate concentration cannot exceed 1.5%, if full cure at 100°C/1 hour is to be obtained, and no adhesion is obtained at levels less than 0.5%.

- In the absence of additional silicone hydride, or with excessive silicone hydride levels, the physical properties of the cured formulation are compromised.

The model for the optimized first-generation formulation is shown in Figure 11.

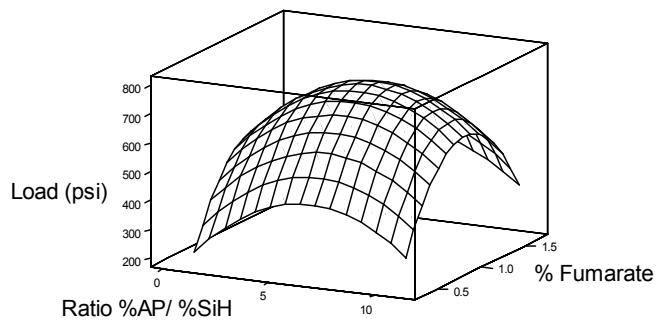


Figure 11. Wire Frame Plot of the Model of the Optimized RTV630 Formulation With First Generation Adhesion Promoter

Regression analysis provided the following transfer function: $Y = -296 + 1465.5x_1 + 91.3x_2 - 713(x_1)^2 - 7(x_2)^2$ where x_1= adhesion promoter and x_2= % adhesion promoter/ % silicone hydride. The optimized formulation which contained 1% adhesion promoter and a ratio of % adhesion promoter/ %silicone hydride of 4.4 provided cohesive failure (658+/-60 psi) after a 1-hour cure cycle at 100°C. The process capability analysis for the 1st generation formulation resulted in a Z_{st} score = 5.9 and a Z_{lt} score= 5.1 (Figure 12).

In order to better understand the addition cure mechanism, molecular modeling was used. The mechanism of the platinum catalyzed hydrosilylation reaction was modeled, and The results were presented at the 221st ACS National Meeting, San Diego and MSI Polymer Consortium 2000 (Eichinger, B., and Stein, J., "Mechanism of the Pt(O) Catalyzed Hydrosilylation Reaction", 221st ACS National Meeting, San Diego, 4/1-5/2001; Stein, J., and Eichinger. B., "The Mechanism of the Pt(O) Catalyzed Hydrosilylation Reaction" MSI Polymer Consortium 2000 Meeting, Key West, Fl, April 2-6, 2000.) and was published in the Polymer Preprints, 2001 (Eichinger, B. E.; Stein, J. Polymer Preprints, 2001, vol. 42, no. 1, pp. 251 Division of Polymer Chemistry, American Chemical Society) (Appendix E).

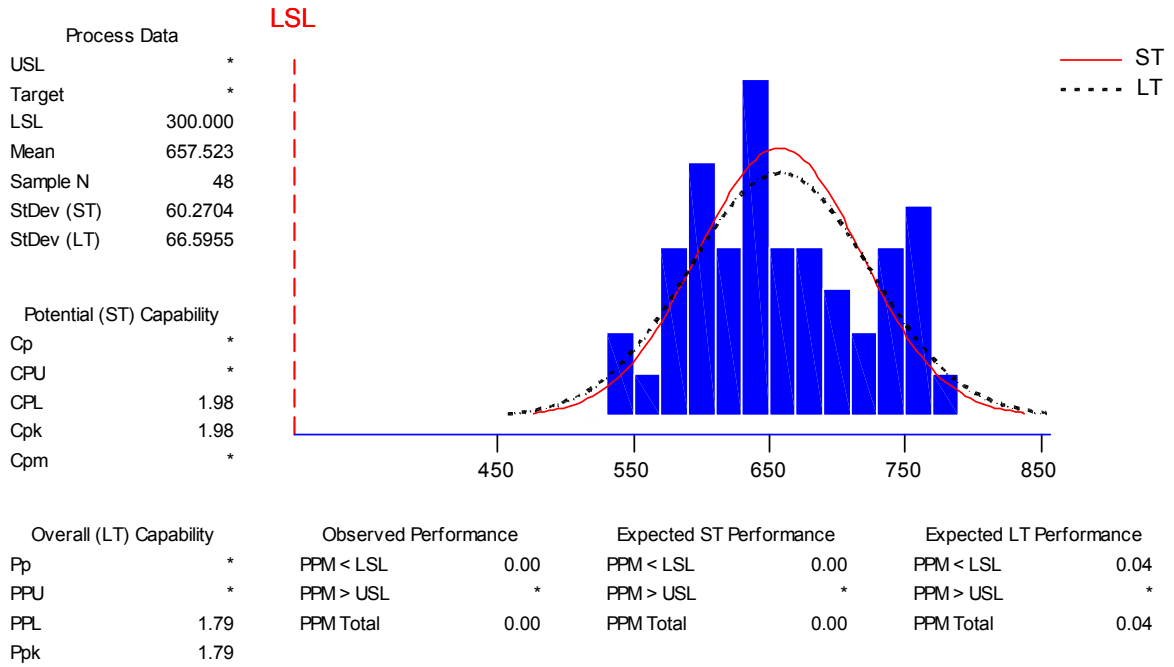


Figure 12. Final Process Capability of First Generation Product

Testing of Unamended and Amended RTV630 Formulations

Tear and tensile properties were measured for baseline unamended RTV630 cured at either 100 ^{o}C/1hour or 70°C/4 hours, and for the optimized first-generation amended RTV630 formulation cured at 100 ^{o}C/1 hour. The values are given in Table 1. Both amended and unamended RTV630 samples had equivalent tear properties (ANOVA, DF 11, P = 0.185). Tensile and elongation at break of the amended formulation were significantly improved ((ANOVA, DF 11, P= 0.022 (tensile strength) P = 0.005 (elongation at break). The hardness of the formulation was reduced with the incorporation of the adhesion promoter. ANOVA analysis of testing conducted at GE indicated no statistical difference between the performances of the unamended baseline and first-generation RTV 630 systems.

Table 1 Physical Properties of Baseline Unamended RTV630 and Amended RTV630

Material (cured for 1 hour at temp)	**Die B tear (pi)**	**Tensile strength (psi)**	**% Elongation**	**Hardness Shore A**
Unamended RTV630 100 ^{o}C	142.15 ± 3.84	815.3 ± 86.7	234.1 ± 89.3	61-62
Unamended RTV630 70 ^{o}C	136.92 ± 5.24	861.6 ± 22.1	293.7 ± 85.5	61
1st gen. Amended RTV630 100 ^{o}C	136.52 ± 4.22	956.7 ± 38.0	446.7 ± 29.9	57

Validation lap-shear tests were conducted at the DoD and DOE facilities with bare 2024 T-3 aluminum and alclad 2024 T-3 aluminum, due to the frequency of use of these substrates in DoD and DOE applications, where addition curable silicones are used for bonding and sealing purposes. Failure loads were found to be well in excess of the design margin over the entire range of testing temperatures and loading rates. A more thorough description of efforts that lead to these results was discussed in the technical report *Primerless RTV Silicone Sealants/Adhesives –PP1135* dated December 1999. Additional spot adhesion tests have been conducted with this formulation and the results of these tests are discussed later in the report.

Aluminum Surface Analysis

Studies were conducted at VPI to compare the durability of bonded aluminum systems using PLS100-630, the first-generation formulation of RTV 630 amended with bis(trimethoxy-silylpropyl)fumarate, and baseline RTV 630 with SS-4155 primer. The objective of these studies was to compare the performance of the unamended and amended RTV silicone adhesive systems and to discern the role of the first-generation adhesion promoter on the adhesive bonding performance of the system. Wedge type specimens were prepared and were tested in the Mode I (peel loading) configuration at room temperature in air and via immersion in water at room temperature. These crack propagation studies were performed with substrates prepared using the base-acid cleaning procedure and the P2 etching procedure; strain energy release rates were obtained by measuring the crack growth rates as a function of time. The results of these studies for the RTV 630 baseline and optimized first-generation materials are shown in Table 2.

Table 2. Baseline and First-Generation RTV 630 Formulation Durability Testing.

Crack Propagation Testing Data (Mode I)				
Formulation	Substrate	Testing Conditions	Failure Mode	Strain Energy Released
				J/m^2
RTV 630 + SS4155 Primer	BA treated	RT air	cohesive	3.50E+03
RTV 630 + SS4155 Primer	P2 treated	RT air	cohesive	3.90E+03
RTV 630 + SS4155 Primer	BA treated	RT water	cohesive	2.20E+03
RTV 630 + SS4155 Primer	P2 treated	RT water	cohesive	2.80E+03
First-Generation Formulation	BA treated	RT air	cohesive	6.80E+03
First-Generation Formulation	P2 treated	RT air	85% cohesive	5.30E+03
First-Generation Formulation	BA treated	RT water	cohesive	3.60E+03
First-Generation Formulation	P2 treated	RT water	75% adhesive	4.40E+03

These results indicate that the first-generation optimized formulation forms more durable bonds with higher corresponding strain energies per unit area than those formed by the baseline RTV 630 system using GE SS-4155 silane primer for P2 etched and base-acid

treated aluminum substrates. It is worth noting, however, that in the case of the P2 etched substrates, mixed failure modes were observed in bonds prepared using the first-generation formulation indicating that this may not be the ideal surface treatment for bonds prepared using this formulation, particularly in applications where the bonds may be exposed to significant amounts of moisture. Regardless of this fact, the data indicated that the performance of the first-generation material was superior to that of the baseline material under the bonding environment examined in these tests. The plots of crack length versus time, used to obtain the data in Table 2, have been included in Appendix H.

Room Temperature, Primerless Adhesion to Metals and Thermoset Plastics

Efforts during the second year of the project were focused on the development of primer-less self-bonding room temperature curable silicones that exhibited adhesion to metal and selected thermoset plastics. It was found that the RTV630 material used in the first-generation formulation did not allow for room temperature curing due to the inhibitory nature of that silicone resin. This necessitated a change to RTV866, another RTV silicone material that was capable of curing at room temperature with adhesion promoters incorporated into the system. The same two "critical to quality" attributes that were used to select the optimized first-generation formulation were applied in selecting the optimized second-generation formulation, namely, entirely cohesive failure in bonded specimens and ultimate lap shear strength values greater than 300 pounds per square inch, while not deviating substantially from the physical properties of the unamended baseline RTV 866 formulation. A more thorough description of efforts that lead to these results was discussed in the technical report *Primerless RTV Silicone Sealants/Adhesives – PP1135* dated December 2000.

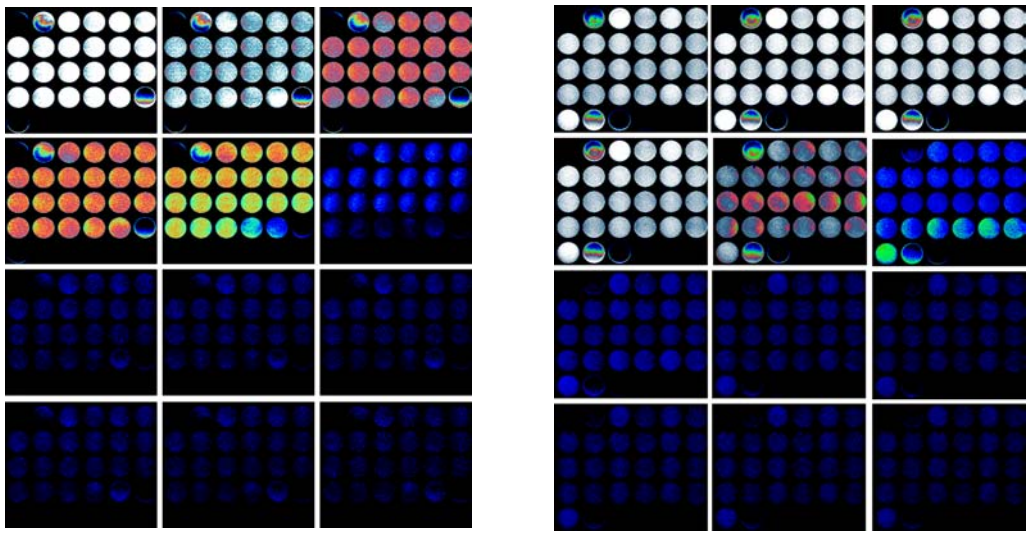
Screening/Down Selection of Adhesion Promoters for RTV 866

The quantum mechanics of the bonding of aluminum and a model adhesion promoter were studied using molecular modeling. These results helped guide the development of the second-generation formulation. This study was published in Surface Science (Eichinger, B.E. and Stein J., A Quantum Mechanical Study of the Bonding of a Silyl Ester to Hydrated Alumina, Surface Science, **492**, 75 (2001)) (Appendix F). Eleven adhesion promoters (listed in appendix I) were evaluated with RTV866 for room temperature adhesion to metal. For each adhesion promoter, a screening DoE was performed to determine if that additive would adhere to Alclad aluminum.

Using the results of these DoE's, the eleven adhesion promoters were down selected to two. This down selection was based on initial adhesion data and physical property evaluation. Both adhesion promoter candidates had pros and cons associated with them. The hydromuconate was difficult to synthesize, but showed robust adhesion to alclad aluminum. The succinate required a much simpler synthesis, but the evaluation of the first batch showed variability within sample sets, which lead to inconsistent results. It was decided to continue to evaluation both of these adhesion promoters. DoE's were conducted to evaluated the adhesion of the RTV866 amended with either the hydromuconate or the succinate to both alclad and bare aluminum (2024). The adhesion promoters were screened using a full factorial design. The factors explored were: adhesion promoter, additional silicon hydride, and additional inhibitor.

The adhesion promoter ranged from 0.77%-1.23% by weight. The weight percent of silicon hydride (88104) was varied from 0% to 0.69%. Finally, the range chosen for the inhibitor (2-methyl-3-butyn-2-ol) was 0.01% to 0.02%. The results of these experiments for the hydromuconate formulations showed good adhesion to alclad, but little or no adhesion to bare aluminum. The succinate showed good adhesion to both substrates and little inter-sample variability. Based on this new data, the succinate adhesion promoter was chosen as the second-generation adhesion promoter.

Nuclear Magnetic Resonance (NMR) Imaging was used to determine the effect of adhesion promoter incorporation on the curing profile of amended RTV866. The cure of RTV866 samples with and without bis (trimethoxysilylpropyl) succinate was monitored using NMR Imaging system (Figure 13). Profiles were recorded every two hours and presented as a frame. In the images below, uncured sample material appears brightest due to relatively long proton relaxation time. As areas of the sample cured, the sample at those voxels (3-D pixels) decreased in signal intensity because the proton relaxation time became shorter and the voxel's color moved from white to red to green to blue to black. In the absence of adhesion promoter, cure was more rapid at the top of the reaction vessel. In contrast, cure was most rapid at the bottom of the reaction vessel for the sample amended with adhesion promoter. The rate of cure did not change with the incorporation of the adhesion promoter.



A **B**

Figure 13. NMR Images of Curing Profile for Polydimethylsiloxane Network

A) unamended (without adhesion promoter)
B) amended (with adhesion promoter)
Grayscale images were colorized so that image intensity from brightest to darkest was mapped to white→red→green→blue→black.
Note: the top of the reaction vessel was at the bottom of each frame

P2 Framework Tool

During an in-process review (IPR), the SERDP board requested that the new adhesion promoters, synthesized for this project, be screened using a Pollution Prevention (P2) computer analysis package. Dr. Farag at the University of New Hampshire employed the P2 framework and screened our second-generation adhesion promoter candidates. The down selected adhesion promoter gave acceptable results in this P2 framework (Table 3). Although this compound showed high aquatic toxicity results, it is most likely to biodegrade and not persist in the water.

Table 3. P2 Evaluation for bis (trimethoxysilylpropyl) succinate

Property	Data	Conclusions/Predictions
ENVIRONMENTAL PERSISTENCE IN:		
Air	OH • ½ life = 0.7 days VP = 3.1 x 10^{-6} mm Hg	Not persistent in air, likely to partition to the air.
Water	Biowin values >0.5	Biodegrades rapidly
	Water half-life <60 days	Not persistent in water
	HLC = nonvolatile	Will not move to air
Soil	Log K_{OC} > 4.5	Will adsorb to soil
	Soil half-life <60 days	Not persistent in soil
Sediment	Sediment half-life >60 days	Persistent in sediment, but not likely to partition to the sediment.
BIOACCUMULATION	BCF = 3.2	Low
AQUATIC TOXICITY	High for acute and chronic	High
CANCER POTENTIAL	At the present time, it is not appropriate to run this structure in OncoLogic.	

Robust Optimization of Second-Generation Formulation

It was previously shown that excellent adhesion could be obtained with RTV866 amended with bis(trimethoxysilylpropyl)succinate on alclad and bare aluminum substrates over a large design space or range of adhesion promoter and inhibitor concentrations. A response surface DoE (with inner and out arrays, three center points and replication at one corner) was designed to investigate and optimize the adhesion of the down selected adhesion promoter on steel, anodized aluminum, bare aluminum, and alclad aluminum. In addition, the range of the adhesion promoter concentration was expanded to include lower levels, since formulation cost is directly proportional to the amount of incorporated adhesion promoter. The inhibitor concentration window also was

widened to go as low as 0%. The DoE ranges were 0.45 to 1.2% by weight bis(trimethoxysilylpropyl)succinate and 0 to 0.02% by weight inhibitor (2-methyl-3-butyn-2-ol). Samples were cured at ambient temperature for seven days and then adhesion bond strength was evaluated. Regression analysis indicated that only the adhesion promoter concentration and its square term were significant; inhibitor level had no effect on adhesion. Also in this design space, adhesion was inversely correlated with adhesion promoter concentration. The equation for the model in coded units was:

Adhesion strength = $568.9 - 83x - 50.4x^2$

where x = bis(trimethoxysilylpropyl)succinate adhesion promoter.

The model, presented as a wire frame plot in Figure 14, had an R^2 value of 89%. Based on the model predictions and screening data the final second-generation formulation was chosen. The second-generation formulation is RTV866 amended with 0.45 % by weight succinate and 0.02% by weight inhibitor (2-methyl-3-butyn-2-ol).

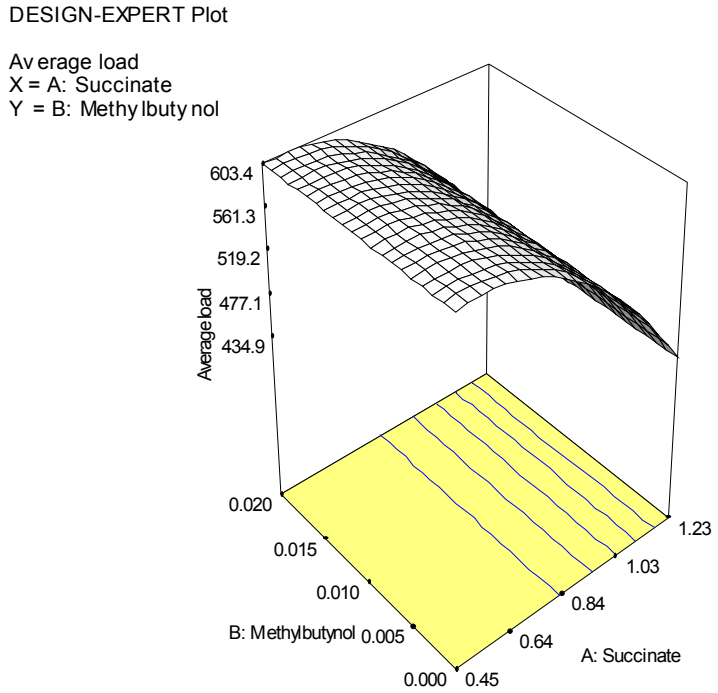


Figure 14. Robust DoE Model Presented as a Wire Frame Plot.

Process capabilities for the Optimized Second-Generation Formulation

A process capability for PLS200-866, the second-generation formulation, comprised of RTV 866 with 0.45% bis(trimethoxysilylpropyl)succinate and 0.02% 2-methyl-3-butyn-2-ol, was determined for adhesion to steel, anodized aluminum, bare aluminum and alclad aluminum. Samples were cured at ambient temperature for seven days and then lap shear adhesion bond strengths were evaluated on an Instron (Table 4, Figure 15). The inhibitor, although shown to have no statistical impact on adhesion, was added to increase the pot life of the formulation. The overall Z_{st} score, independent of substrate for this adhesive system, was found to be 6.11, corresponding to fewer than one failure value of less than 300 psi in lap shear loading per one million opportunities tested. The adhesion of the second-generation formulation also was verified for adhesion to sapphire window material using spot tests.

Table 4. Lap Shear Performance for the Second-Generation Formulation Tested on Selected Substrates

Substrate	Mean (psi)	Std Deviation
Steel	566	43
Anodized Al	600	26
Bare Al	598	52
Alclad Al	633	53
All substrates combined	599	50

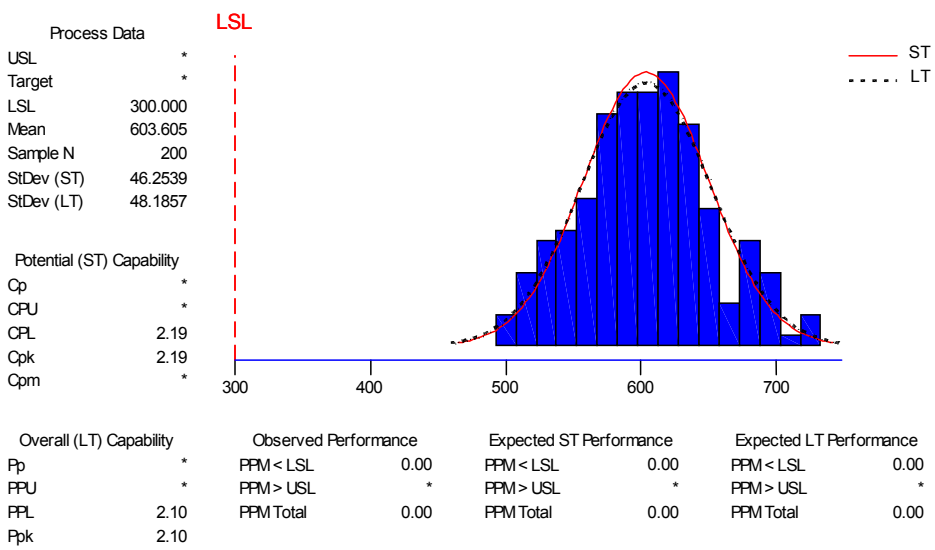


Figure 15. Process Capability of Primerless Second-Generation Formulation.

Testing of Optimized Second-Generation Formulation

The optimized second-generation PLS200-866 formulation also was evaluated for adhesion to epoxy and glass reinforced phenolic substrates using a peel testing method as described in ASTM D903-98. Samples were cured for seven days at ambient temperature or at 100°C for 1 hour prior to testing. In all cases, the failure observed was cohesive, with a mean value of 19.5 ± 0.5 pounds per linear inch for samples of total adhesive thickness between 0.135 and 0.180 inches and a mean value of 15.7 ± 1.5 pounds per linear inch for samples of total adhesive thickness between 0.25 and 0.31 inches using epoxy substrates, and with a mean value of 14.5 ± 1.0 pounds per linear inch for samples of total thickness 0.21 to 0.22 and a mean value of 18.7 ± 0.6 pounds per linear inch for samples of total thickness 0.190 to 0.195 using glass-reinforced phenolic substrates.

Validation lap-shear tests were conducted at the DoD and DOE facilities with bare 2024 T-3 aluminum and alclad 2024 T-3 aluminum substrates; failure loads were found to be well in excess of the design margin over the entire range of testing temperatures and loading rates. Physical property testing also was conducted; the physical properties of the optimized second-generation primerless formulation were found to be essentially identical to those of unamended RTV 866.

In order to further validate the adhesive performance of the primerless second-generation PLS200-866 system, T-Hat tensile tests, derived from ASTM D897-95, were conducted at ARDEC using 4340 steel and glass-reinforced phenolic substrates. For both substrates, predominately cohesive failures were observed in samples tested at all three temperatures (-25°F, room temperature, and 145°F) and similar failure loads were obtained. The results of these tests appear in Table 5.

Table 5. T-Hat Tensile Data for Optimized Second-Generation Formulation.

T-Hat Testing Data					
Formulation	**Substrate**	**Temperature**	**Average Failure Load**	**Standard Deviation**	**Failure Mode**
		(°F)	*(psi)*	*(psi)*	*(% cohesive)*
2nd-Generation	4340 steel	-25	685	65	100%
2nd-Generation	4340 steel	70	575	25.9	100%
2nd-Generation	4340 steel	145	489	16	100%
2nd-Generation	phenolic	-25	685	30.7	100%
2nd-Generation	phenolic	70	456	38.3	80-100%
2nd-Generation	phenolic	145	437	31.4	100%

The specimens prepared with 4340 steel substrates appeared to yield slightly better results at ambient and elevated temperature. However, due to the fact that predominately cohesive failure was seen in all samples, this discrepancy can probably be attributed to either variations in the bond-line thickness of the samples, or to other processing factors that may have been present in preparing the glass-reinforced phenolic samples. A plot of

the ultimate tensile strength of the samples versus the testing temperature (Figure 16) demonstrated that the less than 100% cohesive failure that was observed in some of the RT test specimens, that were prepared using phenolic substrates, was probably due more to geometric variations or processing factors than any temperature dependent characteristics of the adhesive system. In any case, the fact that the failure surface was consistently observed in the bulk of the adhesive rather than at the substrate-adhesive interface is a clear indication that excellent adhesion had been established to steel and glass-reinforced phenolic substrates in this type of loading environment.

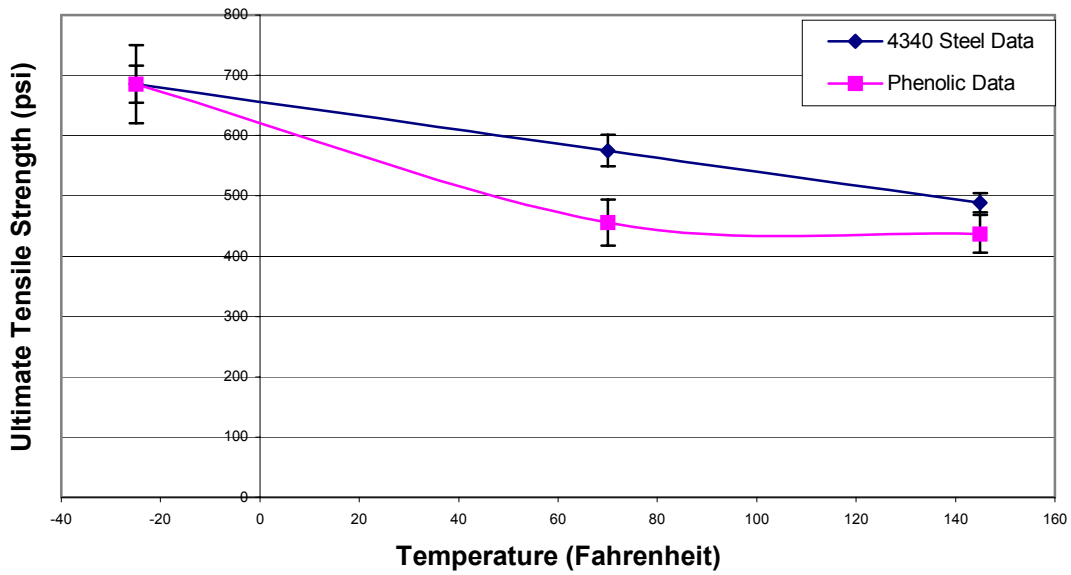


Figure 16. Ultimate Strength vs. Temperature for Second-Generation Formulation.

Durability Studies

Durability studies were performed at VPI with the baseline RTV 866 system and SS-4155 primer, as well as with the optimized PLS200-866 second-generation formulation. To accomplish this task, Mode I (peel loading) crack propagation studies were used to evaluate the performance of the amended and unamended adhesives as a function of surface preparation techniques and environmental exposure conditions. Testing was conducted at room temperature in air and via immersion in water at room temperature. Crack propagation studies were performed with substrates prepared using the base-acid cleaning procedure and the P2 etching procedure; strain energy release rates were obtained by measuring the crack growth rates as a function of time. These strain energy release rates were then used to compare the effects of surface treatments and environmental conditions, moisture in particular, on the durability of the adhesive bonds formed, as well as to quantify the performance of the baseline and optimized second-generation system relative to one another. The results of these studies for the RTV 866 baseline and PLS200-866 optimized second–generation materials are shown in Table 6.

Table 6. Durability Testing of Baseline and Second-Generation RTV Formulations

Crack Propagation Testing Data (Mode I)				
Formulation	Substrate	Testing Conditions	Failure Mode	Strain Energy Released
				J/m^2
RTV 866 + SS4155 Primer	BA treated	RT air	cohesive	2.00E+03
RTV 866 + SS4155 Primer	P2 treated	RT air	cohesive	2.10E+03
RTV 866 + SS4155 Primer	BA treated	RT water	cohesive	1.30E+03
RTV 866 + SS4155 Primer	P2 treated	RT water	cohesive	1.40E+03
Second-Generation Formulation	BA treated	RT air	81% cohesive	1.20E+03
Second-Generation Formulation	P2 treated	RT air	cohesive	1.90E+03
Second-Generation Formulation	BA treated	RT water	cohesive/adhesive	8.00E+02
Second-Generation Formulation	P2 treated	RT water	cohesive	1.40E+03

The Table 6 results indicated that for base-acid treated aluminum substrates, the primerless second-generation PLS200-866 optimized formulation formed slightly less durable bonds with lower corresponding strain energies per unit area than those formed by the baseline RTV 866 system using the SS-4155 silane primer. However, the performance of the primerless system was essentially equivalent on aluminum systems with P2 treated substrates. In the case of the base-acid treated substrates, mixed failure modes were observed in bonds prepared using the second-generation formulation indicating that this may not be the ideal surface treatment for bonds prepared using this formulation, particularly in applications where the bonds may be exposed to significant amounts of moisture. In the samples fabricated with base-acid treated substrates that were tested in room-temperature water, failure was observed to be cohesive during the first one to two hours of testing but it transitioned to adhesive as the test progressed, suggesting that base-acid treated substrates bonded with the second-generation primerless formulation may be sensitive to attack by moisture. In addition to this, the data indicated that adhesive bonds prepared with RTV 866 based adhesives generally yielded less durable bonds than those prepared with RTV 630 adhesives, as can be observed by comparing the strain energy release rates from Tables 2 and 6. The data does indicate, however, that the performance of the second-generation formulation was essentially equivalent to that of the baseline material with the use of the silane primer under the bonding environments examined in these tests using P2 etched substrates. The plots of crack length versus time, used to obtain the data in Table 6 were included in Appendix J.

The specimen failure modes, noted visually (Tables 2 and 6), were further investigated using surface sensitive analysis (XPS) to determine whether the apparent mixed-mode failures that were observed truly exhibited elements of adhesive failure, or if these failures were the result of a weakness in the adhesive-substrate interface. The indication of a thin silicone layer on the "aluminum" failure surface for the second-generation adhesively bonded samples proved that failure was 100% cohesive. It also suggested that components from the adhesive may have produced a weakened region near the aluminum-adhesive interface that facilitated fracture and de-bonding in these tests.

Shelf Life Study of Second-Generation Formulation

A shelf life evaluation study was conducted with the second-generation primerless PLS200-866 formulation at GE in order to identify storage limitations for the optimized formulation, with the adhesion promoter and inhibitor pre-mixed into the RTV 866 B component. Previous studies, conducted at GE, had indicated that pre-mixing the adhesion promoter and inhibitor into the RTV 866 A component yielded formulations that did not exhibit good adhesion even after short periods of time. To conduct the study, the RTV 866 B component was pre-mixed with the bis(trimethoxysilylpropyl)succinate adhesion promoter and the 2-methyl-3butyn-2-ol inhibitor and stored at room temperature. Samples were withdrawn at monthly intervals and compounded with the RTV 866 A component and bonded to 2024 T-3 alclad aluminum, 2024 T-3 bare aluminum, and 4340 steel lap shear substrates. The bonded samples then were allowed to cure for seven days at room temperature prior to testing. The ultimate lap shear strength and mode of failure was noted for each sample. The results of this study appear in Table 7. As can be seen, storing the RTV 866 B component that was pre-mixed with adhesion promoter and inhibitor at room temperature for up to six months prior to compounding with the RTV 866 A component did not have any significant effect on the performance of the second-generation system when bonding alclad 2024 T-3 aluminum and 4340 steel substrates. A significant drop in the performance of the system was, however, seen in samples prepared using bare 2024 T-3 aluminum substrates with the amended RTV 866 B component. A two-part primerless system was seen as desirable for the primerless formulations because it would maintain the packaging, appearance, and preparation and mixing instructions of the traditional two-part RTV 866 system.

Table 7. Shelf Life Lap Shear Properties of PLS200-866*

Months	Adhesion (psi) to Alclad Al	Adhesion (psi) to Bare Al	Adhesion (psi) to Steel
0	633 ± 37	598 ± 33	567 ± 46
1	600 ± 40	561 ± 50	506 ± 30
2	623 ± 41	386 ± 74	600 ± 6
3	632 ± 50	431 ± 47	619 ± 47
4	734 ± 50	367 ± 11	700 ± 32
5	660 ± 24	319 ± 52	645 ± 27
6	665 ± 23	234 ± 29	609 ± 15
11	166 ± 11	283 ± 20	349 ± 100

*PLS200-866 adhesion promoter was incorporated into the RTV 866 B side and both the RTV 866 A and B components then were stored at room temperature. Samples of the A and B formulations were taken at selected time intervals, mixed, and then used to fabricate lap shear samples, which were evaluated for bond adhesion to bare Al, Alclad Al and steel.

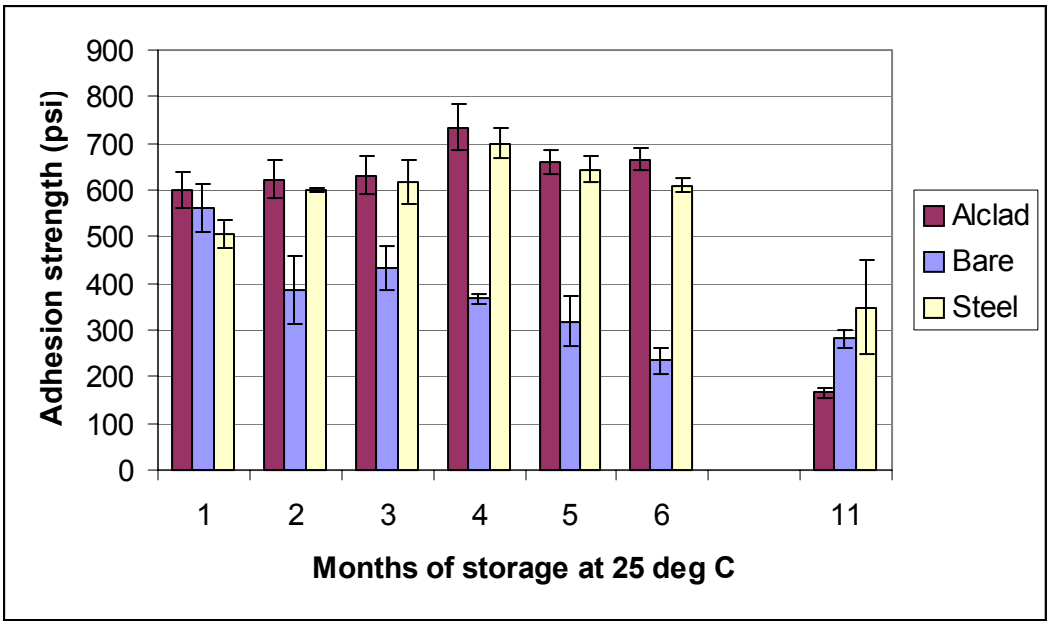


Figure 17. Plot of Shelf Life Lap Shear Properties of PLS200-866

Room Temperature Adhesion to Thermoset Materials

Phenolic glass and epoxy (Humiseal and Amerlock 400 FD) were used to evaluate the bondability of a modified RTV 866 second-generation primerless formulation with 0.78% bis(trimethoxysilylpropyl)succinate, and 0.68% hydride (88104). Lap shears were cured at room temperature for 7 days. The modified second-generation RTV866 with bis(trimethoxysilylpropyl)succinate was much stronger than the substrates themselves.

Peel Evaluation for Second-Generation Adhesion to Thermosets

Due to failure within the lap shear substrate, it was necessary to find an alternative method to evaluate room temperature adhesion of the PLS200-866 second-generation primerless formulation to thermoset materials. The method chosen was the ASTM peel test D429-02 (Reference 10). The Humiseal epoxy was replaced with Amerlock 400FD to increase epoxy to metal substrate adhesion in the final evaluation. The optimized second-generation formulation (0.45 % adhesion promoter, 0.02 % inhibitor) was validated for adhesion to epoxy and phenolic using the peel method. Samples were cured for seven days at ambient temperature prior to testing. In all epoxy samples, the failure was cohesive, with a mean value of 17.6 ± 1.2 pli. The process capability (LSL = 7.3 pli, Z_{st} = 8.04 using the Berryman Scorecard) indicated that second generation formulation could be used on the Amerlock 400FD epoxy with confidence. For the phenolic glass, cohesive failure also was observed in all samples, with a mean value of 15.8 ± 0.9 pli. The process capability of the second-generation formulation to phenolic glass was determined (Z_{st} = 8.6 using the Berryman Scorecard). The performance of the second generation formulation, on both epoxy and phenolic, cured at 100°C for 1 hour also was evaluated using the same peel method as described above. The results indicated good

adhesion to both substrates and similar performance to the room temperature cured samples (Table 8). A milestone was added to this project when it had been shown that the second-generation formulation, which bonded to aluminum and steel, also could be used to bond thermoset substrates.

Table 8. Peel Strength Results for Second-Generation Primerless Formulation Cured at Either Room Temperature or 7 Days or 100°C/1 Hour

	Epoxy		Phenolic	
	Average peel strength (pli)	Z_{st}	Average peel strength (pli)	Z_{st}
Room Temperature for 7 days	17.6 ± 1.2	8.04	15.8 ± 0.9	8.6
100 °C for 1 hour	16.3 ± 1.3	6.8	17.1 ± 1.0	8.8

Adhesion to Thermoplastic Materials

The focus of this phase of the project was the development of primerless, self-bonding, RTV 866 silicones that exhibit adhesion to thermoplastic substrates with no surface pretreatment (other that cleaning). Nylon 6,6 (polyamide 6,6), Lexan ® (polycarbonate), and Ultem ® (polyetherimide) materials were selected as the substrates for designing the third-generation primerless formulations due to their frequency of use in DoD and DOE applications, where RTV silicone rubber sealants and adhesives are employed. As in the second phase of this effort, results obtained from molecular modeling studies and quantum mechanical calculations were utilized to design chemical structures and critical chemical functionalities to help to guide in the identification and selection of the third-generation adhesion promoters. A series of bi-functional chemicals were identified and evaluated based on their potential to form bonds to the modeled substrate surfaces. Screening Designs of Experiments then were employed in conjunction with physical property testing and cure temperature profiling to evaluate the performance of potential primerless RTV 866 systems. Hydrolytic stability testing also was conducted in accordance with ASTM D1151-00 (Reference 11) in order to insure that the primerless systems would develop bonds with good moisture resistance. Molecular modeling was particularly used to better understand the surface of GE Ultem to help identify potential adhesion promoters. The results were published in the proceeding of the Annual Technical Conference of the Society of Plastic Engineers and the journal Polymer, respectively as shown: (Eichinger, B. E., Rigby, D., and Stein, J. Simulating the cohesive properties of Ultem and related molecules. Annu. Tech. Conf. – Soc. Plast. Eng. **59th(Vol. 2**), 1592 (2001).) and (Eichinger, B.E., Rigby, D., and Stein, J., Cohesive Properties of Ultem and Related Molecules from Simulations, Polymer, **43**, 599 (2002). (Appendices D and G). Many adhesion promoters were synthesized and screened for use with the RTV866 formulation at both ambient and elevated temperatures. A list of the adhesion promoters screened for adhesion to these three substrates can be found in Appendix K.

Primerless Adhesion to Thermoplastics at Ambient Temperature

In the process of trying to develop adhesion to Lexan ® and Ultem ® substrates, a series of compounds that were acids and esterifications of other candidate adhesion promoters were evaluated; however, none of these materials resulted in good bond adhesion when compounded with RTV 866. To develop adhesion to Lexan®, polycarbonate copolymers were prepared by a phosgenation reaction; however, no significant increase in adhesion was realized with these materials either. It may be that the surface energies of Lexan ® and Ultem ® are too low to allow them to be suitable for bonding with silicone adhesives with only low levels of adhesion promoters present. Cursory tests have established that good bond adhesion can be obtained for these substrates with the use of surface pretreatments. For example, good adhesion was obtained on Lexan after corona treatment, and on Ultem after exposure to a KOH bath.

The preliminary primerless test formulation was prepared by incorporating 0.78 % bis(trimethoxysilylpropyl)succinate, 0.68% silicone hydride (88104) and 0.02% methyl-butynol into RTV866. One inch by one inch overlap lap shear samples were prepared on corona treated Ultem® and Lexan®. The bonded lap shears were cured for seven days under ambient conditions. For the Lexan, lap shear values could not be obtained because there was failure within the substrate. The adhesive could not be manually removed which indicated acceptable adhesion. The adhesion to corona treated Ultem® showed variability and a low average adhesion strength of 222 +/- 93 psi .

Because of the unacceptable adhesion to Ultem with corona treatment, an alternative treatment was tried. The same RTV formulation as described above, was used in this experiment. The formulation was applied to Ultem® coupons that had been pretreated using the following method: immersed in a 5 molar KOH bath for five minutes, rinsed with distilled water and then air-dried. Samples were cured 7 days at room temperature. The primerless RTV silicone could not be manually removed from the substrate.

Primerless Adhesion to Thermoplastics at Elevated Temperature

Many adhesion promoters, when incorporated into RTV866 and cured at 100°C, were screened for adhesion to Nylon 6,6, Ultem and Lexan. The adhesion promoters listed in Appendix K were down selected based on the screening results. After this screening it was determined that no primerless adhesion could be obtained on Ultem and Lexan without pretreatment with the exception of diallyldiglycidylether. This adhesion promoter was used in conjunction with a Lewis Acid catalyst such as BF_3 or $Al(Me)_3$ and showed good adhesion to all three substrates. Unfortunately these catalysts cannot be used safely in this application due their high reactivity and toxicity. Therefore, the final adhesion promoter was down selected based solely on adhesion to Nylon 6,6.

The Nylon 6,6 adhesion promoters were synthesized and material performance evaluations were carried out employing predetermined physical property and adhesion strength criteria against which formulations were determined to be acceptable or unacceptable. Formulations that passed this initial screening phase then were further

examined using Designs of Experiments and statistical models to establish formulations that provided excellent adhesion to Nylon 6,6. The adhesive performances of all of the optimized formulations then were tested in a variety of bonding configurations over temperature ranges required by end-item applications. A robust primerless, elevated temperature curing, third-generation RTV silicone formulation, that provided excellent adhesion to Nylon 6,6 substrates, was developed. The formulation PLS300-866 was comprised of RTV 866 amended with a third-generation adhesion promoter 2,2'-diallyl bisphenol A. General Electric, GRC has submitted a patent application for this material. Excellent adhesion has been demonstrated to Nylon 6,6 substrates under a variety of substrate preparation conditions with this material.

Lap Shear Specimen and Fixture Variations

RTV 866 amended with adhesion promoter 2,2'-diallyl bisphenol A, was identified to show very little dependence on processes used to clean or dry the Nylon 6,6 lap shear substrates prior to bonding; thus, eliminating the need for a Nylon 6,6 drying process. As the process capability characterization progressed; however, it became apparent that it was difficult to maintain the sample and bond line geometries with the Nylon 6,6 substrates, in order to obtain consistent results with low standard deviations. In order to allow a true optimization of the adhesion of third-generation formulation to Nylon substrates to be conducted, the Nylon lap shear test was redesigned to eliminate the dependence of the test results on factors such as variations in the substrate thickness and bond line thickness. This changed the Nylon 6,6 lap shear strength property variations from 20% to less that 3%.

Bond line control in Nylon 6,6 lap shear samples was maintained by introducing a small amount of calibrated glass beads into the formulation. This significantly reduced the standard deviation observed in Nylon lap shear testing of the amended formulations. Another study was performed varying the percentage of the glass beads in the third-generation formulation between 0.25% and 1%, while maintaining the adhesion promoter concentration at a constant value, in order to determine if the glass beads had a significant effect on the performance of the adhesive bonds formed. The overall result of varying the concentration of glass beads in the formulation was found to be negligible (Table 9).

Table 9. Effect of the % of Glass Beads on Lap Shear Adhesion of RTV300-866

Glass bead amount (g) (%)	Results	
	Failure Mode	Max load (psi)
0.05 (0.25%)	Cohesive	485±12
0.1 (0.5%)	Cohesive	500±10
0.2 (1%)	Cohesive	487±26

The thickness of the Nylon 6,6 substrates also was investigated as a potential source of the large standard deviations that were originally observed in the lap shear samples. It is well known that the single lap geometry, which is usually employed because of its apparent simplicity, often gives rise to complex stress distributions. This is due to the fact that the substrates in the sample are offset from one another and, consequently, the applied forces tend to rotate the bonded section. Generally, this effect is more pronounced in relatively soft substrate materials like Nylon or other plastics. Therefore, an investigation was initiated to reduce or eliminate this effect by increasing the thickness of the Nylon 6,6 substrates and possibly reducing the bond line thickness in the process. Several series of lap shear samples were prepared, with Nylon 6,6 substrates of varying thicknesses, to determine the optimal specimen geometry while using constant concentrations of the 2,2'-diallyl bisphenol A adhesion promoter and 0.5% glass beads in the amended formulation to maintain the bond line thickness. It was determined from this study that good, repeatable results could be obtained using 1/8-inch thick Nylon 6,6 substrates. The effect of the thickness of the Nylon, for systems with identical bond-line thickness and adhesive formulations, can be seen in Table 10 and Figure 18.

Table 10. Effect of Nylon 6,6 Thickness on Lap Shear Adhesion of RTV300-866

Nylon Thickness (inch)	Lap Shear Results	
	Failure Mode	Max load (psi)
1/16	Cohesive	393 ± 21
3/32	Cohesive	514 ± 13
1/8	Cohesive	595 ± 33
3/16	Cohesive	618 ± 41
¼	Cohesive	618 ± 14

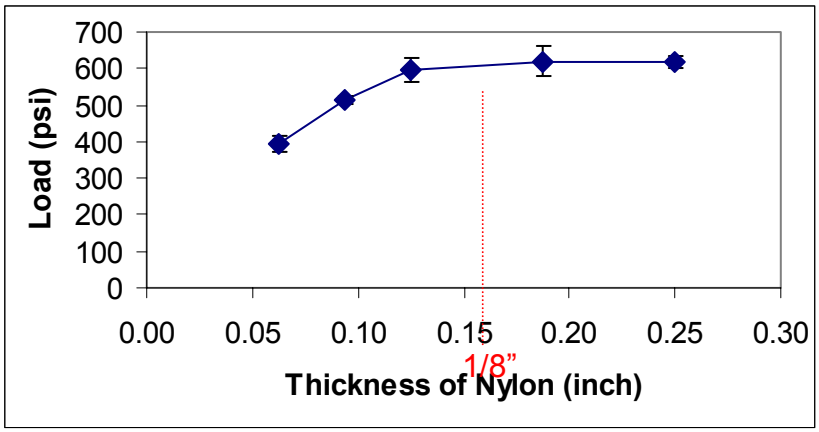


Figure 18. Plot of Adhesion Strength Versus Nylon 6,6 Thickness

A process capability study was carried out using step lap shear molds and a newer system. The step method was the method that was used for the evaluation of adhesion to metals and thermosets. It consisted of a flat metal plate on which a step has been machined so that half of the flat plate is 0.5 mm thinner that the other side. The 1" wide ends of lap shear strips were butted against the side wall of the step, adhesive was applied to the 1 square inch bond area of the strips by the step, and the mating ends of the second set of lap shear strips then were placed over the top edge of the step onto the 1 square inch bond area of the lower strips. The step maintained the bond thickness. When this method was used with the Nylon 6,6, an increase in variability occurred. The increase was related to the fact that the bond line was not uniform (Figure 19). One possible cause of this problem was that plastics are more likely to be warped than the metals; making it difficult to create a uniform bond. Another fixture was used to eliminate this problem.

The new method used a plate with wells to maintain bond orientation. Spacer beads purchased from Potters Industries Inc (0.50-0.59 mm) were incorporated into the adhesive formulation at 0.5% by weight as a positive control for the thickness. This formulation was mixed and degassed according to original procedure. Then the formulation was applied to the coupons in the wells. Next the other coupons were placed on top to complete the lap shear and then a weight (1.26 kg) was placed over the lap shear bond. (Figure 20) The samples then were oven cured 1 hour at 100°C. The results of these studies indicated that good cohesive failure can be observed using both fixtures; however, more reproducible results were obtained using the newer procedure with beads. Note: beads should not be used when this formulation is used on actual parts.

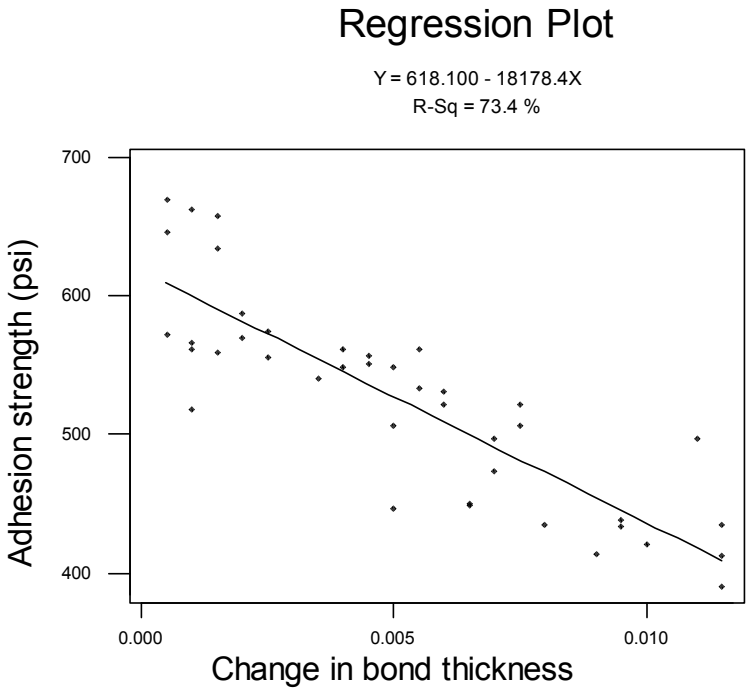


Figure 19. Plot of Adhesion Strength Versus Change in Bond Thickness

Figure 20. Improved Nylon 6,6 Lap Shear Holding Fixture

Robust Optimization of Third-Generation Formulation

Having identified a lap shear sample fabrication fixture, and incorporated the use of glass bead spacers, with which good repeatable results could be obtained, optimization of the third-generation formulation, consisting of RTV 866 resin amended with the 2,2'-diallylbisphenol A adhesion promoter and silicone hydride cross-linker, was conducted. Preliminary studies had shown that using the 2,2'-diallylbisphenol A material in its commercially available form (85% pure), rather than in a more purified form, had a negligible effect on the level of bond adhesion that was developed, so the commercial purity version of the adhesion promoter was used in the central composite Design of Experiments (DoE), designed to optimize adhesion to Nylon 6,6. The adhesion promoter and cross-linker, silicone hydride, concentrations were varied between 0% and 5%, and all samples were allowed to cure at 100 ^{o}C for 1 hour prior to testing. The lap shear results were analyzed using Design Expert software and a model was produced. A graphical representation of the data obtained from this testing is displayed in Figure 21.

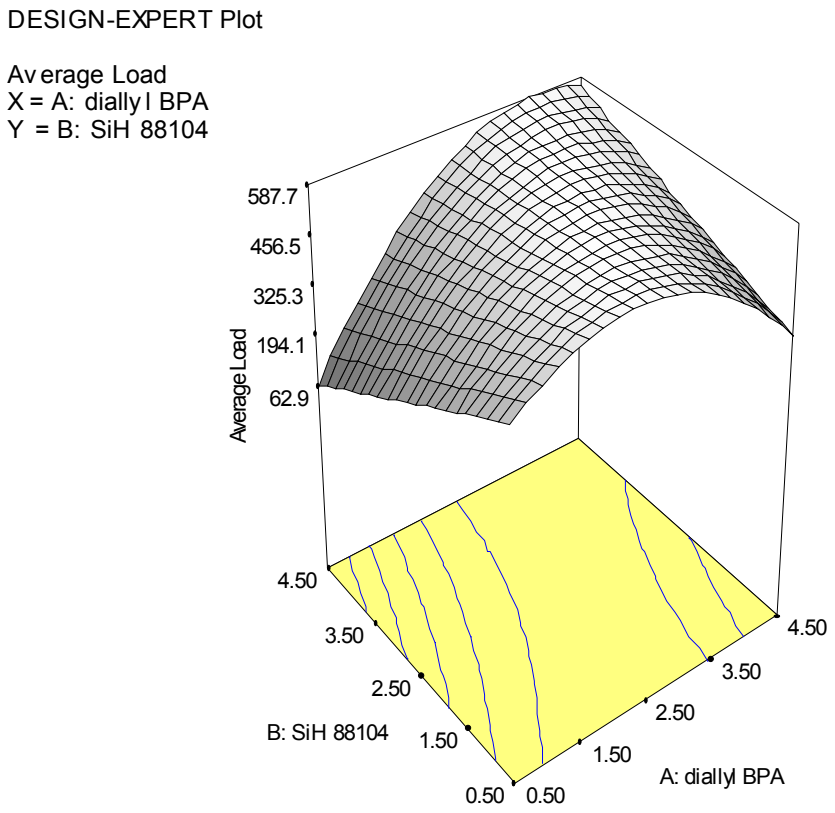


Figure 21 Graphical Model Predicting the Impact of dBPA and Silicone Hydride on Adhesion of Primerless Third-Generation RTV 866 to Nylon 6,6

Regression Equation in coded units-

Load = 535 + 90 (AP) – 31(SiH) – 190$(AP)^2$ + 161(AP*SiH)

Adjusted R^2 = 70%

The model showed a significant lack of fit, therefore a decision was made to take the data that was collected and determine if a simpler formulation could be found. One of the star points (2.5%AP, 0% SiH) of the central composite DoE suggested that good adhesion could be obtained without the silicone hydride. Based on the information from the DoE and formulation considerations, the final formulation was determined by varying the percentage of 2,2'-diallylbisphenol A from 0.25 to 2.5%. Lap-shear samples were prepared, cured for 1 hour at 100 C and tested (Figure 22).

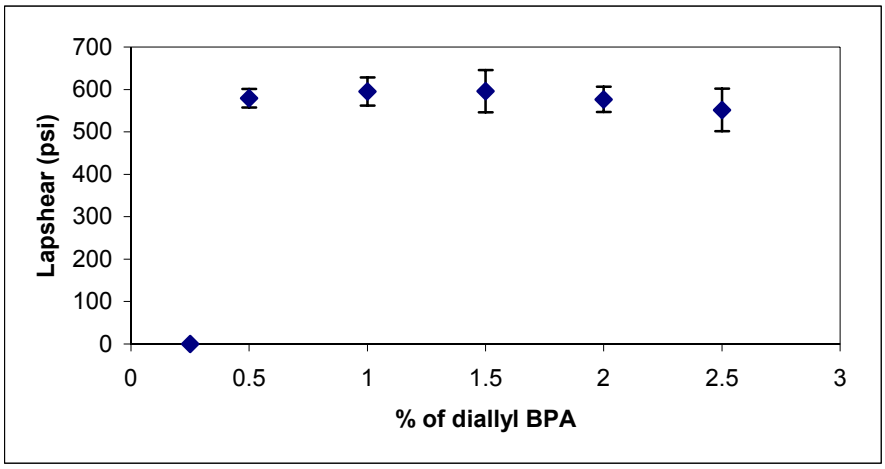


Figure 22. Effect of the Levels of 2,2'-diallylbisphenol A on the Adhesion of Primerless Third-Generation RTV 866 to Nylon 6,6

A statistical analysis of the data collected during this experiment, excluding the 0.25% dBPA, indicated that there was no significant difference between these formulations (df = 25, p = 0.237). The final formulation of 1.25% dBPA was selected in order to ensure that slight errors in the measurement of the adhesion promoter would not impact the adhesion of the final product.

Process Capability

After the final third generation (nylon) formulation was chosen, a process capability was determined. RTV866 amended with 1.25% diallyl bisphenol A and 0.5% glass spacer beads was applied to coupons and cured for 1 hour at 100 ^{o}C (Figure 23). This formulation was found to have a Z_{st} = 8.2 by using the Berryman Score card.

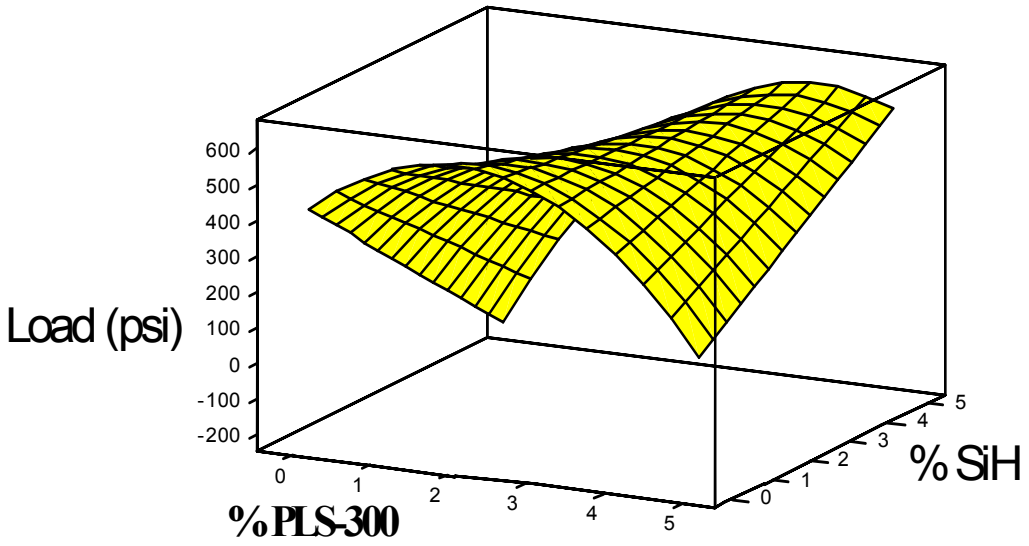


Figure 23. Effect of the Levels of 2,2'-diallylbisphenol A and Silicone Hydride on Adhesion of Primerless Third-Generation RTV 866 to Nylon 6,6

It was apparent in Figure 23 that for low adhesion promoter levels, incorporation of the cross-linker into the amended formulation may not be necessary. In addition to this, it can be seen that good results could be obtained for high levels of adhesion promoter (~5%) and moderate levels of silicon hydride (~2.5%); however, this required the use of a significant amount of additives in the formulation, and adding large amounts of adhesion promoter to the system was found to compromise the material properties of the cured formulation. For this reason, and because the adhesion developed by the cured material was found to be less dependent on slight variations in adhesion promoter concentration in this region, the optimum third-generation primerless formulation for bonding Nylon 6,6 substrates was determined to contain 1.25% 2,2'-diallylbisphenol A adhesion promoter and no cross-linker. The material properties of this system were examined and were determined to be approximately equivalent to those of the unamended baseline RTV 866 system. These results are shown in Table 11. These properties were determined by curing sheets of the material in a press for 1 hour at 100°C. A statistical comparison of this data to base line RTV 866 data indicated that both the tensile and tear properties of the material were changed. The tensile strength of the material was reduced, but the tear strength was enhanced by the addition of dBPA. This reduction in material properties was not large enough to change this formulation's acceptability. Since glass spacer beads were used for the Nylon 6,6 lap shear samples, RTV 866 sheets (with and without dBPA) also were cast with these glass beads. Unfortunately, the physical properties were unable to be accurately measured for these RTV866 sheets with beads incorporated, due to the fact that failure occurred at the beads during the tests.

Table 11. Properties of Baseline and Primerless Third-Generation RTV866

	RTV866 Basic formulation	RTV866+ 2,2'-diallylbisphenol A
Tensile strength (psi)	809.8 ± 17.9	694.9 ± 39.5
Elongation (%)	218±35	320±33
Tear Strength (lbf/in) (Die B)	57.8 ± 1.6	66.2 ± 5.7
Hardness (shore A)	50.8	50

The process capability of the PLS300-866 primerless third-generation formulation for adhesion to Nylon 6,6 substrates then was determined using 1/8-inch thick Nylon lap shear substrates and commercial purity 2,2'-diallylbisphenol A adhesion promoter. The optimized third-generation primerless formulation for bonding Nylon substrates was found to have an average ultimate lap shear bond strength value of 618.4 pounds per square inch under this bonding configuration with a standard deviation of approximately 36 pounds per square inch. This corresponded to a process reliability characterized by less than one defective sample with an adhesion value below the 300 pounds per square inch lower standard limit expected per million samples that are tested. The process capability diagram for this system is shown below in Figure 24.

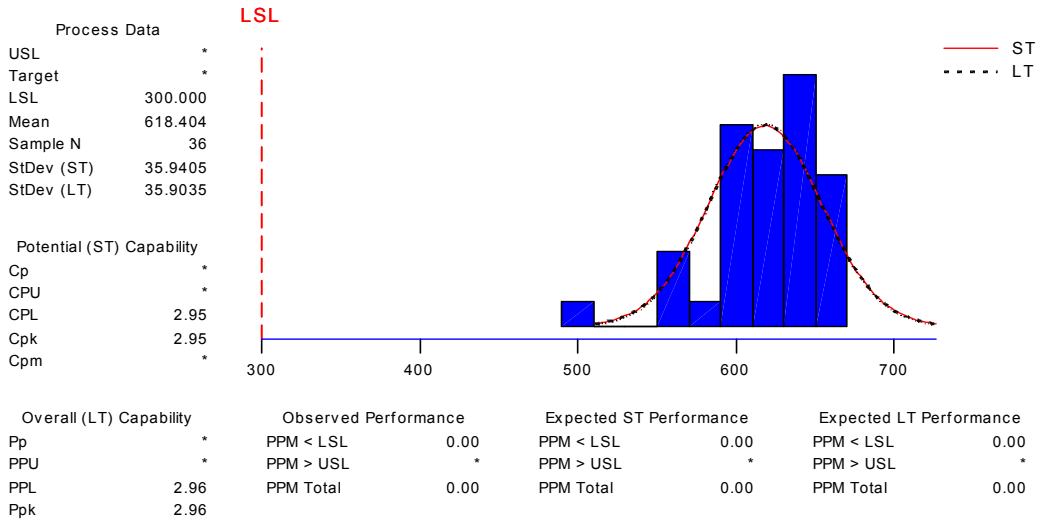


Figure 24. Process Capability for Third-Generation Primerless Formulation on 1/8" Nylon 6,6 Substrates.

Shelf Life Study of Third-Generation Formulation

As with the second-generation formulation, the shelf life of the third-generation PLS300-866 formulation was examined to determine if it were possible to pre-mix the 2,2'-diallylbisphenol A adhesion promoter into either the RTV 866 A component or the RTV 866 B component for storage prior to mixing these components at the time that the adhesive is used.

Previous studies indicated that the 2,2'-diallylbisphenol A adhesion promoter could be stored in the RTV 866 B component for short periods of time, but that it was unstable in the RTV 866 A component. As a result, an evaluation was conducted with the adhesion promoter pre-mixed into the RTV 866 B component and stored at room temperature. Samples were withdrawn at monthly intervals and compounded with the RTV 866 A component and bonded to Nylon 6,6 substrates. The Nylon substrates were solvent cleaned with isopropyl alcohol prior to bonding. The bonded samples then were cured for one hour at 100°C prior to testing. The ultimate lap shear strength and mode of failure was noted for each sample. The results of this study appear in Table 12. As can be seen, storing the RTV 866 B component that was pre-mixed with the 2,2'-diallylbisphenol A adhesion promoter at room temperature for up to eleven months prior to compounding it with the RTV 866 A component did not have any significant effect on the performance of the third-generation system when bonding Nylon 6,6 substrates. As a result, the pre-mixed third-generation appears to exhibit at least an eleven-month shelf life stability guarantee.

Table 12. Shelf Life Lap Shear Properties of PLS300-866*

Months	Average lap shear strength (psi) on Nylon*
0	436 ± 35
1	432 ± 33
2	440 ± 49
3	472 ± 66
4	455 ± 15
5	529 ± 8
6	499 ± 20
11**	650 ± 23

- all test samples had 100% cohesive failure

** different Nylon thickness and different type lap shear sample, but still cohesive failure

General Electric Global Research Center

Alternative to RTV866

GE Specialty Materials (Silicones division) will no longer be making RTV866, which is the base for the second-generation PLS200-866 room temperature cure and the third generation PLS300-866 elevated temperature cure primerless adhesives. Alternative RTV formulations were evaluated with the second generation bistrimethoxysilylpropyl succinate adhesion promoter for adhesion to aluminum and steel. None of these candidate base formulations gave satisfactory results. No alternative has been found for RTV866 base in the room temperature cure system (PLS200). In the short term, 1 – 2 years, RTV866 can be obtained from a GE Silicones distributor who currently has several 55 gal drums of material in stock (The Smith Group, 215-957-7800).

The RTV material developed for primerless adhesion to Nylon 6,6 was optimized in third-generation formulation PLS300-866. The optimal formulation consisted of RTV866 with 1.25% diallyl bisphenol A cured at 100°C for 1 hour. Experiments were carried out to determine if RTV866 could be replaced with RTV630. The RTV630 was amended with the same amount of additive and cured under the same conditions. The results showed a 100% cohesive Nylon 6,6 lap shear failure within the RTV630 base. A process capability study using RTV630 also was performed. The results of RTV630 amended with 1.25% diallyl bisphenol A and 0.5% spacer beads showed an average adhesion strength of 877 ± 42 psi (Figure 25). The z short term determined from this process capability was 13.6. These results clearly indicated that the RTV866 base can be replaced with RTV630 in this formulation without compromising adhesion. The material properties of the amended RTV630 were evaluated and compared with the unamended RTV630 (Table 13). There was no significant change in the tensile or tear strength of these two materials.

Table 13. Physical Properties of RTV630 & Amended RTV630 Cured at 100 ^{o}C/1 Hr

Material	Die B tear (pi)	Tensile strength (psi)	% Elongation	Shore A Hardness
RTV630	142.2 ± 3.8	815.3 ± 86.7	234.1 ± 89.3	61-62
RTV630 + 1.25% dBPA	147.8 ± 3.8	882.3 ± 48.4	410.2 ± 47.3	59-60
Statistics (ANOVA)	df = 7 p = 0.083	df = 7 p = 0.226		

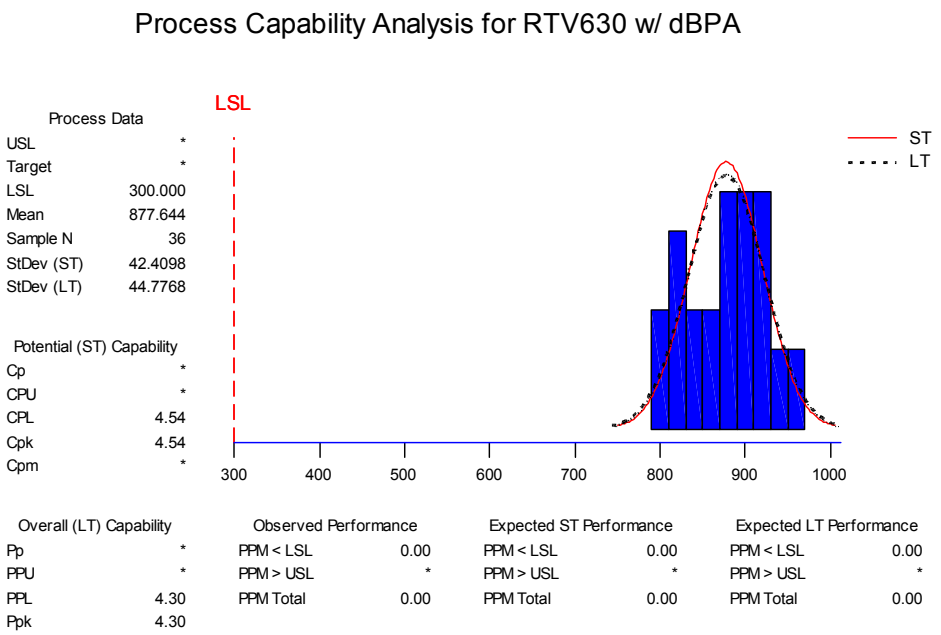


Figure 25. Process Capability of RTV630 with 1.25% diallyl bisphenol A (dBPA)

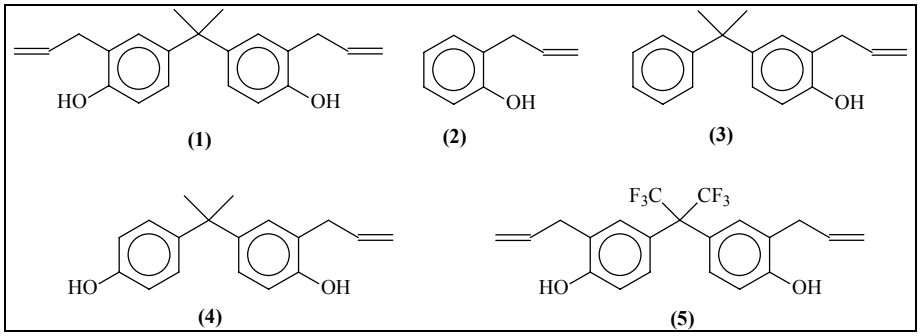
Mechanism of Adhesion to Nylon 6,6

In this section the mechanism of adhesion and the mechanism of the action of diallyl BPA were examined. The role of the chemical structure of the adhesion promoter, the effect of temperature and the interaction between the diallyl BPA and the Nylon 6,6 surface also were evaluated .

Chemical Structure Investigation.

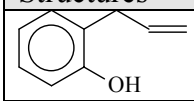
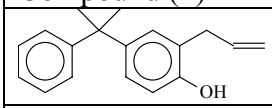
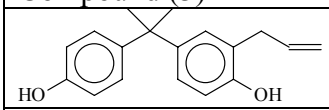
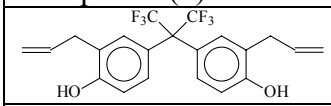
The structures of the different compounds evaluated as third-generation adhesion promoters are shown schematically in Table 14. 2,2'-diallyl bisphenol A and 2-allylphenol (compounds (**1**) and (**2**)) were obtained from Aldrich. 2-Allyl 4-cumylphenol (**3**), 2-allyl bisphenol A (**4**) and 2,2-bis (3-allyl-4-hydroxyphenyl) hexafluoropropane (**5**) were synthesized on site.

Table 14. Structure of the Compounds Evaluated as Third-Generation Adhesion Promoters.



The candidate compounds (**2-5**), depicted in Table 14, were mixed into RTV866 and qualitatively evaluated for bond adhesion. The results are given in Table 15.

Table 15. Effect of Chemical Structure of the Adhesion Promoters on Failure Mode.

Structures	Failure
	No adhesion
Compound (**2**)	
	No adhesion
Compound (**3**)	
	100% Cohesive
Compound (**4**)	
	100% Cohesive
Compound (**5**)	

In the present case, the most probable mechanism involved hydrosylilation of the allylic bond (note: it was previously shown that the O-silylation did not occur in those condition) and polar interaction between the substrate (Nylon) and the phenolic groups. Poor adhesion was obtained by replacing the diallyl BPA (**1**) by a simpler molecule, which contained both allylic and phenolic functions (2-allylphenol –compound (**2**)). One of the possible reason was the fact that 2-allylphenol was able to dissolve the Nylon whereas diallyl BPA didn't dissolve the Nylon. In the case of the compound (**2**), it was possible that the level of the adhesion promoter in the interface was very low due to the diffusion into the substrate leading to a very weak adhesion. One solution to avoid this problem was to prepare a molecule with a structure similar to 2,2'-diallyl bisphenol A in order to decrease the solubility. Accordingly, compound (**3**) was prepared and it was observed that this liquid did not dissolve the Nylon. But in this case too, no improvement of the adhesion between the Nylon and the silicone network was observed. It may be due to a steric effect. After the participation of the allylic bond into the silicon network the OH in the ortho position was too hindered and not able to interact with the plastic surface. However with the 2,2'-diallyl BPA the second OH group could be the link with the plastic since the allylic group had not reacted. To confirm this hypothesis the compound (**5**) was prepared. It contained the same structure of the compound (**4**) with a sterically free OH and in this case it was observed that the efficiency of (**5**) was comparable to 2,2'-diallyl BPA.

Effect of Cure Temperature and Interaction with Nylon 6,6

The RTV cure, based on the hydrosilylation reaction, required one week at room temperature after the mixing of the two parts or less time when cured at higher temperature (1 hour at 100°C). The effect of the cure conditions on the adhesion was investigated by varying the time and the temperature from 1 week at room temperature to 15 minutes at 150°C. Six Nylon 6,6 lap shear samples were evaluated for each condition and the results are given in terms of failure modes (cohesive or adhesive) in Table 16.

Table 16. Effect of Cure Conditions on the Failure Mode of Nylon 6,6 Lap Shear Samples

Cure conditions	Failure
1 week RT	100% Adhesive
1 week 40 C	100% Adhesive
30 hours at 50 C	100% Cohesive
1 hour at 60 C	95% Cohesive
4 hours at 60 C	100% Cohesive
1 hour at 80 C	100% Cohesive
2 hours at 80 C	100% Cohesive
15 hours at 60 C	100% Cohesive
1 hour at 100 C	100% Cohesive
0.25 hour at 150 C	100% Cohesive
0.50 hour at 150 C	100% Cohesive
0.75 hour at 150 C	100% Cohesive

In order to obtain adhesion (cohesive failure), a minimum temperature of 50°C was required. (Note: at this temperature a longer cure process was required). This temperature corresponded to the melting temperature of the amorphous part of the Nylon 6,6. (T_m=285°C and T_g=50°C).

This adhesion promoter links the two interfaces by chemically bonding with the silicon network (hydrosilylation reaction) and strong hydrogen bonding with the Nylon 6,6 surface. The hydrosilylation reaction occurred at room temperature, but the association between the phenolic groups and the polar part of the Nylon 6,6 was activated by the temperature, requiring temperatures above the Tg of the Nylon 6,6 (50°C). The most probable mechanism was the melting of the amorphous part of the Nylon 6,6 and the reassociation of the polar functional groups with the phenolic groups.

Virginia Polytechnic Institute

Surface Chemistry

The surface chemistry for the as received and surface treated Lexan and Nylon 6,6 samples was determined with a Perkin-Elmer model 5400 x-ray photoelectron spectrometer (XPS). Small squares (~10 mm X 10 mm) were cut from the various plastic specimens, and the surfaces were analyzed using the XPS. The area of the sample analyzed was 1 x 3 mm. Photoelectrons were produced by bombarding the samples with Mg K□ x-rays (h□ = 1253.6 eV). The binding energy scale was calibrated by setting the binding energy for the C 1s photopeak for hydrocarbon carbon at 285.0 eV. Elemental composition was calculated by measuring the peak area of the respective photopeaks and correcting the measured area to account for x-ray absorption and analyzer characteristics to obtain results in atomic percent.

The XPS wide-scan spectrum (element identification) for as-received Lexan is shown in Figure 26. The principal elements in the spectrum were carbon and oxygen, with little or no fluorine noted (although the computer identification scheme labeled fluorine). Carbon was the dominant element on the surface, as indicated by the C 1s peak intensity, relative to the O 1s peak. Following a simple surface cleaning with isopropanol, the wide scan XPS spectrum shown in Figure 27 was obtained. It is clear by comparing Figures 26 and 27 that isopropanol cleaning increased the oxygen content significantly. The wide scan spectrum of an isopropanol-cleaned surface using a "corona" discharge gave the plot shown in Figure 28, and Figure 29 shows the plot of the plasma treated surface. For corona and plasma treated Lexan, the spectrum exhibited an O 1s intensity that was significantly greater than for either as-received or isopropanol-cleaned Lexan. In principle, this increase in surface oxygen content should enhance adhesive bond durability. Figure 30 shows the results for the silane treated Lexan surface. Among the changes noted are the appearance of silicon and nitrogen indicating that silane has been incorporated onto the surface of the Lexan. A summary of the atomic concentrations following the various treatments is given in Table 17.

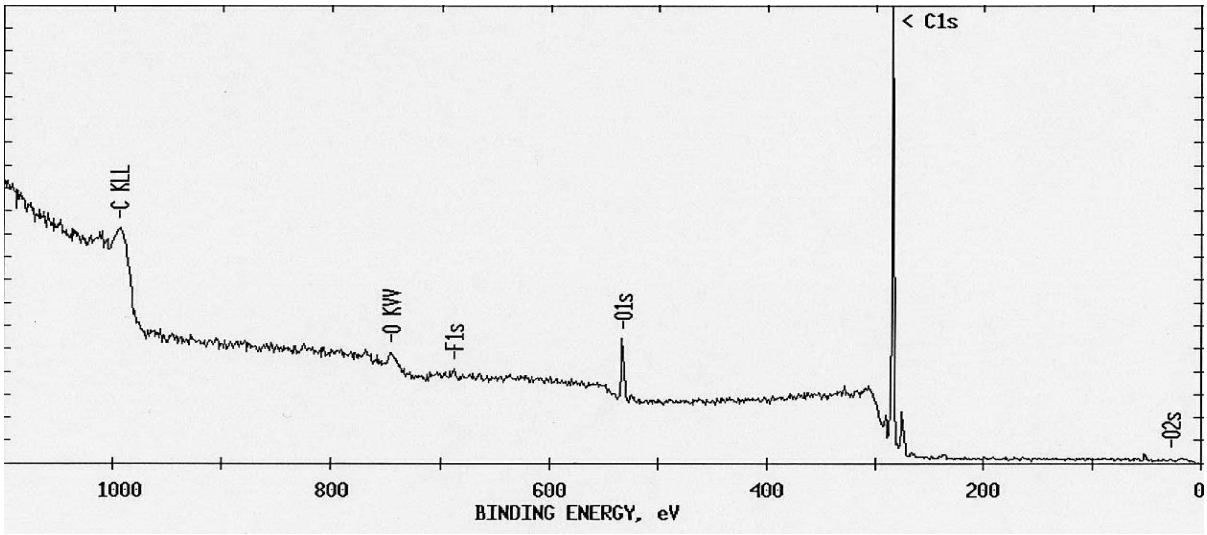


Figure 26. Wide-Scan XPS Spectrum for As Received Lexan.

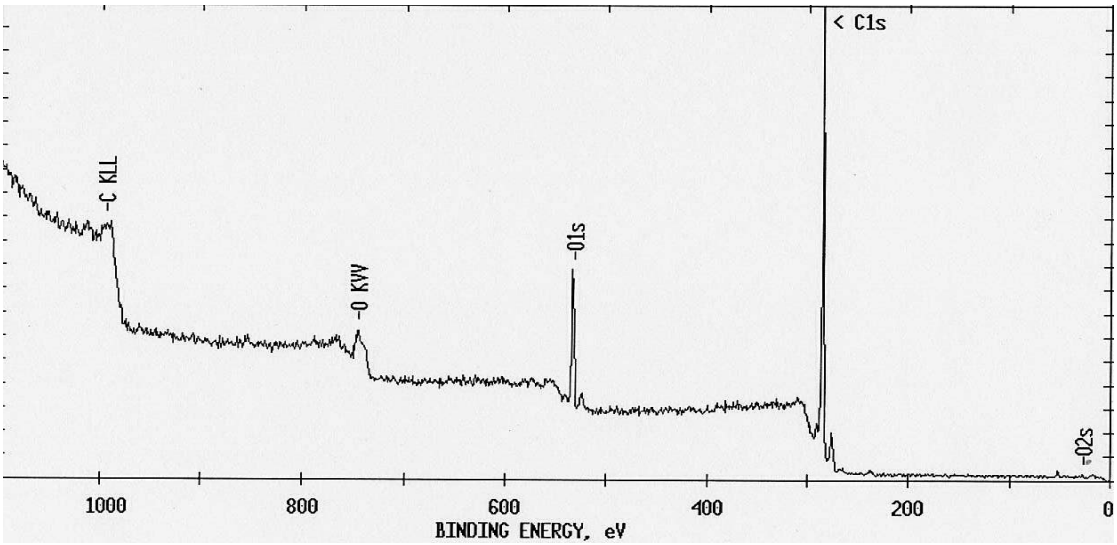


Figure 27. Wide-Scan XPS Spectrum for Isopropanol-Cleaned Lexan

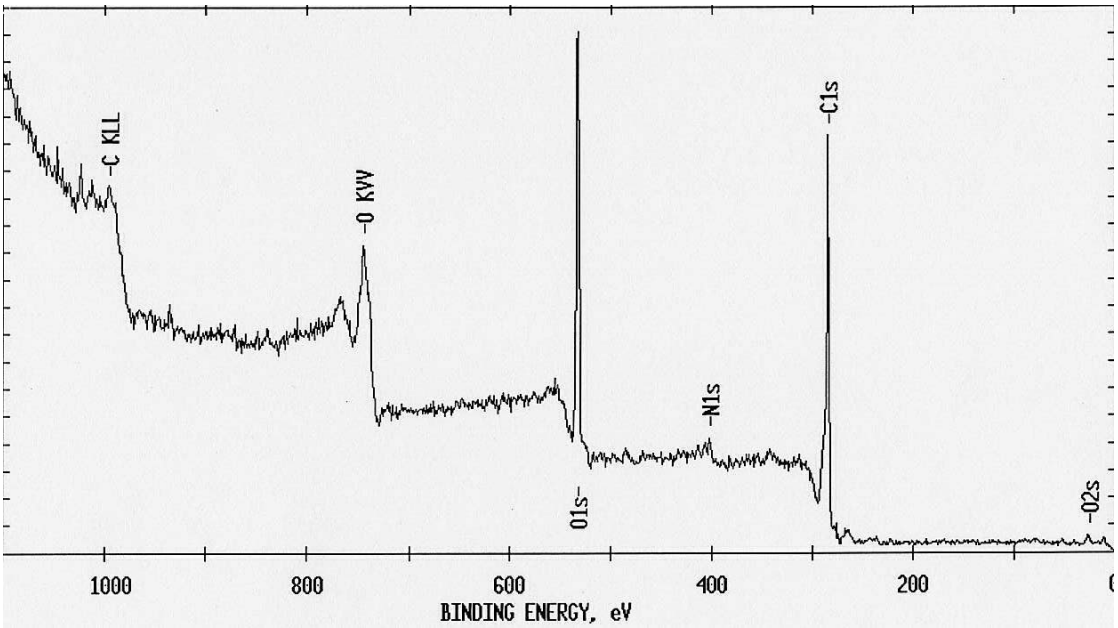


Figure 28. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Corona Treated Lexan

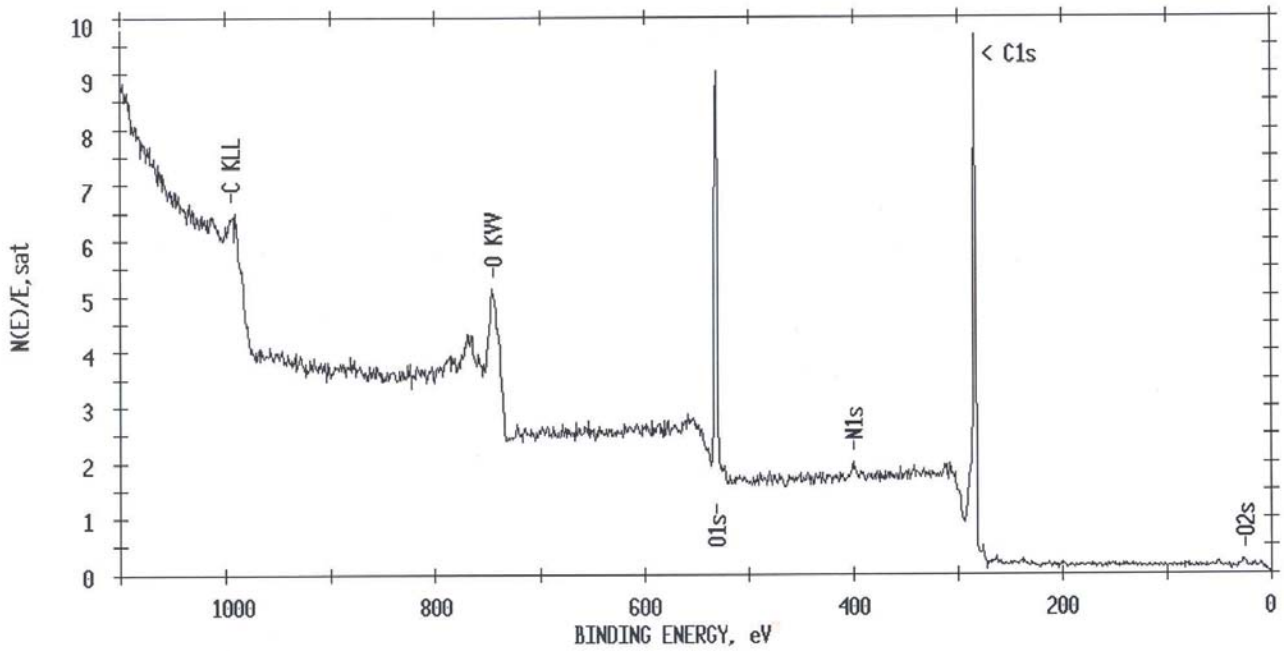


Figure 29. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Plasma Treated Lexan

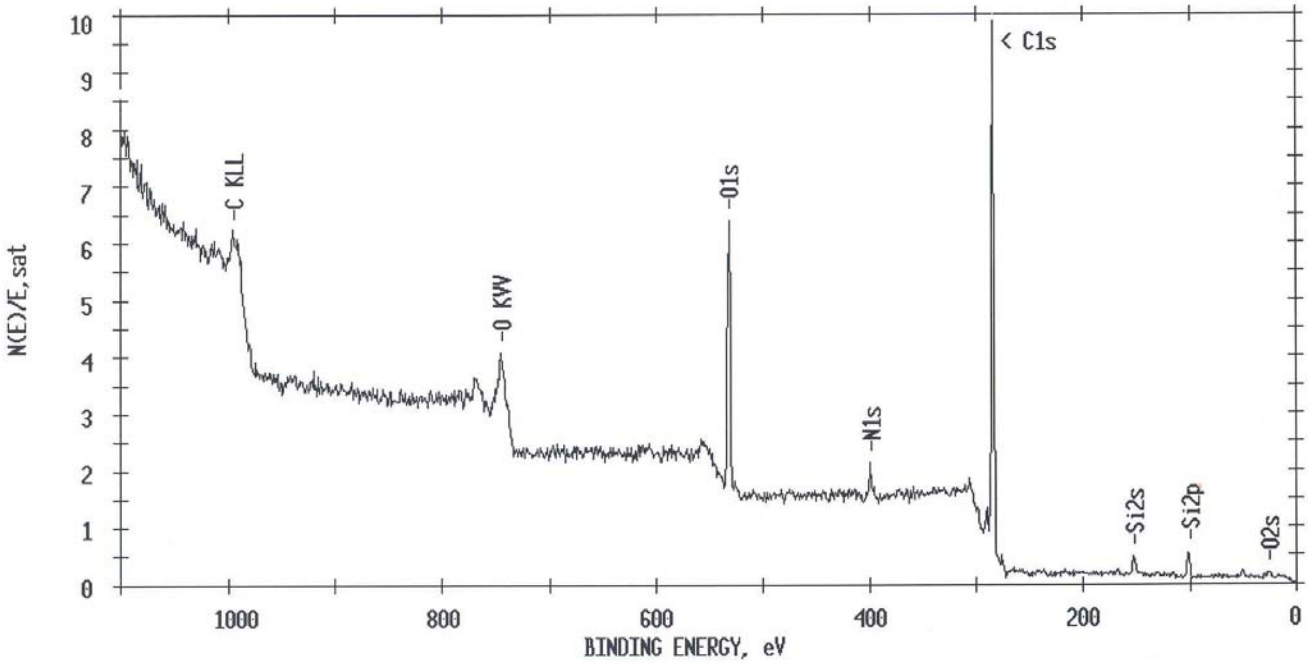


Figure 30. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Silane Modified Lexan

Table 17. XPS Surface Analysis Results for Lexan Adherends (Atomic %)

Sample/element	C	O	N	Si
as rec'd	92.5	7.5	<0.2	<0.2
IPA alcohol clean	86.3	13.7	<0.2	<0.2
corona treat	67.6	29.3	3.1	<0.2
plasma treat Ar/O_2	73.5	25.1	1.4	<0.2
silane modified	76.7	18.0	2.5	2.8

The results indicate, as noted from the wide-scan spectra, that carbon decreased while oxygen increased as the "oxygenating tendency" of the treatment increased. Interestingly elemental compositions for the corona and plasma treatments were similar. It also was

noted, that nitrogen was more prevalent in the corona-treated sample. This result was not surprising since the corona treatment was conducted in air. Although not presented in this report, the C 1s spectra indicated an increase in the C-O, C=O, and COO^- (carbon singly- and multiply-bonded to oxygen) contents for the corona- or plasma-treated Lexan samples compared to the as received- and alcohol-cleaned Lexan specimens. These findings were in accord with previous studies which have shown that oxidation of polymer surfaces occurred when samples were treated via a corona discharge or in an oxygen-containing plasma. The incorporation of the silane coupling agent may enhance the interaction with the PLS300A-630 silicone adhesive via polar interactions. .It was expected that the changes in surface chemistry should increase surface energy and promote wetting, adhesion, and bond durability.

Similar surface modification and characterization procedures were carried out for Nylon 6,6. The wide-scan XPS spectrum for as received Nylon is shown in Figure 31. The spectrum showed the elements carbon, oxygen and nitrogen – as expected, based on the anticipated composition of the polymer. The corresponding spectra following isopropanol cleaning, corona treatment, and plasma treatment are shown in Figures 32 – 34, respectively. The significant observation upon examination of Figs. 31 and 32 is that IPA alcohol cleaning increased the intensity of the oxygen 1s and nitrogen 1s photopeaks relative to the intensities for the as received sample. It also was noteworthy that cleaning with alcohol increased the oxygen and nitrogen content to a level that was approximately equal to that produced following a corona or a plasma treatment. This comparison was more evident when the elemental compositions given in Table 18 were compared.

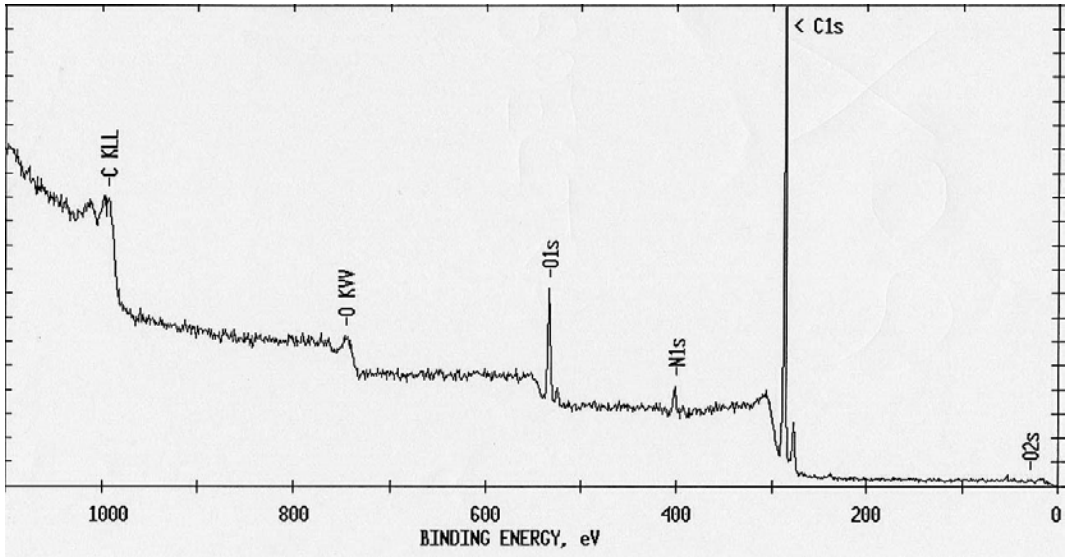


Figure 31. Wide-Scan XPS Spectrum for As Received Nylon 6,6.

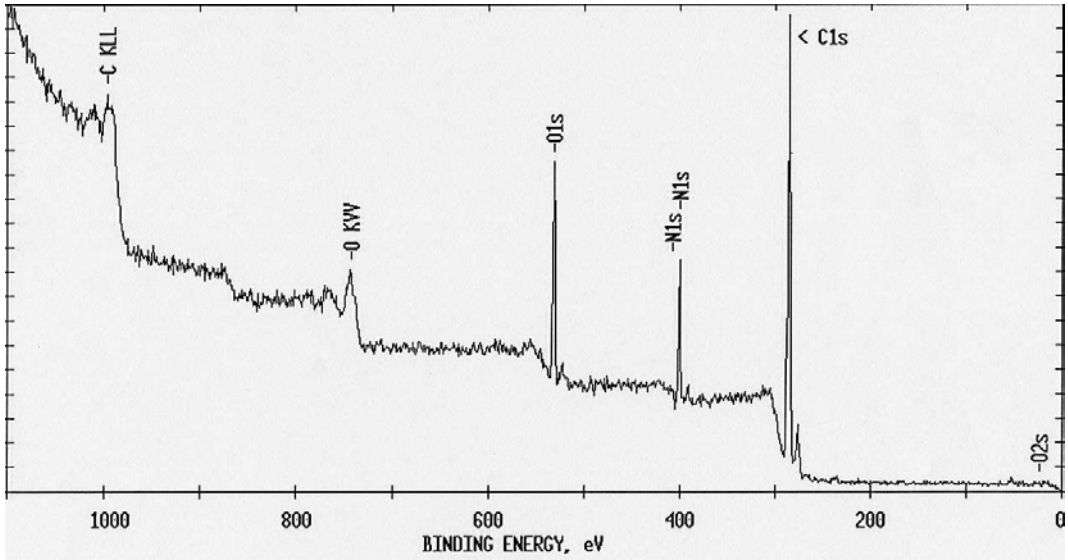


Figure 32. Wide-Scan XPS Spectrum for Isopropanol-Cleaned Nylon 6,6.

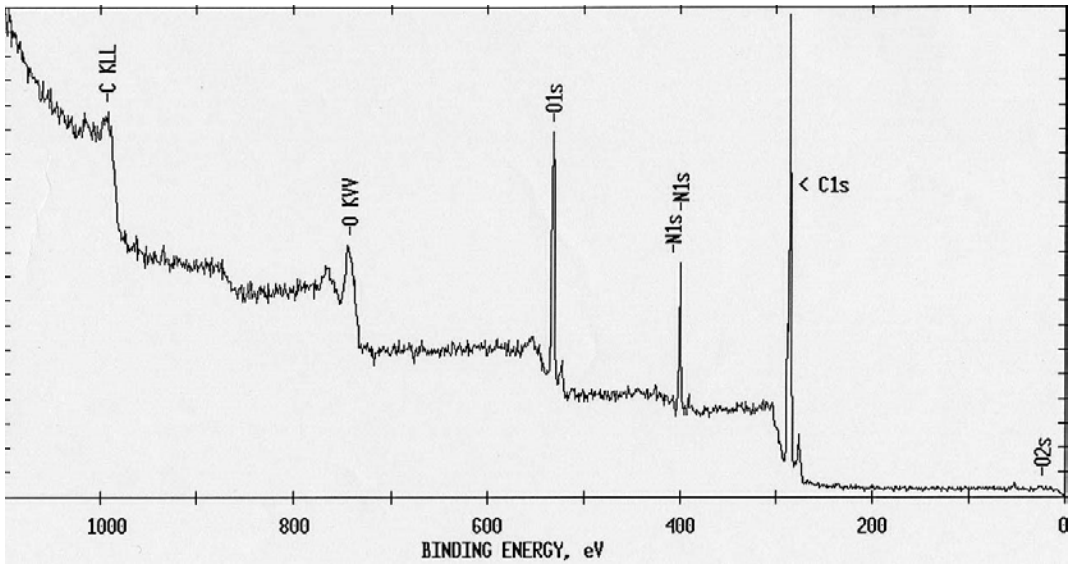


Figure 33. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Corona Treated Nylon 6,6.

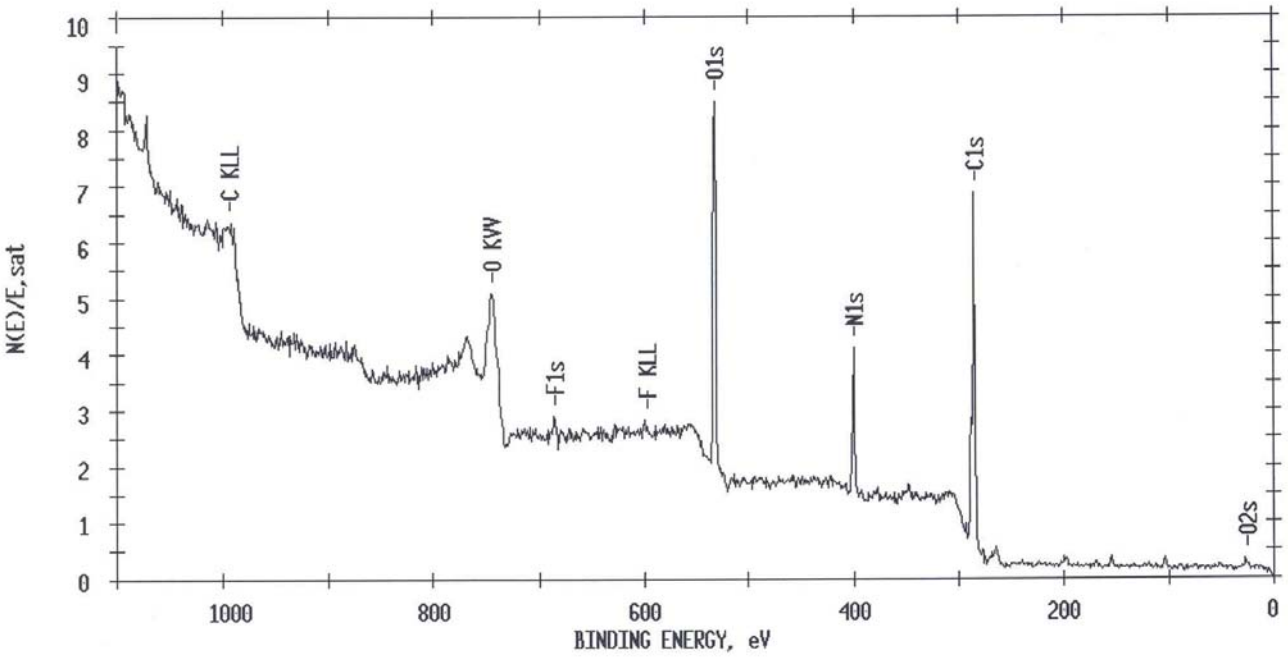


Figure 34. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Plasma Treated Nylon 6,6.

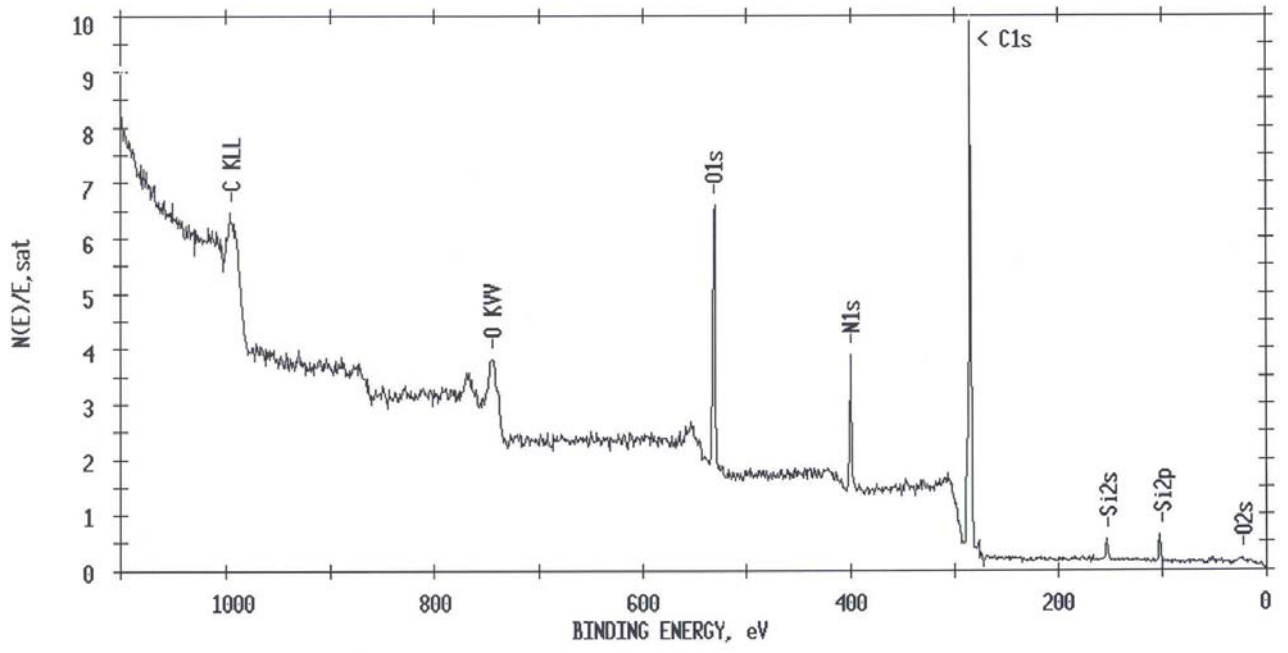


Figure 35. Wide-Scan XPS Spectrum for Isopropanol-Cleaned, Silane Modified Nylon 6,6.

Table 18. XPS Surface Analysis Results for Nylon 6,6 Adherends (Atomic %)

Sample/element	C	O	N	Si
as rec'd	86.8	10.3	2.9	<0.2
alcohol clean	75.9	12.5	11.6	<0.2
corona treat	62.3	25.9	11.8	<0.2
plasma treat Ar/O_2	60.9	25.2	12.3	1.6
silane modified	71.4	14.9	11.0	2.7

The pattern for the change in elemental composition for Nylon 6,6was similar to that noted for Lexan, oxygen increased as the oxidizing content of the treatment increased. In addition, nitrogen concentration increased to a level of about 11-12% and was unaltered even as the severity of the oxygenation treatment increased. It also was observed that silicon and sodium occurred on the surface of Nylon following the plasma treatment. Further it was found that oxidized carbon functionalities, C-O, C=O, COO^-, etc., increased (as apparent in the C 1s spectra, but not show) as the severity of the oxidation treatment increased. On the other hand, little or no change in the shape or binding energy of the N 1s photopeak occurred as the oxidizing capacity of the treatment increased. Silane derivatization was evident from the increase in silicon content relative to the concentration on the IPA cleaned sample.

In summary, the principal effect resulting from the various surface treatments was an increase in the amount of oxidized carbon functionalities. For each polymer this increase in oxidized carbon content appeared as carbon singly- and multiply-bonded to oxygen. The elemental composition (atomic percents) for IPA alcohol-cleaned Nylon 6,6 was in reasonable agreement with the theoretical values: C, 75%, O and N, 12.5 % each. That the nitrogen content remained relatively constant while the oxygen content increased and the carbon percent decreased with the increasing oxidizing severity of the surface treatment indicated, as noted above, that oxidation of carbon, rather than of nitrogen occurred in these processes. It appeared that alcohol cleaning produced a nearly stoichiometric Nylon 6,6 surface.

Contact Angle Measurements

To evaluate the changes in surface chemistry following the surface treatments, contact angle measurements were made using water and ethylene glycol for the cleaned and modified samples. To indicate the changes in surface energy in a more quantitative manner, the work of adhesion was approximated using the Young-Drupe expression: $W_a = \gamma_L(1 + \cos\theta)$. The surface energies for water and ethylene glycol were taken as 72.8 and 48.3 J/m^2, respectively. The results are presented in Table 19 for Lexan and for Nylon 6,6 samples. The principal finding from the surface energy measurements was that the corona and plasma surface modifications increased the surface energy to about the same extent while the increase in surface energy was not as significant for the silane-modified surfaces.

Table 19. Contact Angle and Adhesion Results for Lexan and Nylon 6,6 Adherends

Substrate	contact angle (degrees)		work of adhesion (J/m^2)	
	water	ethylene glycol	water	ethylene glycol
Lexan				
alcohol cleaned	90	64	73	69
corona treated	36	17	132	94
air plasma treated	36	5	132	96
silane treated	63	55	106	76
Nylon				
alcohol cleaned	54	30	116	90
corona treated	34	10	133	95
air plasma treated	34	4	133	96
silane treated	45	26	124	92

Durability Studies

Durability, as measured by crack growth behavior, was determined for Lexan (polycarbonate) and Nylon 6,6 (polyamide), bonded with primerless RTV silicone adhesive, PLS300A-630. Parameters, including surface preparation and environmental exposure conditions, were evaluated using the wedge type specimen. The fracture behavior was studied by inserting a 2 or 3 mm wedge into the bonded specimens and measuring the crack growth in the samples. The thickness of the wedge was selected to produce a stress that promoted reasonable crack growth and extension. The performance characteristics were determined for samples maintained at 1) room temperature in air with normal room humidity (RT), 2) 70°C at low relative humidity (70°C), and 3) 70°C at 100% relative humidity (70°C 100%). For each test condition, three bonded specimens were studied and the resulting crack data was reported as an average for the results obtained from the three specimens. Crack propagation was followed until the specimens debonded completely, or until crack propagation arrested. The results of the durability studies are best presented as crack length *vs* time plots.

To illustrate the variability in these plots for different samples, Figure 36 shows crack length data for silane (APS) modified Nylon 6,6 samples tested at 70°C and 100% RH. The crack length data were quite comparable among the three specimens. It should be noted that specimens for which debonding occurred easily did not usually exhibit such equivalence. Nevertheless, the results for poorly performing specimens indicated the trends in durability. For specimens that exhibit reasonable performance (samples prepared using corona, plasma, and silane modified adherends) the validity of taking the average of the crack growth data for three specimens for subsequent plots given in this report was justified.

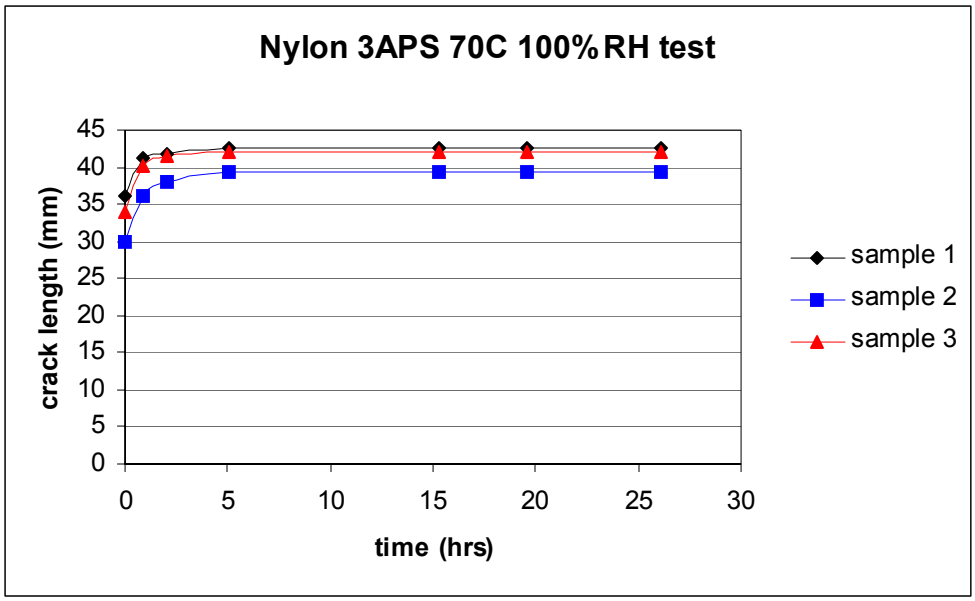


Figure 36. Crack-Length Data for Three Nylon 6,6 Specimens Tested at 70°C/100% RH

The durability results obtained under three environmental conditions for IPA alcohol-cleaned Lexan and Nylon 6,6 samples are given in Figures 37 and 38, respectively. The primary observations were that catastrophic debonding, within a very short time period, occurred for samples prepared via IPA alcohol (I-prOH) cleaning. Itwas interesting to note that crack-growth behavior was not significantly different whether the tests were conducted at room temperature or at elevated temperature (70°C either dry or at high RH). Only for the Nylon 6,6 specimen was crack growth slower for the sample tested at room temperature.

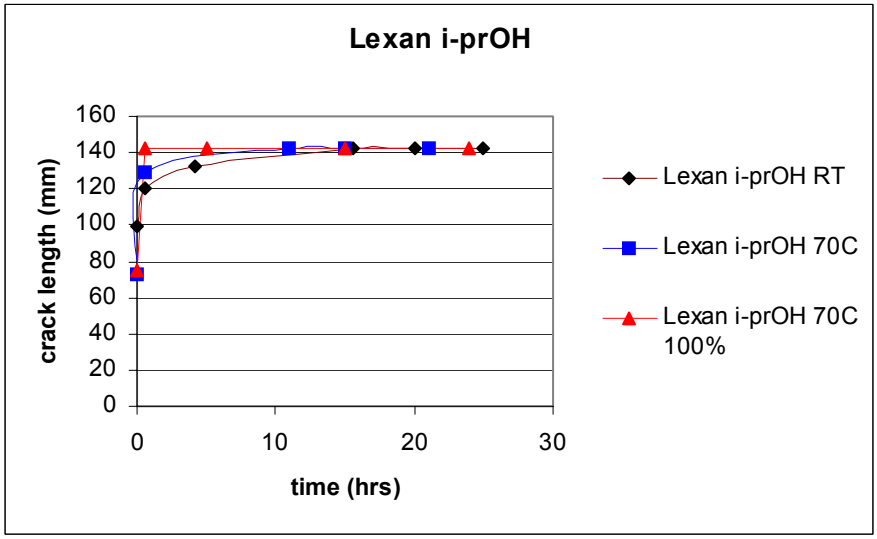


Figure 37. Durability of IPA –cleaned Lexan .

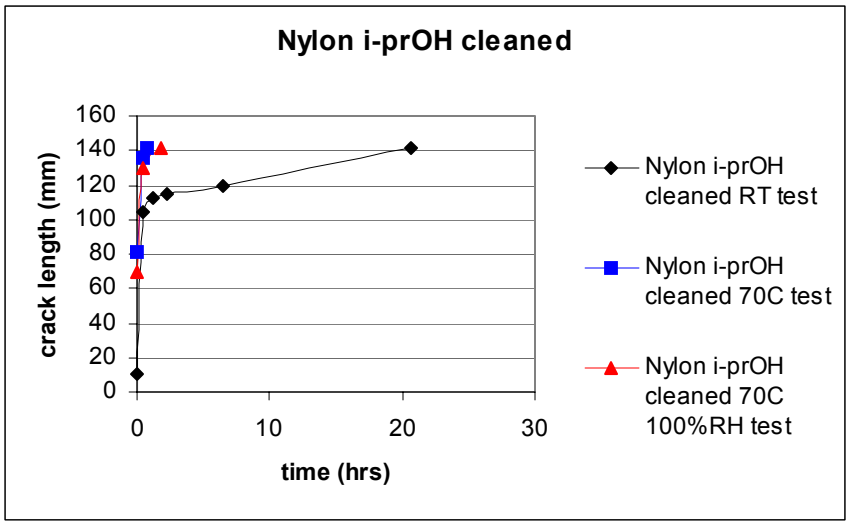


Figure 38 Durability of IPA Cleaned Nylon 6,6.

The durability for samples bonded with PLS300A-630 to Lexan and Nylon 6,6, measured under the most severe conditions (70°C and 100% RH), are shown in Figures 39 and 40, respectively. At crack lengths of about 140 mm, complete debonding of the specimen or crack extension along the full length of the sample occurred These results are presented to illustrate the role that surface treatment plays in influencing durability. Treating the surfaces with the corona improved durability initially, but for longer times, debonding equivalent to that for IPA –cleaned samples took place. For the plasma-treated Lexan samples, durability was initially good but approached the behavior for IPA or corona-treated samples at longer times. The significant finding for each Lexan sample was that performance degraded for tests carried out at high temperature and high humidity, with the exception of the sample treated with the silane coupling agent.

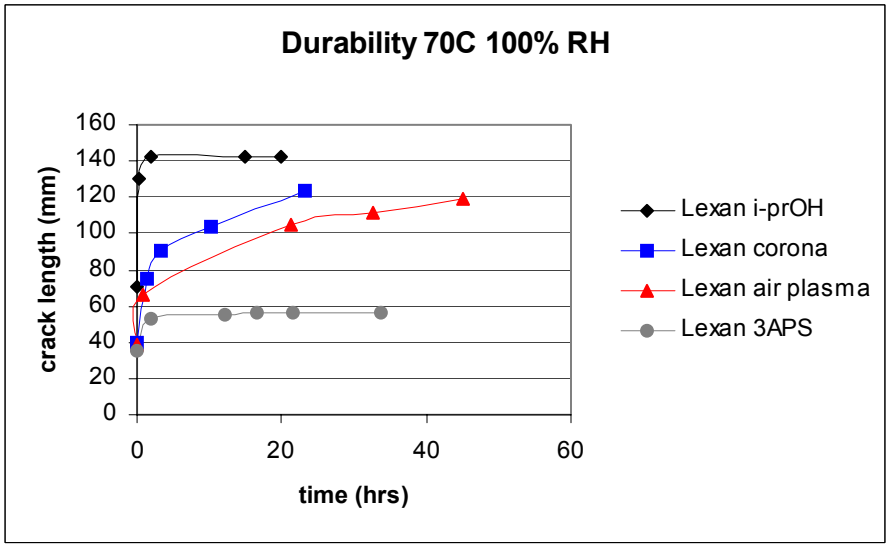


Figure 39. Durability of Lexan Under Severe Environmental Conditions.

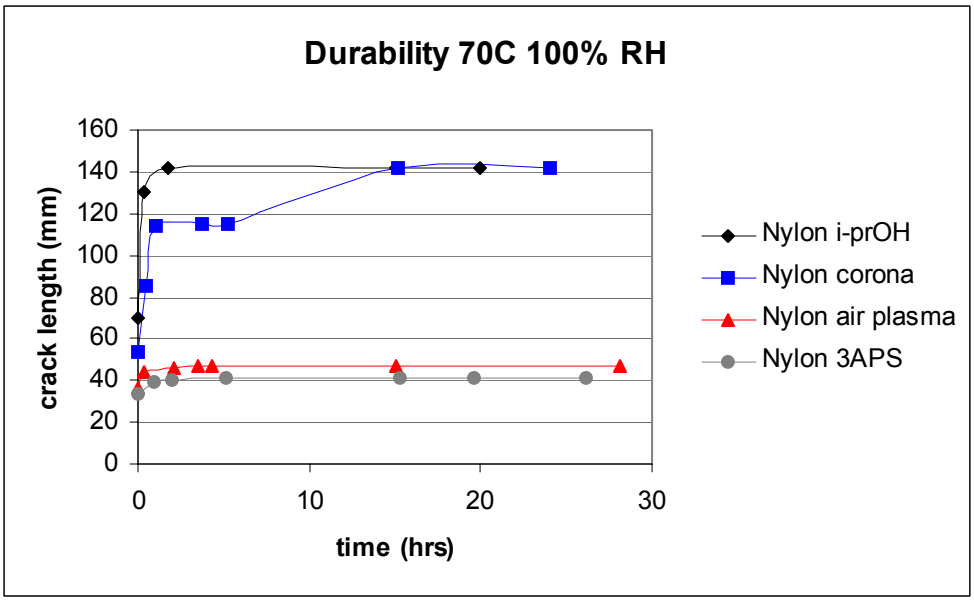


Figure 40. Durability of Nylon 6/6 Under Severe Environmental Conditions.

The crack length results for the PLS300A-630/Nylon 6,6 specimens shown in Figure 40 (tests at 70°C and 100% RH) indicated excellent performance for plasma and silane (APS) treated surfaces. The plasma treated Nylon 6,6 samples performed better than the Lexan. The main difference between Lexan and Nylon 6,6 was the higher concentration of nitrogen in Nylon 6,6. Surface energy results indicated approximately equivalent values for the work of adhesion, and on that basis, durability should be comparable. Perhaps the presence of nitrogen, in the form of an amine, in the silane (APS) sample, facilitated adhesion and enhanced durability. Further experiments would be needed to determine whether nitrogen was the principal factor that enhanced durability.

It was not evident what the reason was for the poor behavior for corona-treated samples. It was possible that the corona treatment had not been optimized, or that it was not as extensive or as "deep" into the surface as the plasma treatment; nor was it determined whether the corona-surface modification "lifetime" was sufficient to allow durable bond formation. No studies of the degradation of the modified surfaces have been carried out. Based on the surface characterization studies, the corona treatment should have enhanced bond formation and durability. Clearly, some as yet unidentified process degraded the surface and decreased bond durability for the corona treated samples.

The results in Figures 41 and 42 show the performance of the silane modified Lexan and Nylon 6,6 samples. The performance was similar under RT, 70°C and 70°C 100% RH conditions. The cracks arrested at very short times and did not exhibit further crack growth or sample degradation even under severe exposure conditions. For most conditions, the crack lengths usually were less for Nylon 6,6 than for Lexan. Such results further indicated the fact that optimum modification conditions for Lexan have not been identified. Incorporation of other heteroatom functionalities could perhaps improve adhesion and durability of Lexan.

The performance of other PLS300A-630 bonded samples following other surface treatments are shown in the Figures in Appendix L. In general, performance varied with respect to environment; RT > 70°C > 70°C and 100% RH; while the variation with surface treatment was Silane > plasma > corona > isopropanol cleaning. It was also noted that the crack lengths were typically less for Nylon 6,6 than Lexan.

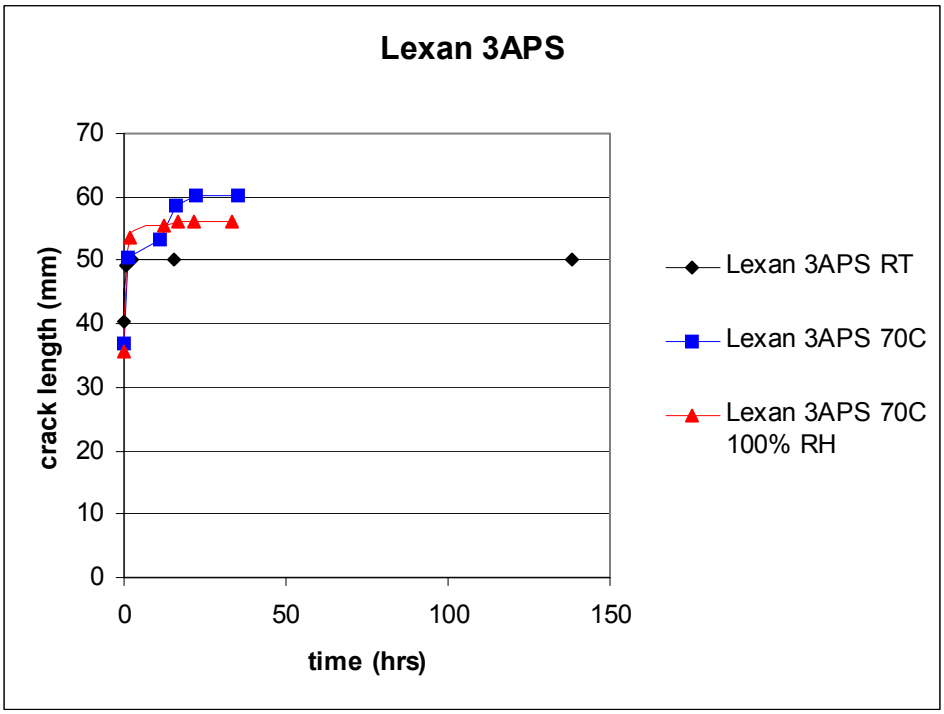


Figure 41. Durability of Silane Treated Lexan: Different Test Conditions

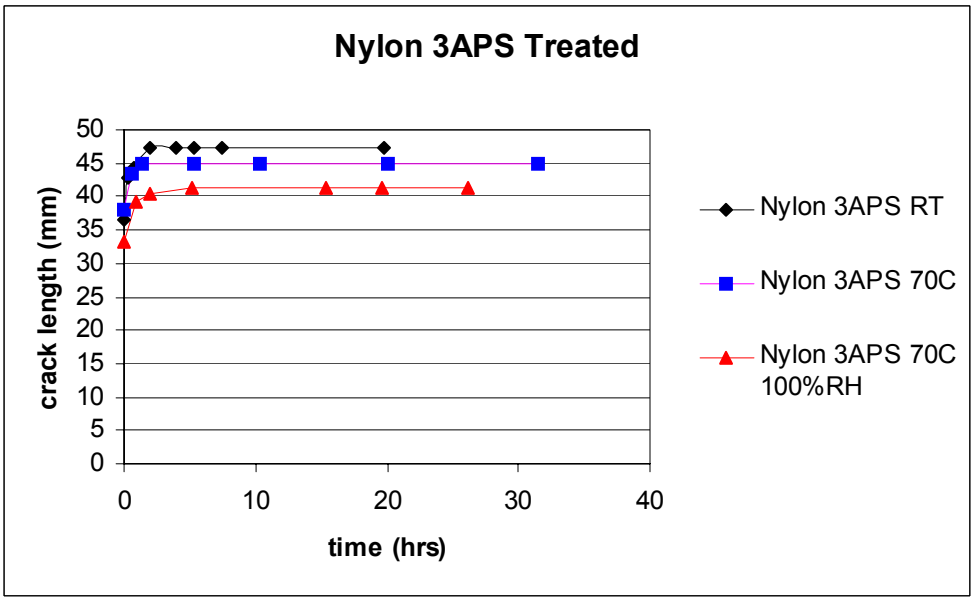


Figure 42. Durability of Silane Treated Nylon 6,6: Different Test Conditions

The surface characterization and durability studies have demonstrated that the surfaces of "plastics" could be modified to increase surface energy and at the same time improve durability. On the other hand, some surface modifications did not have long-term benefits for durability, although initial adhesion and performance was enhanced relative to specimens prepared using non-modified adherends. Among the best performing surface modification approaches in this study, the derivatization of Lexan and Nylon 6,6 using a silane coupling agent facilitated adhesive bonding and improved durability. It is conceivable that modification of surfaces via plasma or corona treatments followed by derivatization with coupling agents could further enhance adhesion and durability in these systems.

Department of Energy

One of the major aims of the final phase of this program was to assess technology in order to identify DoD and DOE applications for the primerless RTV adhesive/sealant materials and to transfer optimized formulations into these areas of interest. The Polymer Production Facility (PPF) at the Department of Energy, Kansas City Plant, which is managed by Honeywell Federal Manufacturing & Technologies, has been working to support this goal. The Polymer Production Facility is a unique facility owned by the federal government. It serves as a small-scale production facility of specialty materials, most of which are not available commercially. The PPF produces a broad range of chemicals including epoxies, urethanes, silicones, polyamide resins, and specialty curing agents, to name a few. It also does repackaging of chemicals and materials, usually into smaller or special configuration containers. The PPF is housed in a 22,000 square foot, stand-alone building. It is equipped with six chemical reactors ranging in size from 22 liters to 500 gallons. Other equipment includes blending, drying, filtration and grinding equipment. The KCP is an ISO 9000 and 14000 certified facility, which includes the PPF. A fully equipped Analytical Laboratory is available on-site to perform testing and certification of raw materials including the primerless silicone products.

The PPF has developed and produced a series of three primerless kits. The first, second, and third-generation primerless formulations, designated PLS100, PLS200, and PLS300, have been packaged in one pound kits that were distributed to the Army, Navy, and Air Force members of this SERDP research team for evaluation. Adhesion promoters and additives (such as the succinate additive) that are not available commercially also were synthesized at the PPF and included in the packaged kits. Appendix B lists the components, along with mixing instructions, for the various DOE primerless RTV kits.

Air Force Materials Laboratory

Lap Shear Testing

AFRL/MLSA evaluated lap shear adhesion of two formulations of primerless RTV materials prepared in kit form by DOE/Honeywell. The first-generation formulation, PLS100-630 (elevated temperature cure on metal), was tested on bare 2024-T3 aluminum substrates and a third-generation formulation, PLS-300-866 (elevated temperature cure on Nylon 6,6), was tested on Nylon 6,6 substrates. The University of Dayton Research Institute (UDRI) conducted all tests. Lap shear test specimens were prepared with the PLS-100-630 primerless RTV silicone on bare 2024-T3 aluminum substrates. Baseline specimens with RTV-630 and SS4155 primer also were prepare and tested. Three sets of 5 specimens were prepared for testing at -65°F, RT, and 400°F (consistent with Air Force requirements). The baseline specimens, RTV-630 using SS-4155 primer, were tested at room temperature only. Test results are shown in Appendix M.

The PLS100-630 and RTV-630 were mixed and cured in accordance with instructions provided with the kit. The mixed materials were degassed in a vacuum chamber for 30 minutes prior to specimen fabrication. All panels were cleaned with acetone prior to assembly. The template used during the fabrication of the lap shear panels had a machined offset of 50 mils, however, the majority of the glue lines were 60 mils. This may have been caused by adhesive swell during cure because there was no weight on the adherends during cure.

The primerless PLS100-630 lap shear specimens were tested at -65°F, 77°F and 400°F in accordance with ASTM D1002. The primed RTV-630 lap shear specimens were tested at 77°F in accordance with ASTM D1002. Crosshead speed was 2 inches per minute.

The PLS100-630 exhibited 100% cohesive failure when tested at -65°F, and 90% cohesive failure when tested at 400°F. The lap shear strengths were 815 psi at -65°F and 330 psi at 400°F. At 77°F, both the PLS100-630 and RTV-630 test specimens exhibited 0% cohesive failures with lap shear strengths of 410 psi for the PLS100-360 and 220 psi for the RTV-630. The RTV-630 test specimens were retested because the first set had considerable entrapped air, potentially resulting in the lower shear strengths observed. However, while the adhesive in the retested specimens contained no entrapped air, the lap shear strength was not noticeably higher. In general, at 77ºF (the only temperature at which the baseline was tested), the performance of the PLS100-630 on unprimed bare aluminum substrates was better than the performance of RTV-630 on bare aluminum substrates primed with SS-4155. The shear strength of the PLS100-630 without primer was approximates double that of the RTV-630; however, failures were adhesive for both.

Lap shear specimens were prepared with the third-generation PLS300-866 primerless RTV silicone on bare Nylon 6,6 substrates. Specimens with RTV-866 using SS4155 primer also were prepared and were used as a baseline. Three sets of 5 specimens were prepared for testing at -65°F, RT, and 200°F (consistent with Air Force requirements).

The PLS300-866 and RTV-866 were mixed and cured in accordance with instructions provided with the kit. The mixed materials were degassed in a vacuum chamber for 30 minutes prior to specimen fabrication. All panels were cleaned with acetone prior to assembly. Glass beads (20-mil diameter) were used to maintain bond line thickness for these Nylon 6,6 lap shear samples. The primerless PLS300-866 and the primed RTV-866 lap shear specimens were tested at -65°F, 77°F and 200°F in accordance with ASTM D1002. Crosshead speed was 2 inches per minute.

The PLS300-866 exhibited 100% cohesive failures with Nylon 6,6 as the adherend at all three test temperatures. The lap shear strengths were 1175 psi at -65°F, 530 psi at 77°F, and 264 psi at 200°F. The RTV-866 on Nylon 6,6 primed with SS-4155 exhibited 100% cohesive failures at -65°F and 77°F. At 200°F the failure mode was 30% cohesive. The lap shear strengths were 925 psi at - 65°F, 612 psi at 77°F, and 268 psi at 200°F.

In general, the performance of the primerless PLS300-866 on Nylon 6,6 substrates was roughly equivalent to the performance of RTV-866 on Nylon 6,6 substrates primed with SS-4155. The exception was that at 200ºF, the RTV-866 primed with SS-4155 exhibited only 30% cohesive failures whereas the PLS300-866 on unprimed Nylon 6,6 exhibited 100% cohesive failure.

NAVAIR Patuxent River

Lap Shear Testing

NAVAIR Patuxent River tested two formulations of primerless RTV materials prepared in kit form by DOE/Honeywell. The first-generation formulation, PLS100-630 (elevated temperature cure on metal), was tested on bare 2024-T3 aluminum and a third-generation formulation, PLS300A-630 (elevated temperature cure on Nylon 6,6), was tested on Nylon 6,6 strips provided by ARDEC (test data shown in Appendix N). The test results discussed below show that the primerless RTV kits prepared by DOE have strength properties comparable to the GE laboratory produced primerless RTV materials.

The PLS100-630 primerless RTV silicone was used to prepare lap shear specimens with bare 2024-T3 aluminum. Specimens with RTV-630 using SS4155 adhesion promoter primer also were prepared and used as a baseline comparison for the primerless formulation. Three sets of 5 specimens were prepared for testing at – 65°F, RT, and 400°F (consistent with Navy requirements and earlier Navy testing). All panels were cleaned prior to assembly with acetone. Glass spacer beads were not needed for bondline thickness because the fixture provided by GE maintained an approximately 40-mil bondline thickness through use of the milled step plate described earlier in this report. Crosshead speed was set at 2 inches per minute.

While none of the specimens exhibited completely cohesive failure, the primerless specimens, except for RT, demonstrated 70 and 75% cohesive failure at 400°F and –65°F respectively vs. 30 and 10% cohesive for the specimens with primer. At RT, the primerless specimens failed 50% cohesive and the primer specimens failed 60%

cohesively. Average failure loads for the baseline/primer specimens were 529, 367, and 714 psi at RT, 400°F, and –65°F, respectively. Average failure loads for the PLS100-630 specimens were 399, 322, and 889 psi at RT, 400°F, and –65°F, respectively. The loads for specimens with primer were higher than the primerless specimens at RT (529 vs. 399 psi) but the primerless samples performed better at –65°F (889 vs. 714 psi). In both of these cases, where there was a significant difference, however, the standard deviation was high (116 for the 889 psi load and 92 for the 529 psi load) for the higher load bringing the primer vs. primerless differences to much less than at first seemed apparent.

The PLS300A-630 primerless RTV silicone was used to prepare lap shear specimens on Nylon 6,6 panels supplied by ARDEC. Specimens with RTV-630 using SS4415 adhesion promoter also were prepared and used as a baseline comparison for the primerless formulation. As with the aluminum, three sets of 5 specimens were prepared for testing at temperatures of – 65°F, RT, and 200°F. All panels were cleaned prior to assembly with acetone. Glass beads (20-mil diameter) were used to maintain bond line thickness for these Nylon lap shear samples. Crosshead speed was 2 inches per minute.

Notable within the Nylon 6,6 tests were the extremely high failure loads (average at 1472 psi) obtained with the primerless specimens at – 65°F. In two of the five specimens, the Nylon 6,6 broke at the edge of the overlap before the silicone adhesive failed. These specimens were not included in either the average load or failure mode calculations. The baseline – 65°F specimens with primer failed at 898 psi. In general, all specimens and all substrates withstood significantly higher shear strengths at – 65°F than at any of the other temperatures. Overall, the primerless silicone performed better than the specimens with primer for all the Nylon 6,6 specimens (all temperatures). At the 200°F test condition, the results with the specimens with primer were comparatively low at 232 psi and the failure mode was 100% adhesive. When inspecting the bond line after testing, there appeared to be excessive primer on these panels where adhesive failure occurred. Beside the environmental impact in using silicone primers, difficulty in proper and consistent application of the primer is one of the biggest drawbacks for using these materials. An alternate explanation for the poor shear strength is that 200°F is above the glass transition temperature of the amorphous element of Nylon 6,6 and adhesion properties may have been compromised. However, due to the significantly higher failure load (400 psi with 65% cohesive failure) generated with the primerless system at 200°F, inconsistent primer application is the more likely reason for the low results. The RT and – 65°F specimens, despite the notably excessive primer, failed at fairly high loads (664 and 898 psi, respectively) but with low cohesive failure (30% and 15%, respectively). The PLS 300-630A primerless specimens had higher load failures (823 and 1472 psi) at RT and –65°F and failed cohesively (100% and 95%, respectively).

ARDEC

Spot Adhesion Testing

Qualitative spot adhesion tests have been conducted on a variety of substrates that are representative of present and possible future applications for RTV silicones with the first-generation and second-generation primerless formulations. These results should only be viewed as a cursory survey of the adhesive capabilities of the primerless systems, rather than as a recommendation for using the primerless materials to bond all of the substrates listed. To conduct these tests, drops of the adhesive formulation were applied to the particular substrates being examined and were allowed to cure. After the adhesive had cured, an attempt was made to manually scrape the adhesive off the surface of the substrate. Excellent adhesion was characterized for samples where the adhesive could not be removed from the sample without tearing the adhesive and leaving a layer of adhesive on the surface of the substrate, analogous to the cohesive mode of failure observed in lap shear samples. Fair adhesion and poor adhesion were characterized by adhesives that peeled cleanly from the surface in some places while tearing from the surface in some places and by peeling easily from the surface upon scraping, respectively. In general, excellent adhesion was obtained to metals, composites, and thermoset plastics while poorer adhesion was observed for thermoplastic materials. The substrates were prepared by abrading followed by solvent wiping or simply by solvent wiping alone. In some cases, additional surface treatment techniques such as corona treating were employed. The adhesive was allowed to cure for seven days at room temperature or for one hour at 100°C, depending on the formulation being used, prior to testing. The results of these tests indicate that the primerless material should lend itself to a broad array of applications. A complete listing of the results of spot adhesion testing completed to date can be found in Appendix O.

Lap Shear Testing

ARDEC tested three formulations of primerless RTV materials prepared in kit form by DOE/Honeywell. The first-generation formulation, PLS100-630 (elevated temperature cure on metal), was tested on alclad 2024-T3 aluminum and the two third-genertion formulations PLS300A-630 and PLS300-866 (elevated temperature cure on Nylon 6,6) were tested on Nylon 6,6 strips. (test data shown in Appendix P). The test results discussed below show that the primerless RTV kits prepared by DOE have strength properties comparable to those obtained with the GE laboratory produced primerless RTV materials.

The PLS100-630 primerless RTV silicone was used to prepare lap shear specimens with alclad 2024-T3 aluminum. Specimens with RTV-630 using SS4155 adhesion promoter primer also were prepared and used as a baseline comparison for the primerless formulation. Three sets of 5 specimens were prepared for testing at –25°F, RT, and 145°F (consistent with Army requirements and earlier Army testing). All panels were cleaned with IPA prior to assembly. Glass spacer beads were not needed for controlling

bondline thickness, because the fixture provided by GE maintained a bondline thickness of approximately 40-mil through use of the milled step plate described earlier in this report. Crosshead speed was set at 2 inches per minute.

All of the PLS100-630 2024-T3 alclad aluminum specimens exhibited complete cohesive failure. Average failure load for the baseline/primer specimens was 606 psi at RT, which was about equal to the PLS100-630 specimens with a failure at 656 psi. As was expected from prior tests, the low temperature primerless samples had a higher failure value, 910 psi, and the elevated temperature primerless samples had a slightly lower failure value, 530 psi, as compared to the RT primerless samples.

The PLS300A-630 and PLS 300-866 primerless RTV silicones were used to prepare lap shear specimens on Nylon 6,6 panels. Specimens with RTV-630 and RTV 866 using SS4415 adhesion promoter also were prepared and used as a baseline comparison for the comparable primerless formulations. As with the aluminum, three sets of 5 specimens were prepared for testing at temperatures of –25°F, RT, and 145°F. All panels were cleaned prior to assembly with IPA. Glass beads (20-mil diameter) were used to maintain bond line thickness for these Nylon 6,6 lap shear samples. Crosshead speed was 2 inches per minute.

As was observed with the first-generation aluminum samples, The low temperature primerless third-generation samples had higher failure values, 1,008 and 888 psi, while the elevated temperature third-generation primerless samples had slightly lower failure values, 549 and 411 psi, as compared to the RT primerless samples, PLS300A-630 and PLS300-866, respectively.

Technology Transition

Technology transition work on this program has included transitioning the PLS200-866 formulation to the XM984 120 millimeter extended range mortar program (Figure 43).

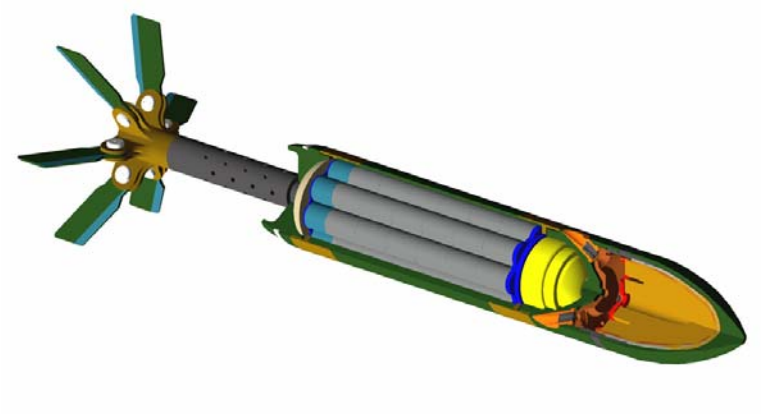


Figure 43: XM984 120-Millimeter Extended Range Mortar

The PLS200-866 formulation was used in bonding glass reinforced phenolic insulators into rocket motor assemblies (Figure 44). A successful ballistic test was held with mortars that were fabricated using the primerless formulation, and the material exhibited superior performance in meeting the thermal, mechanical, and adhesive requirements of this demanding application.

Figure 44: Bonding of Phenolic Insulator into Rocket Motor Assembly.

CONCLUSIONS

The first-generation objective to develop a primerless elevated temperature addition curing RTV silicone adhesive/sealant was successfully accomplished. The formulation consisted of GE RTV 630 modified with bis(trimethoxysilylpropyl) fumarate adhesion promoter. ANOVA analysis of testing indicated no statistical difference between the first-generation PLS100-630 and baseline RTV 630 + SS4155 primer formulations.

The second-generation objective to develop a primerless, room temperature addition curing RTV silicone adhesive/sealant was successfully accomplished. The PLS200-866 formulation consisted of GE RTV 866 modified with bis(trimethoxysilylpropyl)succinate adhesion promoter and 2-methyl-3-butyn-2-ol inhibitor. Excellent adhesion, without the use of a primer, was demonstrated for alclad, bare, and anodized aluminum as well as to steel, epoxy, and phenolic resin substrates.

The third-generation objective to develop a primerless, elevated temperature addition curing RTV silicone adhesive/sealant for thermoplastic (Nylon 6,6) materials was successfully accomplished. The two formulations, PLS300A630 and PLS300-866, consisted of GE RTV 630 and GE RTV 866 silicone adhesive/sealants each modified with adhesion promoter 2,2'-diallyl bisphenol A. Excellent adhesion has been demonstrated to Nylon 6,6 substrates under a variety of substrate preparation conditions with these materials, and the development of repeatable, durable, moisture resistant bonds has been established without compromising the material properties of the cured RTV silicone material. Shelf life stability testing for these new third-generation primerless systems with the adhesion promoter pre-mixed into the RTV B component has been established to be greater than eleven months.

General Electric (GE) Company's Silicone Business Unit issued a release indicating that they will discontinue manufacturing RTV 866 and it will not be commercially available within 2 years. This impacts PLS-200 and PLS-300 formulations in the long term.

GE's technical representatives recommended several alternatives. An amended PLS-300 formulation was evaluated which substituted RTV 630 for RTV 866 with 1.25% DBPA adhesion promoter. A full Design of Experiment test was conducted using RTV 630 in place of RTV 866. This substitute was determined to be an excellent replacement without compromising performance. Process capabilities exceeded GE's six-sigma requirements.

A substitute silicone for RTV 866, meeting critical to quality requirements, in the PLS-200 formulation, which utilizes succinate adhesion promoter, has not been determined.

In order to conduct durability studies, VPI treated both Lexan and Nylon 6,6 wedge crack test samples with IPA wiped, corona discharge, activated gas plasma, and silane modified treatments prior to primerless silicone bonding. XPS surface characterization analysis was conducted on the treated surfaces prior to bonding to establish the "oxygenating tendency" of the specific treatments. Increased oxidation of thermoplastic substrates usually will enhance bond performance and is critical for durability evaluations, which subject samples to severe environmental conditions. Wedge crack bond durability results on Nylon were better than Lexan using similar surface treatments. Wedge crack bond durability on corona treated Lexan was inferior to surfaces which were not corona treated. An explanation for this unexpected result has not been determined. The general findings are that modification of Lexan and Nylon 6,6 using the Plasma or derivation with the silane coupling agent significantly enhanced adhesion as indicated by performance in the environmental test measurements. It is theorized that treating the surface of Lexan and Nylon 6,6 with either the corona or plasma treatment prior to using the silane modification may further enhance adhesion and bond durability.

The Polymer Production Facility (PPF), DOE/KCP has completed all material/processing specifications and received all required approvals/authorizations to synthesize, process and distribute the four primerless silicone formulations. The PPF also had distributed primerless RTV "kits" (PLS100, PLS200, and PLS300) to the DoD team – Navy, Air Force and Army Laboratories for qualification evaluations.

The NAVAIR, Patuxent River Materials Lab, along with the Air Force and Army have completed their evaluations of PPF supplied primerless silicone formulations; the performance of the DOE kits was equal to comparable PLS primerless materials fabricated by GE. These results qualified PPF as a supplier for primerless formulations. The evaluations showed that bond strengths with primerless formulations met or exceeded bond strengths of samples bonded with high VOC containing primers. Evaluations of primerless silicones on bare aluminum at excessively high temperatures (400°F) also showed excellent bond strengths, comparable to primed silicone samples. High temperature bond capability is a unique characteristic of RTV silicones. The primerless silicone formulations developed in this study maintained this unique capability.

Spot adhesion testing has demonstrated the ability of the first-generation and second-generation formulations to develop adhesion to a wide variety of substrates varying from metal substrates such as titanium and sol-gel treated aluminum substrates to thermoset plastic substrates and composite substrates such as carbon fiber reinforced epoxy substrates and glass reinforced phenolic substrates. Excellent adhesion was also obtained on some crystalline surfaces such as sapphire and to coatings such as phosphated steel.

Technology transition and demonstration work has continued, and the performance of the second-generation primerless RTV silicone formulation in bonding a glass fiber reinforced, phenolic insulator to a rocket motor housing in the XM984 120 millimeter extended range mortar, was demonstrated in a successful ballistic test.

REFERENCES

1. SERDP Year End Report, "Primerless RTV Silicone Sealants/Adhesives PP-1135", December 1999.

2. SERDP Year End Report, "Primerless RTV Silicone Sealants/Adhesives PP-1135", December 2000.

3. SERDP Year End Report, "Primerless RTV Silicone Sealants/Adhesives PP-1135", December 2001.

4. SERDP Year End Report, "Primerless RTV Silicone Sealants/Adhesives PP-1135", December 2002.

5. ASTM D1002-99 Standard Test Method for Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading

6. ASTM D903-98 Standard Test Method for Peel or Stripping Strength of Adhesive Bonds

7. ASTM D897-01 Standard Test Method for Tensile Properties of Adhesive Bonds

8. ASTM D3762-98 Standard Test Method for Adhesive Bonded Surface Durability of Aluminum (Wedge Test).

9. ASTM D3808-01 Standard Test Method for Qualitative Determination of Adhesion of Adhesives to Substrates by Spot Adhesion

10. ASTM D 429-02 Standard Test Method for Rubber Property – Adhesion to Rigid Substrates

11. ASTM D1151-00 Standard Test Method for Determining the Effect of Moisture on Adhesive Bonds.

Appendix A:

Adhesion Promoter Synthesis

Synthetic Procedures

Synthesis of bis(trimethoxysilylpropyl) succinate

A 50 mL round bottom flask was charged with (10.00 g, 50.44mmol) of diallyl succinate and 100.0 µL of 6% Karstedt catalyst. The mixture was stirred at 50 °C for 10 min, then (18.50 g, 19.30mL, 151.2 mmol) of trimethoxysilane was added slowly. The reaction mixture was stirred at 50 °C overnight. After the reaction was complete according to ^{1}H-NMR spectroscopy, excess trimethoxysilane was stripped under high vacuum. The product was isolated in 95% yield.
^{1}H-NMR: δ 4.06 (t, 2H, OC$\underline{H}_2$), 3.55 (s, 9H, Si(OC$\underline{H}_3$)$_3$), 2.58 (s, 2H, OCC$\underline{H}_2$), 1.7 (q, 2H, $Ch_2C\underline{H}_2CH_2$), 0.65 (t, 2H, SiC$\underline{H}_2$).

Synthesis of bis(trimethoxysilylpropyl) hydromuconate

A 2000 mL round bottom flask equipped with magnetic stir bar and Dean Stark apparatus was charged with trans-hydromuconic acid (100g, 0.70mol), *p*-toluenesulfonic acid (1.40 g, 0.0070 mol), 4-methoxyphenol (0.86 g, 0.0070 mol), allylalcohol (205 g, 3.5 mol) and 500 ml of toluene. The mixture was stirred at 110 °C for 6 h. Excess allylalcohol and toluene were removed in vacuo and 200 mL of diethyl ether was added. The crude solution was washed with a saturated solution of sodium bicarbonate (5 x 200 mL), a saturated solution of sodium chloride (3 x 200 mL) and water (3 x 200 mL). The crude product was dried over $MgSO_4$, filtered, and the solvent was evaporated. Distillation at 110°C/2.0 mmHg afforded 129 g of diallyl hydromuconate. A 500 mL round bottom flask was charged with diallyl hydromuconate (129 g, 0.58 mol) and Karstedt catalyst (37 µL, 13%by weight Pt). The mixture was stirred at 55 °C for 10 minutes followed by slow addition of trimethoxysilane (156 g, 1.28 mol, 162 mL). The reaction mixture was stirred overnight at 100 °C. After the reaction was complete according to ^{1}H-NMR spectroscopy, excess trimethoxysilane was stripped under vacuum to yield 258.08 g (95.6% yield) of bis(trimethoxysilylpropyl) hydromuconate.
^{1}H-NMR: δ 5.6 (t, 1H, H2CC$\underline{H}$=), 3.95 (t, 2H, OC$\underline{H}_2$), 3.52 (s, 9H, Si(OC$\underline{H}_3$)$_3$), 3.02 (d, 2H, $O_2CC\underline{H}_2$), 1.66 (q, 2H, $CH_2C\underline{H}_2CH_2$), 0.65 (t, 2H, SiC$\underline{H}_2$).
^{13}C-NMR: δ 172 ($H_2C\underline{C}O_2$), 126 ($CH_2H\underline{C}$=), 67 (O$\underline{C}H_2$), 51 (Si(O$\underline{C}H_3$)$_3$), 38.5 ($O_2C\underline{C}H_2$), 22 ($H_2C\underline{C}H_2CH_2$), 5 ($\underline{C}H_2Si$).

Appendix B

PRIMERLESS SILICONE (PLS) KIT FORMULATIONS AND MIXING DIRECTIONS

The following is a summary of the various PLS silicone kit formulations (including mix ratios)

Kit Designation: PLS-100-630

KC Part#	Name	PBW	Comments	Supplier
2070140	RTV 630 A	89.41	RTV Base	GE Silicones
2070140	RTV 630 B	8.94	RTV Curing Agent	GE Silicones
2070141	bis(trimethoxysilylpropyl) fumarate	0.98	Fumarate Adhesion Promoter (UV9450A)	GE Silicones
2070145	silicon hydride	0.67	Needed for optimized properties (88104)	GE Silicones

PBW = parts by weight

Recommended Cure Time: 1 hour at 100°C

Recommended Mixing Procedure

- Weight and mix all components together in a metal, plastic or glass container. Do not use paper containers. Also, when components are mixed together, material in corners of the container must be thoroughly mixed into the bulk mixture. This is very important as the additives are very small quantities and must be incorporated into the bulk mixture. A new, wooden tongue depressor is recommended for mixing the ingredients.
- A single container is used for weighing and mixing the ingredients. The container should be large enough for subsequent de-gassing the mixture (with a full vacuum applied a 5x volumetric expansion may be expected.
- Weigh out the correct amount of additive(s). Next, add the RTV 630 Part B. Mix thoroughly!
- In the same container, add the correct amount of RTV 630 Part A. Mix thoroughly!
- De-gas the blended mixture in a vacuum, breaking the rising foam by repeatedly releasing the vacuum. This should be done several times (each time opening the de-gassing tank to break the gas bubbles and to scrap the sidewalls of the container to keep all the mixture together). The multi-step de-gassing is optional, depending on the efficiency of the vacuum.
- Apply the mixed and degassed PLS silicone material to each substrate surface to be bonded. If any air bubbles become visible, break them before assembling the test substrates. Once the test specimens are assembled cure for 1 hour at 100 degrees C.

Appendix B

PRIMERLESS SILICONE (PLS) KIT FORMULATIONS AND MIXING DIRECTIONS (continued)

Kit Designation: PLS-200-866

MS	Name	PBW	Comments	Supplier
2070139	RTV 866 A	90.48	-	GE Silicones
2070139	RTV 866 B	9.05	-	GE Silicones
2070148	Succinate	0.41	Synthesized (Appendix A)	
2070143	2-methyl-3-butyn-2-ol	0.02	Inhibitor	Aldrich

PBW = parts by weight

Recommended Cure Time: 7 days at room temperature

Recommended Mixing Procedure

- Weight and mix all components together in a metal, plastic or glass container. Do not use paper containers. Also, when components are mixed together, material in corners of the container must be thoroughly mixed into the bulk mixture. This is very important as the additives are very small quantities and must be incorporated into the bulk mixture. A new, wooden tongue depressor is recommended for mixing the ingredients.
- A single container is used for weighing and mixing the ingredients. The container should be large enough for subsequent de-gassing the mixture (with a full vacuum applied a 5x volumetric expansion may be expected.
- Weigh out the correct amount of additive(s). Next, add the RTV 866 Part B. Mix thoroughly!
- In the same container, add the correct amount of RTV 866 Part A. Mix thoroughly!
- De-gas the blended mixture in a vacuum, breaking the rising foam by repeatedly releasing the vacuum. This should be done several times (each time opening the de-gassing tank to break the gas bubbles and to scrap the sidewalls of the container to keep all the mixture together). The multi-step de-gassing is optional, depending on the efficiency of the vacuum.
- Apply the mixed and degassed PLS silicone material to each substrate surface to be bonded. If any air bubbles become visible, break them before assembling the test substrates. Once the test specimens are assembled cure for 7 days at room temperature.

Appendix B

PRIMERLESS SILICONE (PLS) KIT FORMULATIONS AND MIXING DIRECTIONS (continued)

Kit Designation: PLS-300-630A
Designed for use with Nylon

MS	Name	PBW	Comments	Supplier
2070140	RTV 630 A	89.4	-	GE Silicones
2070140	RTV 630 B	8.94	-	GE Silicones
2070142	2,2'-diallyl bisphenol A	1.25	85% technical grade	Aldrich 41352-6

PBW = parts by weight

Recommended Cure Time: 1 hour at 100°C

Recommended Mixing Procedure

- Weight and mix all components together in a metal, plastic or glass container. Do not use paper containers. Also, when components are mixed together, material in corners of the container must be thoroughly mixed into the bulk mixture. This is very important as the additives are very small quantities and must be incorporated into the bulk mixture. A new, wooden tongue depressor is recommended for mixing the ingredients.
- A single container is used for weighing and mixing the ingredients. The container should be large enough for subsequent de-gassing the mixture (with a full vacuum applied a 5x volumetric expansion may be expected.
- Weigh out the correct amount of additive(s). Next, add the RTV 630 Part B. Mix thoroughly!
- In the same container, add the correct amount of RTV 630 Part A. Mix thoroughly!
- De-gas the blended mixture in a vacuum, breaking the rising foam by repeatedly releasing the vacuum. This should be done several times (each time opening the de-gassing tank to break the gas bubbles and to scrap the sidewalls of the container to keep all the mixture together). The multi-step de-gassing is optional, depending on the efficiency of the vacuum.
- Apply the mixed and degassed PLS silicone material to each substrate surface to be bonded. If any air bubbles become visible, break them before assembling the test substrates. Once the test specimens are assembled cure for 1 hour at 100 degrees C.

Appendix B

PRIMERLESS SILICONE (PLS) KIT FORMULATIONS AND MIXING DIRECTIONS (continued)

Kit Designation: PLS-300-866
Designed for use with Nylon

MS	Name	PBW	Comments	Supplier
2070139	RTV 866 A	89.4	-	GE Silicones
2070139	RTV 866 B	8.94	-	GE Silicones
2070142	2,2'-diallyl bisphenol A	1.25	85% technical grade	Aldrich 41352-6

PBW = parts by weight

Recommended Cure Time: 1 hour at 100°C

Recommended Mixing Procedure

- Weight and mix all components together in a metal, plastic or glass container. Do not use paper containers. Also, when components are mixed together, material in corners of the container must be thoroughly mixed into the bulk mixture. This is very important as the additives are very small quantities and must be incorporated into the bulk mixture. A new, wooden tongue depressor is recommended for mixing the ingredients.
- A single container is used for weighing and mixing the ingredients. The container should be large enough for subsequent de-gassing the mixture (with a full vacuum applied a 5x volumetric expansion may be expected.
- Weigh out the correct amount of additive(s). Next, add the RTV 866 Part B. Mix thoroughly!
- In the same container, add the correct amount of RTV 866 Part A. Mix thoroughly!
- De-gas the blended mixture in a vacuum, breaking the rising foam by repeatedly releasing the vacuum. This should be done several times (each time opening the de-gassing tank to break the gas bubbles and to scrap the sidewalls of the container to keep all the mixture together). The multi-step de-gassing is optional, depending on the efficiency of the vacuum.
- Apply the mixed and degassed PLS silicone material to each substrate surface to be bonded. If any air bubbles become visible, break them before assembling the test substrates. Once the test specimens are assembled cure for 1 hour at 100 degrees C.

Appendix C

A New Class of Adhesion Promoters for Addition Curable Silicone Adhesives

Judith Stein*[1], B.E. Eichinger[2], Thomas Early[1] and Christina Darkangelo Wood[1"],
MST Conference Proceedings, Newark, NJ May 2000.

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Abstract

Silicones intrinsically have low surface free energy and therefore either primers or additives, which function as adhesion promoters, must be utilized in order for silicones to adhere to surfaces. Alkoxysilanes, which are typically added to promote adhesion in condensation curable silicones, function by chemically coupling the silicone network to the substrate providing a deformable interfacial layer. We have developed a new class of addition curable silicones that are self-priming. These bifunctional materials are only partly miscible in the silicone matrix and bloom to the surface upon curing. The interfacial layer is comprised of an entanglement of the condensed adhesion promoter and the silicone matrix.

X-ray Photoelectron Spectroscopy confirmed that the adhesion promoter concentration is enhanced at the adherend interface after cure. Molecular simulations support the hypothesis that the adhesion promoter most likely bonds to a hydroxyl defect site on the metal. The effect of adhesion promoter incorporation upon the curing profile of the silicone has been determined using NMR Imaging.

Keywords: Silicones, adhesion promoters, primers, hydrosilylation

- **Introduction**

Addition curable silicone coatings are formed by the reaction of multifunctional silicone hydride polymers with multifunctional silicone vinyl polymers in the presence of a hydrosilylation catalyst such as Karstedt's catalyst, $Pt_2(M^{vi}M^{vi})_3$, where $M^{vi}M^{vi}$= 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. Coatings prepared in this manner do not typically adhere to surfaces for a variety of reasons including the low surface free energy of the coatings, their low polarity and high flexibility of the polymer backbone and their incompatibility with organic polymers [1]. Priming of the adherend surface enhances the adhesive nature of these materials [2]. Unfortunately, there are many issues with the use of primers. Application is an art and is not generally robust. Adhesion is dependent upon the degree of primer condensation. Primers have very high volatile organic compound levels and thus their use has a negative impact on the environment.

[1]GE Corporate Research and Development, 1 Research Circle, Niskayuna, NY 12309
[2]Accelrys, 9685 Scranton Road, San Diego, CA 92121
*To whom correspondence should be addressed
518-387-7342
518-387-7403 (fax)
steinj@crd.ge.com

An alternative method to obtain adhesion of addition curable silicones to substrates is by incorporation of adhesion promoters into the pre-cured silicone. Adhesion promoters typically contain functionality for chemically bonding into the polymer network and for chemically bonding at the surface [3]. The first material to be employed as an adhesion promoter in an addition curable silicone was a combination of vinyltrichlorosilane and vinyltrialkoxysilane by Ballard in 1970 [4]. Since that time, hundreds of patents have been written most of which describe compositions containing adhesion promoting compounds with at least one functionality selected from alkoxy, alkenoxy, epoxy, acryl, alkenyl or silicon hydride [5,6,7]. Other concepts that have been employed include combinations of addition curable silicone with condensation curable catalysts such as aluminum or zirconium, and functionalization of fillers with methoxy groups [8,9,10].

In this paper, we describe a new self-priming addition curable silicone. In this case, the adhesion promoter does not chemically bond to the silicone network but rather phase separates to the silicone-adherend interface.

2.1 Experimental

- Materials

Karstedt's catalyst, bis(trimethoxysilylpropyl)fumarate and addition curable silicone compositions (RTV630, LIM 6040 and RTV866) were generously supplied by GE Silicones. Bis(trimethoxysilylpropyl)succinate was prepared by reaction of diallylsuccinate with two equivalents of trimethoxysilane in the presence of Karstedt's catalyst. The appropriate adhesion promoter was incorporated into the formulations at 1.2%. After incorporation of the adhesion promoter, the formulations were degassed either by centrifugation or a combination of devolatization in vacuum/centrifugation cycles. Samples were allowed to cure either at room temperature for 7 days or 2 hours at 100°C prior to analysis by X-ray photoelectron spectroscopy. For the adhesion studies, 22 grams of RTV630 was combined with 0.5 mmoles of either glycidoxypropyltrimethoxysilane (0.11g) or bis(trimethoxysilylpropyl)fumarate (0.22g) and 0.15g of silicone hydride resin(9.5mmol H per gram). Lap shear samples of 2.54 cm x 2.54 cm were cured at 115°C and tested using an Instron 4202 with a crosshead speed of 5.08 cm per minute.

- NMR Imaging

Images at 2 Tesla field strength (85.2 MHz proton frequency) were obtained on a General Electric 33-cm horizontal bore imaging NMR spectrometer. Actively shielded gradient coils produced about 7 Gauss/cm gradients. A 70 mm diameter quadrature "bird cage" coil was used with approximately 55 microsecond 90° pulses at full RF power. A standard spin warp imaging sequence was used to obtain a 64 x 64 x 32 mm image with a 1 x 1 x 1 mm voxel (volume element) size [11]. Two scans per block were acquired with a spin warp echo time of 4.2 ms, acquiring a scan every second. This resulted in a 1 hour 8 minute total acquisition time. Sample components were mixed as quickly as possible before the first image acquisition was acquired. The starting material was liquid and became solid upon cuing. Subsequent image acquisitions were initialized two hours after the start of the previous image acquisition. Raw image data were apodized and Fourier

transformed by the General Electric Omega spectrometer software. Tiled, grayscale TIFF images were developed from the three-dimensional data with a custom program developed at GE. Image colorization was performed on a PC with standard imaging processing software.

- X-ray Photoelectron Spectroscopy

Data were acquired on a PHI 3500 instrument with an Al K monochromator. Survey scans were performed with the energy analyzer set at a pass energy of 187 eV. High-resolution scans of individual core levels were obtained with a pass energy of 12 eV.

- Secondary Ion Mass Spectrometry

Data were acquired on a PHI 3500 instrument using a 4 kV Xe^+ source with a one nA beam current. The analyzed area was 4x4 mm. Secondary ions were detected using a quadrupole mass spectrometer.

- Calculations

Quantum mechanical calculations were performed on a representative hydrated alumina cluster with the density functional programDMol[3] [12]. The cluster was constructed by extracting a core of 6 Al atoms together with all neighboring oxygens from the (001) surface of alumina. To this structure were added sufficient H atoms to yield a cluster having the stoichiometry $(Al_2O_3)_3 \bullet 15H_2O$. The geometry of the cluster was then optimized using the VWN ltem silan in Dmol[3] [13]. During the minimization, several H atom transfers occurred to yield the structure shown in Scheme I. The high accuracy dnp numerical basis set (equivalent to a 6-31G**) was used for all calculations. Subsequent to locating a stable local minimum, a single point energy evaluation was performed using the higher order approximation provided by BP gradient corrections [14]. (This procedure, using VWN geometries with BP energies, is a recognized standard method for obtaining the most accurate energies for the best molecular structures.) The geometry of the optimized cluster was fixed for subsequent work.

A relatively small model of the adhesion promoter was used for bonding studies. Methyltrimethoxysilane was bonded to tuck-in sites with one, two, and three oxygen atoms (see Fig. 5). A hydroxyl site on the edge of the cluster was also selected for study, but here only one bond was formed with the silane. The heat of reaction (electronic energies only, exclusive of zero point vibrations) at 0 K was determined for the reaction

$$R_1R_2R_3SiOCH_3 + HOX \longrightarrow R_1R_2R_3SiOX + CH_3OH$$

where X represents the remainder of the cluster.

In addition to studies on the binding of the silyl ester to the alumina cluster, the first few steps of the condensation polymerization were investigated. In this case, the reaction studied was

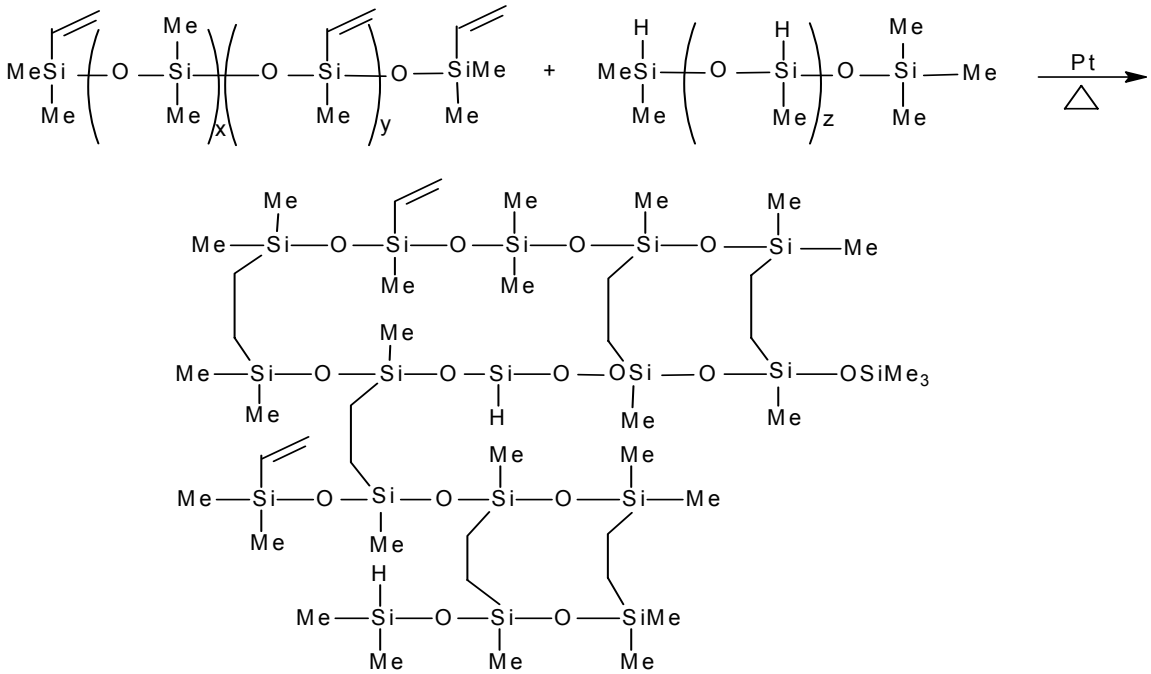
$$R_1R_2R_3SiOCH_3 + CH_3OSiR'_1R'_2R'_3 + H_2O \longrightarrow R_1R_2R_3SiOSiR'_1R'_2R'_3 + 2CH_3OH$$

The heats of reaction for formation of ltem and trimer were investigated.

3.0 Results and Discussion

- Silicone Adhesive Compositions

Silicone networks were prepared by reaction of silicone hydride polymers with silicone vinyl polymers in the presence of a hydrosilylation catalyst, a cure inhibitor and an adhesion promoter as shown in Scheme 1 [2].



Scheme 1. Addition Cured Silicone Network

Adhesion promoters were exemplified by the bifunctional structure (**1**) below which contains both ester and silylmethoxy functionalities.

$$(CH_3O)_3SiCH_2CH_2CH_2(O)C(=O)RC(=O)CH_2CH_2CH_2Si(OCH_3)_3$$

(1)

In most cases, bis(trimethoxysilylpropyl)fumarate was used as the adhesion promoter (R is CH=CH) [15]. Inhibitors such as fumarates, maleates or acetylenic alcohols were added to the formulation to prevent premature gelation of the silicone [16].

We have shown previously that these networks contain small amounts of residual silicon hydride groups[1]. These hydride groups could possibly hydrolyze and condense with silicon hydrides to form more crosslinks or alternatively, it might be possible for the silanols thus generated to react with the methoxy groups of the adhesion promoter. However, adhesion to the surface occurs more rapidly than disappearance of the residual silicon-hydride as evidenced by FIT-IR spectroscopy. Adhesion values for the

unamended formulation, and for formulations comprising a traditional adhesion promoter (glycidoxypropyltrimethoxysilane) and the new adhesion promoter are given in Table 1.

Table 1. Effect of adhesion promoter incorporation on lap shear strength

Adhesion Promoter	**Lap Shear Strength (Mpa)**	**Failure Mode**
none	0.49+/-0.20	interfacial
glycidoxypropyltrimethoxysilane	1.27+/-0.39	interfacial
bis(trimethoxysilylpropyl)fumarate	4.77+/-0.27	interfacial

- Location of the Adhesion Promoter in Cured Silicone Networks

Previously, we described the use of dynamic Secondary Ion Mass Spectrometry to locate the adhesion promoter, -aminopropyltrimethoxysilane, in a condensation-cured silicone matrix [17]. In this case, the adhesion promoter was uniformly distributed throughout the cured silicone. This is not unexpected since the adhesion promoter is miscible with the uncured silanol polymer and in addition contains functionality that can condense with either the crosslinker or silanol polymer. In contrast, X-ray Photoelectron Spectroscopy revealed that incorporation of bis(trimethoxysilylpropyl)fumarate in an addition cured silicone resulted in enhancement of the adhesion promoter at the surface (Fig. 1). The amount of adhesion promoter in the bulk was below the detection limit. Concentration at the surface is a consequence of the partial immiscibility of the adhesion promoter in the silicone phase after cure.

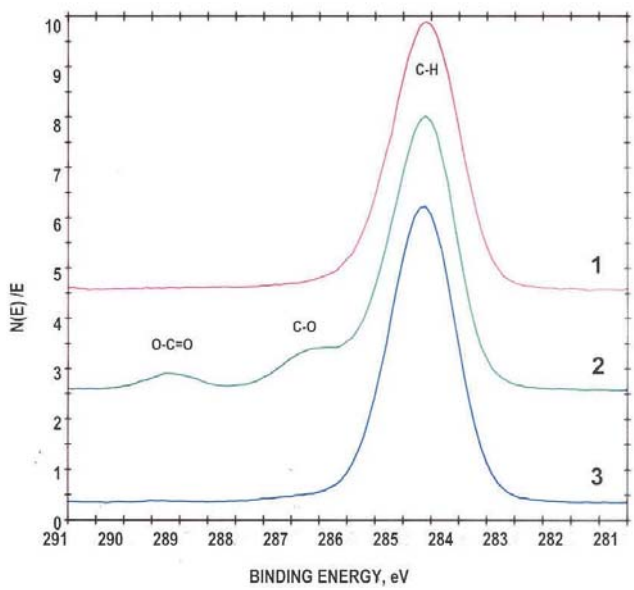


Fig. 1. X-ray Photoelectron Spectra of:

1) Surface of polydimethylsiloxane network without adhesion promoter
- Surface of polydimethylsiloxane network with adhesion promoter
- Interior section (sample of 150 mm sliced in half) of polydimethylsiloxane network with adhesion promoter

3.3 NMR Imaging of Silicone Network

The following experiment demonstrated that the catalyst preferentially resided in the adhesion promoter phase. The pale yellow catalyst was suspended in the silicone and then adhesion promoter was added. The pale yellow catalyst separated into the adhesion promoter as determined by transfer of the yellow color to the adhesion promoter. Thus, the platinum is more likely to be sequestered in the adhesion promoter phase rather than the silicone during the initial curing process. One might expect that sequestering of the platinum would change the cure profile relative to a coating not containing the adhesion promoter. The cure profile was measured using NMR Imaging for samples with and without bis(trimethoxysilylpropyl) succinate (a non –cure-inhibiting adhesion promoter) inclusion. Profiles were recorded every two hours. In the images below, uncured sample material appears brightest due to relatively long T_2 proton relaxation time (Fig. 2). As areas of the sample cured, the sample at those voxels decreased in signal intensity because the proton relaxation time became shorter and the voxel color moved from white to red to green to blue to black[18]. In the absence of adhesion promoter, cure is more rapid at the top of the reaction vessel. Hydrosilylation occurs more rapidly in the presence of higher concentrations of oxygen [19]. In contrast, cure occurs more uniformly for the sample amended with adhesion promoter consistent with containment of the platinum in the adhesion promoter. In fact, the amended sample appears to be less cured on the top consistent with migration of the adhesion promoters to interfaces.

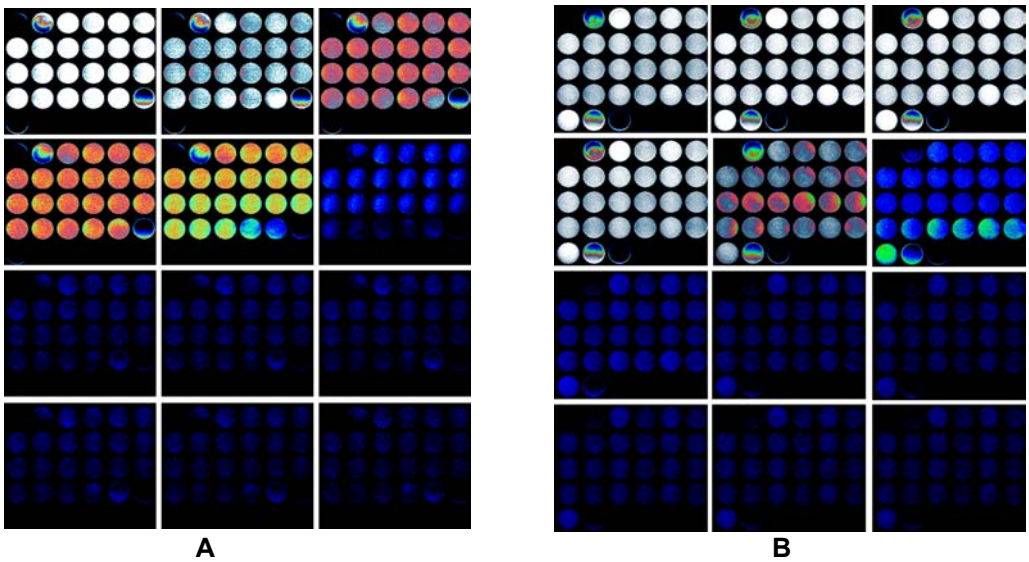


Fig. 2. NMR Images of curing profile for polydimethylsiloxane network at two hour intervals

- Without adhesion promoter

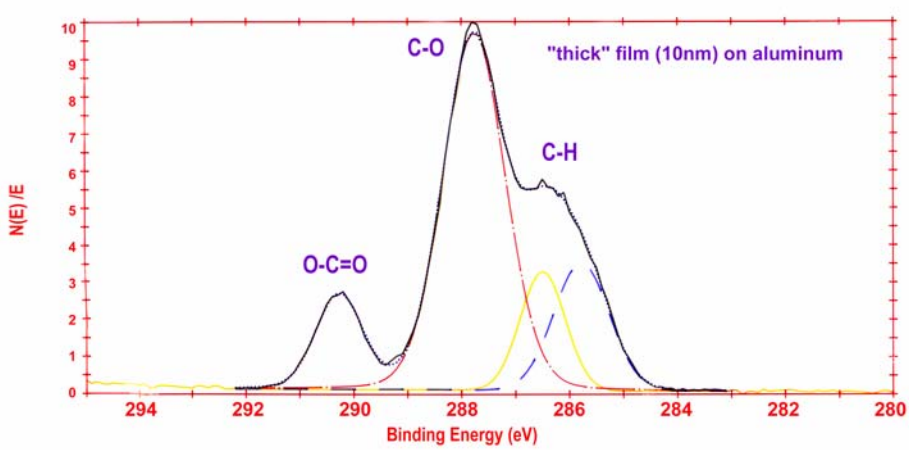
B) With adhesion promoter

Gray scale images were colorized so that image intensities from brightest to darkest were mapped to white→red→green→blue→black.

Note: the top of the reaction vessel is at the bottom of each frame

- Interaction of the Adhesion Promoter with Aluminum Surfaces

The interaction of the adhesion promoter with an aluminum surface was studied by X-ray Photoelectron Spectroscopy and Secondary Ion Mass Spectrometry. A stock solution of 1% adhesion promoter was applied to aluminum coupons. Subsequent to the application, one coupon set was copiously washed with toluene to remove physisorbed adhesion promoter. This sample had a coating thickness of less than 2 nm whereas the coating containing both physisorbed and chemisorbed adhesion promoter had a coating thickness greater than 10 nm. In the case of the unwashed sample, the x-ray photoectron spectrum was dominated by the C-O peak, which was attributed to the carbon of the methoxy groups. In bis(trimethoxysilylpropyl)fumarate, the percentages of each type of carbon group are: C-H, 37.5%, C-O, 50%; and O-C=O, 12.5%. In the washed sample, the largest peak was assigned to the C-H group. In addition, the ratio of the C-O-Si carbons to O-C=O carbons was less in the chemisorbed film, indicative of a diminished quantity of methoxy groups. If the methoxy groups were completely reacted, then the ratio of the different types of carbon would be C-H, 60%; C-O, 20% and O-C= O, 20% (Fig. 3). Our results are consistent with approximately 4-5 of the methoxy groups being condensed or reacted. These observations are supported by the results of the Secondary Ion Mass Spectrometry study which showed a decrease in the peak at 121 amu (assigned to $Si(OCH_3)_3$ for the chemisorbed film(Fig 4). These results suggest that the adhesion promoter was either bound to the surface or polymerized on the metal surface, or more likely, both.



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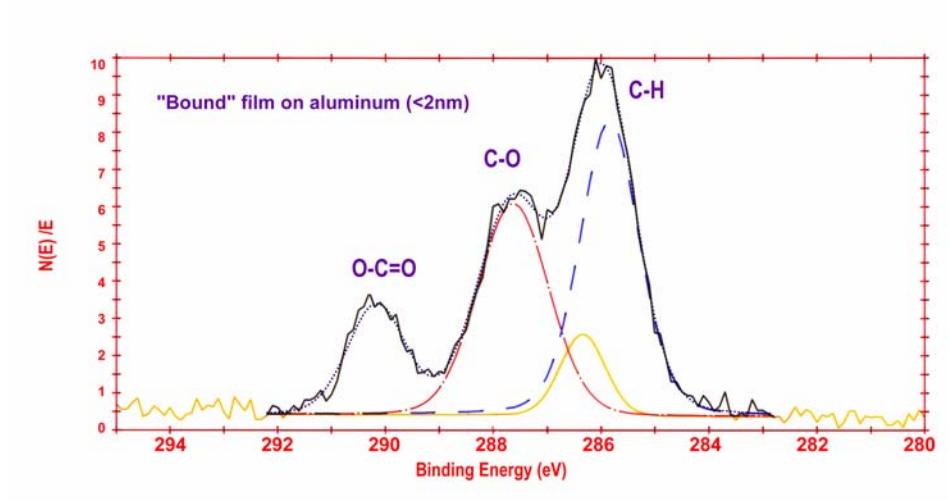

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Fig 3. X-ray Photoelectron Spectra of:
A) physisorbed and chemisorbed adhesion promoter on aluminum
B) only chemisorbed adhesion promoter on aluminum

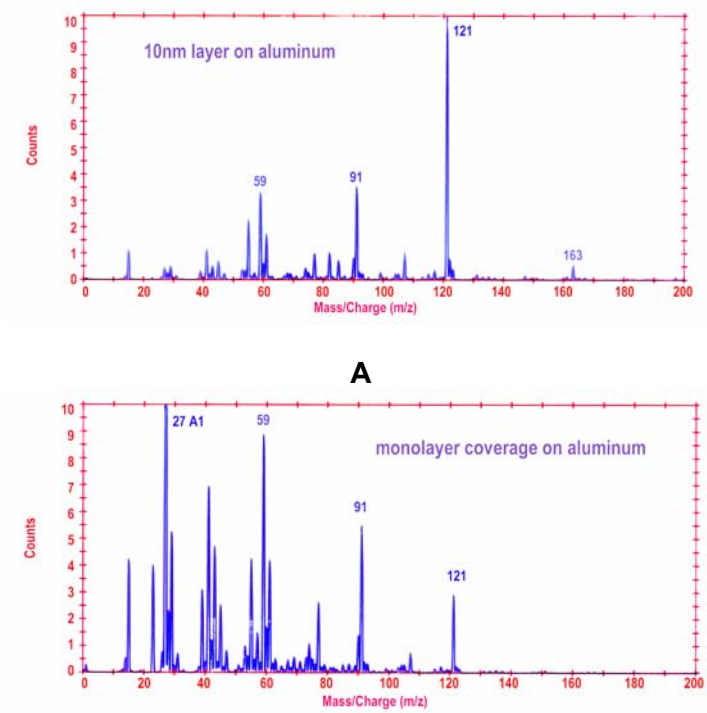
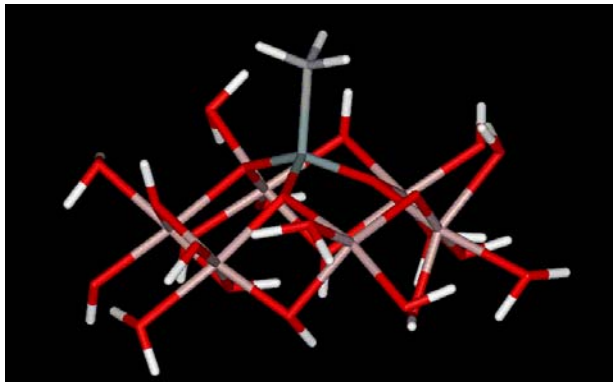
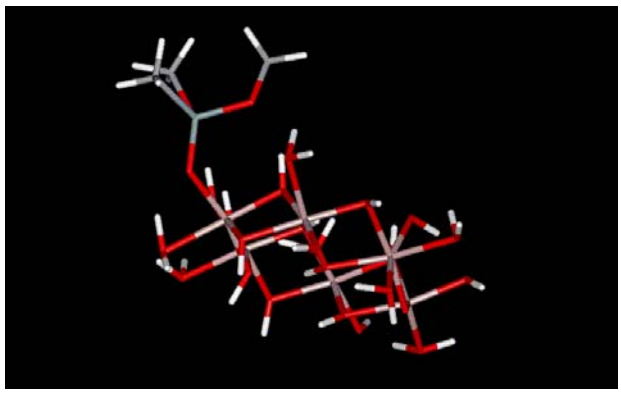


Fig.4. Secondary Ion Mass Spectra of:
A) both physisorbed and chemisorbed adhesion promoter on aluminum
B) only chemisorbed adhesion promoter on aluminum

DFT calculations suggest that the model adhesion promoter $CH_3Si(OCH_3)_3$ is more likely to interact with a hydroxyl defect site rather than at a "tuck in" site on aluminum surfaces (Fig. 5.). The first reaction at the tuck-in site is strongly endothermic, and only when the last of the three bonds to the surface has formed does the overall heat of reaction become mildly exothermic. On the contrary, the first reaction at a surface defect hydroxyl is moderately exothermic, and thus much more probable than at the tuck-in site. Furthermore, inspection of models suggests that the activation energy for the first reaction at the tuck-in site would be quite high, as the steric hindrance for approach of the Si atom to an embedded O atom is severe. These results are consistent with those of White and Tripp [20] who reported on the reaction of methoxymethylsilanes with silica.



A



B

Fig. 5. Coordination of $CH_3Si(OCH_3)_3$ at:

- a "tuck in" site on aluminum
- a defect hydroxyl site

Calculations also suggest that the adhesion promoter can easily polymerize as well on the metal surface. Condensation polymerization of the adhesion promoter is virtually athermal and most likely driven by the favorable entropy accompanying the release of methanol (Fig. 6).

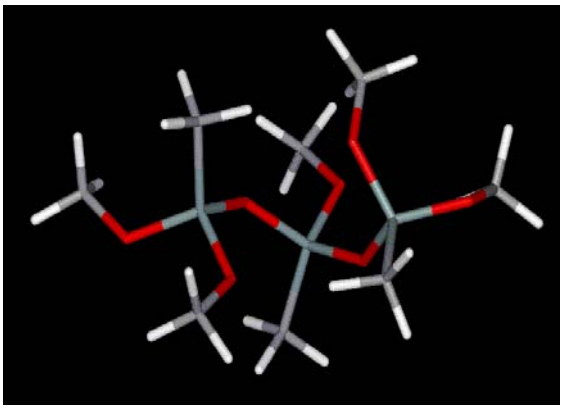


Fig. 6. Model of trimer of condensed adhesion promoter

- **Conclusions**

Incorporation of members of the class of bifunctional adhesion promoters represented by the prototypical bis(trimethoxysilylpropyl)fumarate into addition curable silicones results in the formation of self-priming systems. In these systems, the adhesion promoter migrates to the surface during the curing process. This results in an enrichment of the adhesion promoter at the surface and also changes the cure profile such that the material cures more rapidly at the interface. The adhesion promoter reacts rapidly with any accessible surface hydroxyls as well as undergoing self-condensation reactions. The interfacial layer is a random organosilicate thermoset bonded tightly to aluminum surface hydroxyl sites on the hydrated aluminum surface. The silicone elastomer is most likely entangled with the organosilicate thermoset in the interfacial layer.

The self-priming adhesion promoting systems utilize some of the concepts previously described for bonding to surfaces such as the need for methoxy groups on the adhesion promotor to effect bonding to the metal surface. However, in most previously developed systems, adhesion was enhanced by miscibility of the adhesion promoter in the silicone matrix and by chemical coupling the silicone elastomer to the surface. There is a study in which interdiffusion of the adhesion promoter into a polymer has been reported to enhance adhesion, however, in this case, the surface was primed rather than forming the interfacial layer by self-assembly [21].

References

- J. Stein, H. Grade, E.A. Williams, P.J. Codella, and J.F. Smith, , *J. Appl. Polym. Sci.,* **47**, 2257 (1993).
- E.P. Plueddemann, Silane Coupling Agents, Plenum Press, New York 1982.

3. T. Suzuki, and M. Kasuya, J. *Adhesion Sci. Techol.*, **3**, 463 (1989).
4. U.S. Patent No. 3, 527, 655 assigned to GE (1970).
5. U.S. Patent No. 4,311739 assigned to GE (1982).
6. U.S. Patent No. 4,677,161 assigned to Toray (1987).
7. U.S. Patent No. 4,737,562 assigned to Dow Corning (1988).
8. U.S. Patent No. 4,754,013 assigned to Dow Corning (1988).

9. U.S. Patent No. 4,742,103 assigned to Toray(1988).
- U.S. Patent No. 4,891,393 assigned to Toray (1990).
- W. Edelstein, J. Hutchison, G. Johnson, and T. Redpath, *Physics in Medicine and Biology,* **25,** 751 (1980).
- B. Delley, *J. Chem. Phys*., **92,** 508-517 (1990)
- S.J. Vosko, L. Wilk, and M. Nusair. *Can. J. Phys*. **58,** 1200 (1980).

14. A.D.Becke, *Phys. Rev. A* **38,** 3098 (1988) J.P. Perdew, *Phys. Rev. B* **33** 8822, (1986)
15. U.S. Patent No. 5,164,461 assigned to GE (1992).
16. L.N. Lewis, J. Stein, R.E. Colborn, Y. Gao, and J. Dong, *J. Organometallic. Chem*. **521**, 221, (1996).

- J. Stein, S.J. Valenty, G.A. Smith, D.V. Bresniak and L.C. Prutzman, *Macromolecules*, **19**, 2291 (1986).

18. N. Bloembergen, E.M. Purcell and R.V. Pound, *Phys. Rev.*, **73**, 679 (1948).
19. J. Stein, L.N. Lewis, Y. Gao, and R.A. Scott, *J. Amer. Chem. Soc.* **121**, 3693 (1999).
20. L.D. White, and C.P. Tripp, *J. Colloid Interface Sci*., **224**, 417 (2000).
21. N.H. Sung, A. Kaul, I. Chin, and C. Sung, *Polym. Eng Sci.*, **22**, 637 (1982).

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Appendix D

SIMULATING THE COHESIVE PROPERTIES OF ULTEM AND RELATED MOLECULES

Annu. Tech. Conf. – Soc. Plast. Eng. **59th (Vol 2),** 1592 (2001

B. E. Eichinger, Molecular Simulations Inc.
David Rigby, Molecular Simulations Inc.
Judith Stein, General Electric-CRD

Abstract

The cohesive properties of many engineering plastics are difficult to determine experimentally, as the polymers are frequently insoluble, have high T_g's, and are sometimes poorly characterized. Molecular modeling can provide useful information of higher quality than might be obtained by other methods for these difficult polymers. A series of simulations on Ultem® and related molecules have been performed to evaluate the cohesive energy density of the polymer and determine interfacial interactions with small molecules. These methods yield a value near 22.0(Mpa)^{½} for the solubility parameter of the polymer, and it is shown that benzyl alcohol has the most favorable interactions.

Introduction

Molecular modeling of bulk materials has advanced to the point where several properties can be reliably computed with an accuracy that rivals experiment.[1] This is especially helpful for those systems that are inherently difficult to study experimentally, and for which experimental data is therefore not available or is of uncertain quality. Foremost amongst difficult systems are the engineering plastics, which are often only soluble in extremely aggressive solvents, have high T_g's, and may be poorly characterized. While these systems are difficult to study experimentally, they also pose challenges to simulations because they relax slowly owing to their structural complexity and rigidity. By study of oligomers and related small molecules, with extrapolation to high MW,[2] one can partially circumvent many of these problems. This plan requires a high quality force field, and we use COMPASS for this purpose, as it has been specifically optimized to provide accurate condensed phase equation of state and cohesive properties for molecules containing a wide range of functional groups.[1]

The primary purpose of this research has been to identify potential adhesives that might be used with Ultem®. Structural homology recommended benzyl alcohol as a candidate fragment that might fulfill these requirements. Furthermore, the published solubility parameters for the polymer[3] [23.7(Mpa)^{½}] and benzyl alcohol[4] [24.8(Mpa)^{½}] are very similar, suggesting that they should be compatible. To determine whether or not simulations might shed further light on these considerations, we have undertaken a study of the interactions of a range of low molecular liquids with a model for the surface of Ultem.

The strategy that we chose to adopt for these calculations avoids the direct computation of surface tensions as required by the Dupré equation. We opted to use software to calculate the energy of interaction between the polymer and fluid phases directly, without having to subtract out the polymer-polymer and fluid-fluid contributions. A part of what we will show here is that the method is relatively simple yet very informative.

Methods

Simulations were performed with the *Discover* molecular mechanics and dynamics simulation module from MSI. Periodic cells containing from about 1500 to 5000 atoms were built with *Amorphous Cell*. The constructions were subsequently refined to provide input for production runs. The smaller cells were used for homogeneous systems and the larger for the heterogeneous (interfacial) systems. The homogeneous systems were built with 3D periodicity, and were equilibrated in the NPT ensemble at 298K and zero applied pressure using the Berendsen[5] barostat. This equilibration was usually done for 5-10ps with dynamics, and this was followed by a data accumulation run lasting at least 100ps, with configurations being saved every 5ps. Sun and Rigby[6] have shown that this gives statistically independent samples of the energy for systems of small molecules.

Group-based cut-offs were used (the molecules having been subdivided into neutral charge groups), with explicit atom sums being calculated out to 9.5Å to 10.5Å, depending on the polarity of the molecule (however, the differences between calculated densities and solubility parameters was not outside the statistical noise for these two cut-offs). A "tail correction" was applied to evaluate the compressive effect on the cell arising from the dispersion interaction between molecules in the cell and all others in the shell from the cutoff to infinity. The temperature of 298K in all of the simulations was equilibrated with the Andersen algorithm,[7] with the velocities being randomized to a Boltzmann distribution every 400-800fs, depending on the size of the system. The velocity Verlet algorithm[8] was used for integration of the equations of motion.

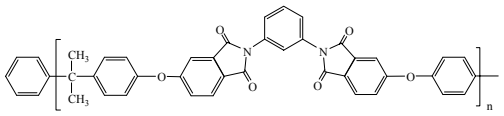
Methods for constructing polymer surfaces have been described by Mansfield and Theodorou[9] as well as by Mattice and coworkers.[10-12] The method used in the *Amorphous Cell* module of *Materials Studio*[13] is similar to the Mansfield and Theodorou method. A "glass wall" potential is applied to two plane faces [conventionally taken to be orthogonal to the *c*-axis of the cell] separated by a specified distance of an otherwise periodic box containing the growing polymer. A segment of any molecule that approaches either wall experiences a strong inverse power repulsive force with a singularity outside the box, and this biases the Metropolis ballot criterion encouraging the growing molecule to stay within the box. These slabs or films are then equilibrated to the point where their energy is within the bounds that minimizers can easily handle when the potential is removed or the cells are assembled with other surfaces.

For our studies, 2D boxes of the small molecules were also built using the algorithm described above, whereupon the two slabs were merged and the box extended by 100Å in the *c*-direction. This super-cell was treated as a 3D periodic system for the dynamics simulations (overall dimensions *ca.* 37Å ×37Å ×150Å). The fluids were constructed with 1500-2000 atoms each. The glass wall potential between the two interfaces was removed and the surfaces allowed to equilibrate naturally against the vacuum for approximately 20-100ps, following which 250ps production runs were executed. Neutral charge group cut-offs of 9.5Å were used for propagating the dynamics, with a tail correction being applied to the films in an effort to mimic bulk conditions.

The same initial polymer configuration was used for all solvents, and no attempt was made to average over polymer configurations apart from what is realized during the run for any one of the solvents. The thickness of the polymer layer in the equilibrated systems was about 28Å and the repeat unit is about 21Å long. This cell is too thin, relative to the repeat unit length, to have an accurate representation of the configuration statistics of the polymer at the interface,[10-12] but it would have been prohibitively costly to make larger simulations or better averages over configurations. Simulations on the heterogeneous systems were run in the NVT ensemble at 298K, and every 500fs the energy of interaction between polymer and fluid layers was evaluated using an 18Å cutoff without tail correction. Exploration of the dependence of computed interaction energies on this cutoff distance showed that there was no advantage to using a larger cutoff, but a smaller one would have omitted significant contributions to the energy evaluation. This gives a consistent and reasonably accurate measure of the total energy of interaction of the two layers. A total of 500 energy evaluations were performed for each system (250ps total simulation time).

Visual inspection of the energy as a function of time generally revealed plateaus where the energy fluctuated about a reasonably stationary mean value, and averages over these time intervals were taken. Relatively large excursions of the energy were often seen, and these are associated with diffusion of one or two solvent molecules into the polymer. The polymer film was usually very rough when equilibrated against each of the fluids, and probably had significant voids that allowed diffusion. No attempt was made to correct for molecules that had diffused into the polymer matrix; since each solvent diffused to some extent, it is probable that the trends in the results are not significantly influenced by this phenomenon.

Results



The repeat unit[3] of Ultem with end groups is shown in structure I. Rather than leave a phenolic group at the chain end, the oligomers used in calculations were terminated with phenyl groups. Neutral charge groups for the phenyl terminated chains were easily assigned. Owing to the cited difficulties in equilibrating the polymers, it was deemed essential to survey smaller fragments of the repeat unit. Bulk amorphous phases of N-

phenylphthalimide, 2,2-diphenylpropane, and diphenyl ether were studied, and the results are given in Table I along with the results for the Ultem oligomers. A crude estimate for the solubility parameter for the polymer is provided by a weighted average of the values for the two imide and ether groups and one diphenylpropane:

$$\delta \approx \left[2(23.78+21.13)+18.82\right]/5 = 21.7(\mathrm{MPa})^{1/2}.$$

However, the polymer is denser than the average of these structural units, and an additional correction to increase the solubility parameter by about 10% to account for this effect makes the solubility parameter very near the literature value 23.7 $(\mathrm{Mpa})^{1/2}$. The values computed for the Ultem oligomers can be likewise corrected to the experimental density; this gives values of approximately 21.5 for the 1-mer, 21.9 for the 2-mer, and 19.7 for the 4-mer. The average over the oligomers is about 21.0$(\mathrm{Mpa})^{1/2}$. We conclude that the best estimate of the solubility parameter for the polymer is about 22.0$(\mathrm{Mpa})^{1/2}$.

Sorption Studies

Solubility parameters of the small molecules used in these studies—*iso*-amyl acetate, *n*-amyl acetate, toluene, isopropanol, benzyl alcohol, propylene glycol and ethylene glycol—were evaluated so as to validate the COMPASS force field. The results of these simulations are given in Table 2. The table also contains data allowing comparison of densities of the fluids obtained from the NPT simulations with the available literature values. On average, densities agree with the literature to slightly better than 1%, with the largest deviation being for isopropanol. Solubility parameters agree with the literature values to within an average of about 3.7%, with the largest deviations (for isopropanol and ethylene glycol) being for fluids having the most uncertain literature values. (It is important in making comparison between simulations and experiment that the influence of gas phase dimerization be accounted for. This has not been done for isopropanol. As previously pointed out by us,[2] the experimental values for ethylene glycol are highly scattered.) For the other liquids, solubility parameters from simulations are on average within 0.3% of the reported experimental values.

The interaction energies of the 5 fluids with the Ultem surface model are contained in the last column of Table 2. A plot of the energies against the solubility parameters of the fluids is shown in Fig. 1. It is seen that the energy appears to have a minimum near $\delta = 24(\mathrm{MPa})^{1/2}$, i.e., near the value for benzyl alcohol. Qualitative experiments show that benzyl alcohol wets the surface of an Ultem sample, as do some of the other solvents reported here that have solubility parameters smaller than benzyl alcohol. However, using the same experimental protocols, ethylene glycol is found not to wet Ultem. The results also suggest that solubility parameters may not capture all the interactions. The solubility parameters for isopropanol and benzyl alcohol are very nearly equal, yet the modeling predicts that benzyl alcohol interacts more favorably with Ultem than does isopropanol. This conclusion is also consistent with general chemical principle of structural homology yielding greater compatibility.

Conclusions

Simulations on Ultem and related compounds suggest that the solubility parameter for the polymer is approximately 22.0$(\mathrm{Mpa})^{1/2}$, a value that is slightly lower than that estimated from group additivity methods. Models of interfaces of Ultem in interaction with a variety of low molecular liquids having a range of solubility parameters show that the relatively simple determination of the molecular interaction energies advocated here suffices to identify molecules that interact most favorably with the polymer surface. A good correlation is obtained between the solubility parameters for the liquids and the interface interaction energy, showing that this energy is approximately quadratic in the difference between the solubility parameters for the polymer and the fluids. However, the results suggest that benzyl alcohol interacts more favorably than isopropanol, a conclusion that could not be drawn from solubility parameters alone. There seems to be a fairly wide window of solubility parameters that are consistent with interfacial compatibility with Ultem. Densities and solubility parameters for a range of low molecular liquids have been obtained from simulations with use of the COMPASS force field, and these are shown to compare favorably with literature data.

Acknowledgement

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References

1. Sun, H., *J. Phys. Chem. B* 1998, 102, 7338-64.
2. Rigby, D., Sun, H., Eichinger, B.E., *Polymer Int.* 1997, 44, 311-30.
3. Bicerano, J. “Prediction of Polymer Properties,” Dekker, New York, 1993, p. 157.

4. Bandrup, J., Immergut, E.H., Grulke, E.A., Eds, "Polymer Handbook, 4th Ed.," John Wiley & Sons, Inc., New York, 1999.
5. Berendsen, H.J.C., Postma, J.P.M., van Gunsteren, W.F., DiNola, A., Haak, J.R., *J. Chem. Phys.* 1984, 81, 3684-90.
6. Sun, H., Rigby, .D., *Spectro. Acta* 1997, A153, 1301-23.
7. Andrea, T.A., Swope, W.D., Andersen, .H.C., *J. Chem. Phys*. 1983, 79, 4576-83.
8. Verlet, L., *Phys. Rev.* 1967, 159, 98-103.
9. Mansfield, K.F., Theodorou, D.N., *Macromolecules* 1990, 23, 4430-45.
10. Zhan, Y., Mattice, W.L., *Macromolecules* 1994, 27, 7056-62.
11. Misra, S., Fleming, P.D. III, Mattice, W.L., *J. Comput.-Aided Mat. Des*. 1994, 2, 101-12.
12. Natarajan, U., Tanaka, G., Mattice, W.L., *J. Comput.-Aided Mat. Des.* 1997, 4, 193-205.
13. *Materials Studio* is available from Molecular Simulations Inc., San Diego, CA.
14. Frenkel, M., Gadalla, N.M., Marsh, K.N., Wilhoit, R.C., Eds, "TRC Thermochemical Tables, Hydrocarbons," Thermodynamics Research Center, College Station, TX, 1996.
15. Frenkel, M., Gadalla, N.M., Marsh, K.N., Wilhoit, R.C., Eds, "TRC Thermochemical Tables, Non-Hydrocarbons," Thermodynamics Research Center, College Station, TX, 1996.
16. "The Merck Index" 11th Ed., Merck & Co., Inc. 1989.
17. Barton, A.F.M., "CRC Handbook of Solubility Parameters and Other Cohesion Parameters," 2nd Ed., CRC Press, Boca Raton, FL, 1991.
18. Majer, V.; Svoboda, V., "Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation," Blackwell Scientific Publications, Oxford, 1985, 300.
19. Knauth, P., Sabbah, R., *Thermochim. Acta*, 1990, 164, 145-152.
20. Pedley, J.B., Naylor, R.D., Kirby, S.P., "Thermochemical Data of Organic Compounds," Chapman and Hall, New York, 1986, 1-792. Data available from NIST Chemistry WebBook; http://webbook.nist.gov/chemistry/
21. Beaton, C.F., Hewitt, G.F., "Physical Property Data for the Design Engineer," Hemisphere Publishing Co., New York, 1989.

Table 1
Densities and Solubility Parameters for Ultem® Oligomers and Related Molecules

Molecule	ρ (g/cm^3) *Sim.*	ρ (g/cm^3) *Lit.*	δ (Mpa)$^{1/2}$ *Sim.*
N-phenylphthalimide	1.213(0.041)[a]	—	23.78(0.10)
2,2-diphenylpropane	0.984(0.010)	0.9943[b]	18.82(0.16)
diphenyl ether	1.093(0.006)	1.075[c]	21.13(0.13)
Ultem 1-mer	1.177(0.013)	—	20.7(0.3)
Ultem 2-mer	1.201(0.006)	—	21.3(0.1)
Ultem 4-mer	1.182(0.008)	1.27[d]	19.0(0.1)

[a] Standard deviations in parentheses; [b] Ref. 14, p. a-3420 (this value is for the under-cooled liquid); [c] Ref. 16, p. 1158 (density at 20°C); [d] Value for Ultem® 1000 from General Electric website: http://www.geplastics.com/resins/index.html

Table 2
Densities and Solubility Parameters for Solvents and Their Interactions with Ultem®

Solvent	ρ (g/cm^3) *Sim.*	ρ (g/cm^3) *Lit.*	δ (Mpa)^{½} *Sim.*	δ (Mpa)^{½} *Lit.*	E×10^5/(J/cm^2)
iso-Amyl Acetate	0.856(0.009)	0.8719[a]	16.88(0.20)	16.0[g]	-2.10(0.03)
n-Amyl Acetate	0.865(0.008)	0.8719[a]	17.63(0.22)	17.6[h],17.1[i]	-2.23(0.01)
Toluene	0.870(0.008)	0.8622[b]	18.35(0.19)	18.23[j]	-2.36(0.02)
iso-Propanol	0.811(0.008)	0.781[c]	24.86(0.25)	23.58[k]	-2.20(0.01)
Benzyl alcohol	1.035(0.008)	1.041[d]	24.81(0.19)	23.59[k], 24.8[g]	-2.66(0.02)
Propylene glycol	1.044(0.012)	1.042[e]	30.98(0.25)	30.59[k]	-1.78(0.01)
Ethylene glycol	1.103(0.010)	1.1100[f]	35.00(0.20)	33.89[l],29.9[m]	-1.49(0.01)

[a] Ref. 15, p. a-5560; [b] Ref. 15, p. a-3290; [c] Ref. 21, p. 128; [d] Ref. 21, p. 134; [e] Ref. 16, p. 176; [f] Ref. 15, p. a-5180; [g] Ref. 4, p. VII/688;[h] Ref. 15, p. m-5550; [i] Ref. 17, p. 253; [j] Ref. 14, p. m-3290; [k] Ref. 20; [l] Ref. 15, p. m-5230; [m] Ref. 17, p. 253

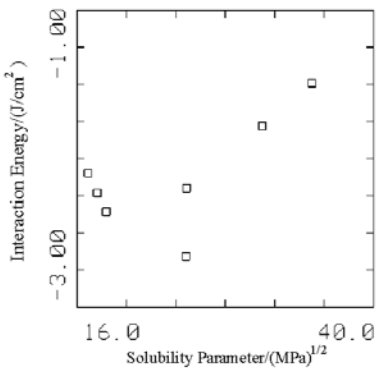


Fig. 1: The energy of interaction between an Ultem® model surface and several low molecular liquids plotted as a function of the solubility parameter. Tabulated results are contained in Table 2

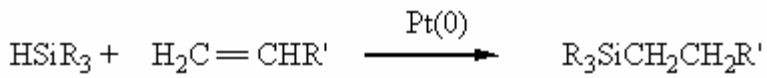
Appendix E

The Mechanism of the Pt(0) Catalyzed Hydrosilylation Reaction

Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **42 (1),** 251 (2001)

B. E. Eichinger
Molecular Simulations Inc.
9685 Scranton Road
San Diego, CA 92121-3752
Judith Stein
General Electric – CRD
1 River Road
Niskayuna, NY 12308

Karstedt's catalyst, $Pt_2(M^{vinyl}M^{vinyl})_3$, is a useful compound for introducing Pt(0) to reaction mixtures of silanes and vinyl compounds, whereby it effects the hydrosilylation reaction:



The commercial importance of this reaction for crosslinking silicone elastomers is well-known, as is its general synthetic utility. The virtue of Karstedt's catalyst is that it does not need to go through the poorly understood reductive steps that chloroplatinic acid undergoes before it can arrive at the Pt(0) catalytic state.

The first step in the reaction is either the loss of a vinyl ligand or the insertion of Pt into the silane bond. We find that both processes are probable, with the energy for the various options being determined primarily by steric factors. Relative reaction energies for model compounds can be found in Table 1 below. (All calculations were performed with Dmol^3, a DFT program from MSI, using the best available numerical basis set with a relativistic core potential for Pt. Geometries were optimized with the VWN functional[1], and energies were gradient and correlation corrected with the Becke-Perdue functional[2] at the VWN geometry.)

The general mechanism for the catalytic cycle was first proposed by Chalk and Herrod [3], and was subsequently modified by Stein, et al.[4,5]. The steps are: complexation of vinyl; oxidative addition of silane; hydrogen transfer from Pt to C; formation of Si-C bond in the reductive elimination of hydrosilylated olefin, followed by complexation with vinyl to re-initiate the catalytic cycle. We find that there is no activation energy for addition of olefin or silane, provided the Pt center is not too crowded.

The hydrogen transfer reaction has an activation energy of about 10.8 kcal/mol above the optimized $PtEt_3(H)SiMe_2Ome$ energy. The transition state for the formation of the Si-C bond from $MeOMe_2SiPt(Eth)Et_3$ lies 27.7 kcal/mol above the starting pentacoordinate complex. The products lie 45.8 kcal/mol below the latter transition state. Clearly the reductive elimination is the rate determining step. The "modified" Chalk-Herrod reaction, in which the Si-C bond is formed before the H-transfer, has a higher activation energy in our hands as well as those of Sakaki and coworkers[6,7]. Our results are in substantial agreement with the conclusions of the Sakaki group.

Acknowledgement

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Table 1. **Heats of Reaction of Model Compounds**

Reactants	Products	ΔE/(kcal/mol) [VWN[a]]	[BP[b]]
Ethylene + $SiHMe_2Ome$	Si(Ethyl)Me_2Ome	-44.5	-28.8
Pt + Et	Pt(Et)	-85.7	-67.2
Pt(Et) + Et	$Pt(Et)_2$	-62.7	-42.7
$Pt(Et)_2$ + Et	$Pt(Et)_3^*$	-49.1	-27.7
$Pt(Et)_3^*$ + Et	$Pt(Et)_4$	-32.0	-6.0
$Pt(Et)_3[D_{3h}]$	$Pt(Et)_3[C_{2v}]$	0.3	-2.3
$Pt(Et)_3^*$	$Pt(Et)_2$ + $Pt(Et)_4$	17.1	21.7
$2Pt(Et)_2$	$Pt_2(Et)_4$	-45.8	-22.0
Pt + $SiHMe_2Ome$	Pt(H)($SiMe_2Ome$)	-104.9	-82.0
Pt(Et) + $SiHMe_2Ome$	Pt(Et)(H)($SiMe_2Ome$)	-68.8	-45.9
$Pt(Et)_2$ + $SiHMe_2Ome$	$Pt(Et)_2$(H)($SiMe_2Ome$)	-50.6	-26.5
$Pt(Et)_3$ + $SiHMe_2Ome$	$Pt(Et)_3$(H)($SiMe_2Ome$)	-30.0	-4.1

Et = ethylene(C_2H_4)
Ethyl = ethyl(C_2H_5)

[a] The VWN column is calculated with an LDA □Item□silan based on ref. 1.
[b] The BP column has been calculated with nonlocal corrections according to Ref. 2.

- Simple average of energies of D_{3h} and C_{2v} isomers.

References

1. Vosko, S. J., Wilk, L., and Nusair, M. *Can. J. Phys*. **1980**, *58*,1200.
2. Becke, A. D., *Phys. Rev. A* **1988,** *38,* 3098; Perdew, J. P. *Phys. Rev. B* **1986**, *33,* 8822.
3. Harrod, J.F.; Chalk, A.J. In *Organic Synthesis via Metal Carbonyls*; Wender, I.; Pino, P., Eds.: Wiley: New York, 1977; Vol. 2, 673.
4. Stein, J.; Lewis, L.N.; Gao, Y.; Scott, R.A., *J. Am. Chem. Soc.* **1999**, *121*, 3693.
5. Lewis, L.N.; Stein, J.; Colborn, R.E.; Gao, Y.; Dong, J. *J. Organomet. Chem.* **1996**, *521*, 221.
6. Sakaki, S.; Mizoe, N.; Sugimoto, M. *Organometallics* **1998**, *17*, 2510.
7. Sakaki, S.; Mizoe, N.; Sugimoto, M.; Musashi, Y. *Coord. Chem. Rev.* **1999**, *190-192*, 933.

Appendix F

A Quantum Mechanical Study of the Bonding of a Silyl Ester to Hydrated Alumina

B. E. Eichinger
Molecular Simulations Inc.
9685 Scranton Road
San Diego, CA 92121-3752
Judith Stein
General Electric-CRD
1 Research Circle
Niskayuna, NY 12309

Abstract

The bonding of methyltrimethoxysilane (MTMS), a model for alkoxysilane primers and adhesion promoters, to a hydrated alumina cluster has been studied with density functional theory. We find that the most probable site for formation of an aluminosiloxane bond is at a surface hydroxyl defect site, such as might exist at a step dislocation on a hydrated alumina surface. The more symmetric tuck-in site with pseudo-C_{3v} symmetry on the (0001) surface is less favorable than the more exposed and readily accessible defect site. In addition, the energetics of the step-growth polymerization reaction of MTMS have been studied, and it is concluded that the oligomerization/ polymerization reaction, which consumes water and releases methanol, is practically athermal. It is argued that the polymerization reaction is primarily driven by entropic factors. At low coverage, chemisorbed □Item□silanes will most likely be unevenly distributed as determined by the irregularity of the surface defects and as influenced by the relative humidity at the time of application. At high coverage, well-aged □Item□silanes on metal or semi-metal oxide surfaces are probably best represented as polymerized (thermoset) resins that are chemically bonded to the substrate at most, if not all, accessible hydroxyl sites.

Introduction

The interaction of Item silanes with metal and semi-metal oxide surfaces is extremely important for a number of technologies. A typical example of a surface active agent from this class of compounds is GAPS, γ-aminopropyltrialkoxysilane. In the coatings industry, functionalized Item silanes are used as primers for metals; in adhesive applications they function as adhesion promoters by functionalizing the substrate; and they are used in the glass industry for surface coatings of silica for a variety of applications. Much is known about the interaction of Item silanes with substrates, and there is a monograph devoted to the topic.[1] However, the subject remains somewhat controversial, perhaps owing to the several difficulties in characterizing substrate surface chemistry, in analyzing thin surface coatings, and in the inherent complexity of the chemistry of this class of molecules.

In the presence of H_2O it is almost certain that the Item silanes are at least partially hydrolyzed.[2-6] At typical substrate surfaces, such as silica or alumina, the hydrolysis will almost certainly be catalyzed by acidic or basic groups that are inherent in the surface that has formed naturally by the reaction of atmospheric moisture with the oxidized substrates. Once the alkoxysilane has been hydrolyzed, it is susceptible to oligomerization and polymerization, up to and including branching and random network formation.[7] Depending on the nature of the substrate surface and the relative humidity, a molecule like GAPS may: (*i*) react with the surface through formation of metalosiloxane bonds, (*ii*) hydrogen bond to the surface through silanol groups, (*iii*) hydrogen bond with hydroxylated surfaces through the alkoxysilyl group, (*iv*) interact by proton transfer to the amine function from surface sites having high Brønsted acidity, (*v*) interact by dipolar interactions through the amine function, (*vi*) form metalazanes or silazanes with the amine function, (vii) form looser van der Waals complexes with no specific group. Given this range of possibilities, it is not surprising that a variety of proposals have been suggested to account for the function of this class of molecules.[1,6-9]

Modeling studies on physisorbed monolayers of organosilanes on metal oxide surfaces have been reported by Kinloch and Hobbs.[10] In that work, silanes with long alkyl groups were studied in an effort to comprehend the relation between chain length of the alkyl group and the degree of order of adsorbed monolayers. Thin film infrared studies of methoxymethylsilanes on dry fumed silica have been reported by White and Tripp.[11] They show that physisorption dominates at low temperatures, whereas chemisorption is more important at high temperatures. White and Tripp present evidence for hydrogen bonding between surface silanols and the alkoxy groups of their adsorbates, but offer only indirect evidence for polymerization of the latter.

The calculations to be described were undertaken in an effort to validate or possibly formulate new plausible models for the structure of chemisorbed Item silanes on hydrated alumina. While the study is limited in scope, our chosen model system should be typical of a range of well-cured alkoxysilane coatings on a variety of metal and semi-metal oxide surfaces. In

addition to the thermodynamics of the reactions of alkoxylated silanes with the hydrated alumina surfaces, we were motivated to investigate the step-growth polymerization reactions of Item silanes owing to the reported incidence of this reaction in the presence of moisture. Unfortunately, there is but one report of polymerization calorimetry[12] on this important class of molecules, and no combustion calorimetry data has been located. Quantum calculations of equilibrium structures and their energies are likely to be the most reliable means to obtain thermochemical information.

The interaction of water with alumina has been studied in great detail recently with a molecular dynamics/density functional (Car-Parrinello) code by Hass*, et al.*[13] In addition to thoroughly exploring proton transfer reactions between H_2O and alumina surfaces, they show that clusters are poor models for extended surfaces. Nonetheless, we are content to study a cluster, since our interest here is in the relative stability of only two chemisorption sites. It is likely that the relative stability of reactions at the two selected sites on the cluster would be mirrored in more extensive calculations on a periodic model. A preliminary account of this work, as well as the application setting, has appeared elsewhere.[14]

Methods

The density functional[15] program Dmol[3] from MSI was used for all calculations. A high quality double-numeric basis set with p-polarization functions on all atoms (dnp), roughly comparable to a 6-31G** basis set in Hartree-Fock programs, was used. The geometries of all structures were obtained by minimization of the energies in the local density approximation (LDA) using the Vosko-Wilk-Nusair (VWN) exchange-correlation terms.[16] Subsequent to locating the optimal local geometries, single point evaluations of the energy were performed with the Becke-Perdew (BP) functional,[17] which applies non-local corrections for exchange and correlation effects. This procedure is a recognized standard method in DFT calculations: Local Hamiltonians tend to overbind but give good geometries, whereas the non-local corrections give improved energies but at the cost of somewhat poorer geometries. The hybrid method gives good (VWN) structures and reliable (BP) energies. For completeness, we report the energies obtained from both.

Calculations were done on the hydrated alumina cluster having the stoichiometry $(Al_2O_3)_3{\cdot}15H_2O$ as shown in Fig. 1. This cluster was constructed by first extracting a set of six Al atoms with bonded O atoms from the (0001) surface of alumina. H atoms were added to saturate all open valences on O atoms, while H_2O molecules were added by hand to make up a six-coordinate environment around each metal center. The structure was then optimized with the VWN functional using a cascade of refinements, which resulted in several H atom transfers to yield the structure shown. The three O atoms at the pseudo-C_{3v} (ψ-C_{3v}) site at the center of the cluster were protonated as shown so as to keep the stoichiometry tidy for the reactions to be

studied. Calculations on the bonding of silanes to the hydrated alumina cluster were performed by fixing all atoms of the cluster except for the O atoms directly involved in bond formation with the silane.

In the interests of saving computer time and since our exclusive interest was in the chemistry of the alkoxy groups of the silane, calculations were performed on the model compound methyltrimethoxysilane (MTMS), $CH_3Si(OCH_3)_3$, and its hydrolysis and condensation products. In addition to the alumina cluster bonding calculations, the energies of the gas phase monomer, Item and trimer of MTMS were also determined.

Results-Chemisorption

There is some belief that the most probable site for chemisorption of trialkoxysilanes on the alumina surface is at the ψ-C_{3v} site formed by three O atoms. There is potential for the incoming silane to react once, twice, or three times with the oxygen atoms at this site, so we investigated this sequence of possibilities. The energies of the pertinent molecules (with both VWN and BP functionals) are contained in Table I. These energies are combined into energies of reaction in Table II for the reaction of the first alkoxy with the ψ-C_{3v} site and with a surface defect hydroxyl, which was taken to be an Al atom at the edge of the cluster. The molecular structures of the two are seen in Figs. 2 and 3. It is seen that the first reaction is far more favorable at the defect site hydroxyl than it is at the ψ-C_{3v} site. (In the tables, a reaction product of structure X with a alkoxysilyl group is denoted by X®*n*, where *n* is the number of Si–O–X bonds that have formed.)

But, might the subsequent reactions of the second and third alkoxides of the incoming silane make up for the unfavorable energy of the first reaction? The answer is yes, partially. Table III contains the energy changes for the second and third aluminosilane bonds that may form (in addition to a repetition of one line from Table II for completeness). It is seen that the second bond is strongly endothermic in the VWN approximation, and essentially athermal at the BP level. Not until the third bond forms is the unfavorable endothermic heat (at the BP level) of the first reaction paid back. Overall, at the VWN level the formation of the fully aluminated silane shown in Fig. 4 is fairly strongly endothermic, while at the BP level it is weakly exothermic.

The next question to be addressed is whether or not the selected hydrated alumina structure with the protonated ψ-C_{3v} site biases the calculation. At the very least, protonation of the cluster at these sites is not expected to artificially lower the energy of the cluster. If the energy is lowered by protonation, then it is proper that the protons should be where they are at this level of level of quantum theory. If the energy is increased, then it can only serve to diminish the apparent energy of reaction. So, at the very least, the cluster structure is biased in favor of reaction at the ψ-C_{3v} site. Yet the reaction at the defect site still appears to be much more probable. If the ψ-C_{3v} site is not protonated, it cannot offer an acidic proton to catalyze the ester

interchange reaction. Overall, it seems that protonation of the ψ-C_{3v} site makes it more favorable for reaction, and at the very least makes the site more nearly equivalent chemically to the defect site with its pendant hydroxyls.

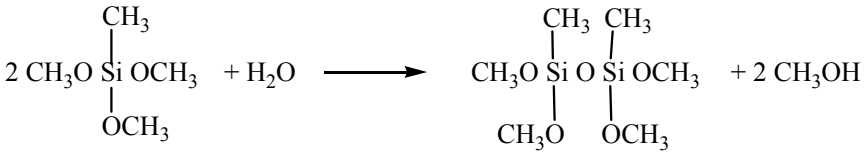
While we have not explored the transition states for the reactions with the defect site and the ψ-C_{3v} site, inspection of the models suggests that the activation energy for the latter site would be substantially larger than for the former. The O atoms at this site are relatively inaccessible, and the incoming bulky trialkoxysilane may have difficulty in making intimate contact with an O atom. If the silane is partially hydrolyzed the steric factor is relieved to some extent, but this relief applies to the defect site as well, so it is hard to see a relative advantage to the ψ-C_{3v} that might attend partial hydrolysis of the silane. The defect site has, by comparison, relatively accessible OH groups that appear to be sufficiently open to react directly with the Si atom of the trialkoxylated species. In addition, it is probable that defect sites are quite acidic, thereby providing a proton to catalyze the ester interchange reaction.

Results-Oligomerization

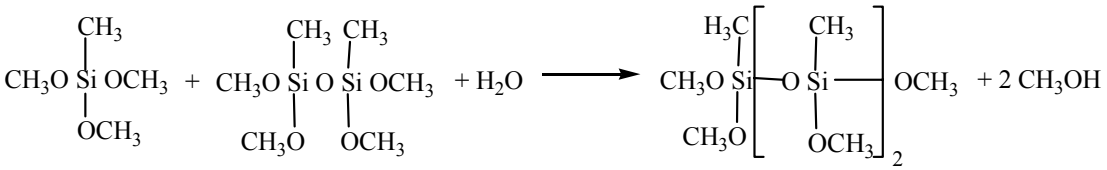
In the presence of water, □Item□silanes will hydrolyze and oligomerize. The enthalpies of reactions in this sequence have been reported for the series of molecules $(CH_3)_xSi(OC_2H_5)_{4-x}$ $x = \{0, 1, 3\}$. In this work, Tiller, *et al.*,[12] attempt to decompose the enthalpy of the overall reaction into contributions from hydrolysis, condensation, and gelation. (We hasten to point out that gelation is not a first order phase transition, so their conclusions regarding the last step require revision.) In any event, the hydrolysis reaction is fast relative to condensation,[3,12] so they are able to measure a value of –6.2 ± 0.3 kJ/mol for this step (the abstract of their paper reports an endothermic heat of this magnitude). The condensation step then appears to have an associated heat of approximately –4.7 ± 0.3 kJ/mol. An alternative measure of the overall heat of reaction is provided by using just the measured heats for polymerization reported for $CH_3Si(OC_2H_5)3$ and $Si(OC_2H_5)_4$. One obtains an enthalpy of hydrolysis and condensation of about –10.7 kJ/(mol of reactant ethoxy groups), which is very close to the sum of the heats for hydrolysis and condensation (-6.2 – 4.7 = -10.9 kJ/mol) cited above.

A potent contribution to the measured heat of reaction, not considered by Tiller*, et al.*, is the heat of solution of the products. Each ethanol that is released in the hydrolysis reaction mixes exothermically with water, and depending on the concentration of the mixture, this could release up to about 4 kJ/(mol ethanol),[18] thereby accounting for the major portion of the observed heat of reaction. This is an important consideration in making comparisons with the results of quantum calculations.

The results in Table I can be used to calculate the energies of oligomerization, as shown in Table IV. The reactions considered are



and



It is seen that the first reaction is very weakly exothermic, whereas the second is weakly endothermic at the BP level (both exothermic, averaging –2.8 kcal/mol with VWN). In other words, at this level of theory, the polymerization is athermal to mildly exothermic. The reactions as written conserve numbers of molecules, so that the change in translational entropy for the reaction is expected to be small. The final factor to consider is the entropy of the growing chain, and that can be expected to be positive. The ring opening polymerization of octamethylcyclotetrasiloxane is accompanied by a large positive entropy, which is ascribed to the great flexibility of the polydimethylsiloxane chain. The same flexibility can be expected for the linear molecules considered here. But, in addition, the trialkoxysilanes are capable of forming branched and even cross-linked structures, and the multitude of possibilities for these structures greatly increases the entropy on the product side of the oligomerization reaction. In summary, then, we claim that the oligomerization/ polymerization of trialkoxysilanes is nearly athermal, and is driven by the positive entropy change that results from the large configuration space that is available to the mixed oligomer/polymer system. This conclusion differs from that of Tiller, *et al.*,[12] whose calorimetric measurements support a heat of reaction of about –5.1 kcal/(mol of SiOSi bonds). They assume that the reaction is accompanied by a negative entropy change, and so require that the reaction be exothermic to compensate. More extensive calorimetric studies of this reaction would be welcomed.

Conclusions

The picture of the reaction of Item silanes with hydrated alumina, and by inference other hydrated oxide surfaces as well, that has emerged from this investigation is one in which the silanes chemically bond to advantageous surface hydroxyl sites. The density and geometry of these sites will be highly dependent on the planarity of the underlying bulk metal or oxide phase and on factors such as relative humidity and surface purity. In the presence of moisture, an excess of alkoxysilane will likely hydrolyze and oligomerize/polymerize. At the extreme of low coverage, it is probable that chemisorbed silanes are not distributed uniformly, but rather congregate at imperfections on the surface. The silanes will be more or less isolated depending on the coverage and surface defect density and distribution, and they could be bonded to the surface once, twice, or three times, depending on the local density of hydroxyl groups. The unbonded alkoxy groups may or may not have been hydrolyzed, depending on the relative humidity. For high coverage and high humidity, the silane likely forms a mat of branched or even crosslinked (thermoset) polymer that is covalently attached to the surface at available hydroxyl sites. (The importance of cyclization in the condensation polymerization of GAPS and related molecules has been emphasized by Rankin, *et al.*[19]) Owing to the importance of entropic factors in the oligomerization/polymerization of the silanes, it is probable that there is a wide range of imperfections in the coating, as any opportunity for a defect increases the entropy of the system.

Acknowledgement

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References

1. Plueddemann, E. P. *Silane Coupling Agents*, 2nd Ed.; Plenum: New York, 1991.
2. Smith, K. A. *J. Org. Chem.* **1986**, *51*, 3827.
3. Smith, K. A. *Macromolecules* **1987**, *20*, 2514.
4. Vainrub, A.; Devreux, F.; Boilot, J. P.; Chaput, F.; Sarkar, M. *Materials Sci. Eng.* **1996**, *B37*, 197.
5. Rankin, S. E.; McCormick, A. V. *Mag. Res. Chem.* **1999**, *37*, S27.
6. Britcher, L.; Kempson, S.; Matisons, J. in *Adhesion Promotion Techniques*, Mittal, K.; L., Pizzi, A., Eds.; Marcel Dekker: New York, 1999. Chpt. 12, pp347-385.
7. Abel, M.-L.; Watts, J. F.; Digby, R. P. *Int. J. Adhesion and Adhesives* **1998**, *18*, 179.

8. Miller, J. D.; Ishida, H. *Langmuir* **1986**, *2*, 127.
9. Ramsier, R. D.; Zhuang, G. R.; Henriksen, P. N. *J. Vac Sci. Technol.* **1989**, *A7*, 1724.
10. Kinloch, A. J.; Hobbs, P. M. *Polym. Mat. Sci. Eng.* **1999**, *81*, 442.
11. White, L. D.; Tripp, C. P. *J. Colloid Interface Sci.* **2000**, *224*, 417.
12. Tiller, H.-J.; Göbel, R.; Hartung, U. *J. Non-Cryst. Solids* **1988**, *105*, 162.
13. Hass, K. C.; Schneider, W. F.; Curioni, A.; Andreoni, W. *J. Phys. Chem B* **2000**, *104,* 5527.
14. Stein; J.; Eichinger, B. E.; Early, T. manuscript submitted for *MST Proceedings*, Newark, NJ May 22,2000.
15. Delley, B. *J. Chem. Phys*. **1990**, *92***,** 508. $Dmol^3$ is a density functional quantum mechanics code based on this reference and is available from Molecular Simulations Inc.
16. Vosko, S. J.; Wilk, L., Nusair; M. *Can. J. Phys*. **1980**, *58*, 1200.
17. Becke, A. D. *Phys. Rev. A* 1988, *38***,** 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
18. Rowlinson, J.S.; Swinton, F.L. *Liquids and Liquid Mixtures*, 3rd Ed., Butterworth Scientific, London (1982), p. 177.
19. Rankin, S. E.; Macosko, C. W.; McCormick, A. V. *Chem. Mater.* **1998**, *10*, 2037.

Table I
Energies of Model Compounds

Molecule	ShortName	Binding Energy/Ha VWN	BP
H_2O		-0.4229036	-0.3784936
CH_3OH	[MeOH]	-0.9293677	-0.8276141
$MeSi(Ome)_3$	[MTMS]	-3.4419096	-3.0408304
$(Al_2O_3)_3{\cdot}15H_2O$	[Clst]	-10.4886127	-9.0662170
$Clst{\cdot}[Osi(Me)(Ome)_2]$	[Clst®1]	-13.0024582	-11.2480304
$Clst{\cdot}[O_2Si(Me)(Ome)]$	[Clst®2]	-12.0381154	-10.4220189
$Clst{\cdot}[O_3Si(Me)]$	[Clst®3]	-11.1151503	-9.6295099
$Clst{\cdot}[Osi(Me)(Ome)_2]^*$	[Edge®1]	-13.0276527	-11.2910972
$(Me(MeO)_2Si)_2O$	[$MTMS_2$]	-5.4518877	-4.8082982
$MTMS_3$		-7.4628711	-6.5692988

- In this structure MTMS is attached to an edge site.

Table II
Energies of Attachment of Trimethoxymethylsilane
to Alumina Surface Sites

Reactants	Products	ΔE/(kcal/mol) VWN	BP
Clst + MTMS	(Clust®1) + MeOH	-0.82	19.71
Clst + MTMS	(Edge®1) + MeOH	-16.6	-7.3

Table III
Energies of Reaction of Model Compounds

Reactants	Products	ΔE/(kcal/mol) VWN	BP
Clust + MTMS	Clust®1+ MeOH	-0.82	19.71
Clust®1	Clust®2 + MeOH	21.95	-1.00
Clust®2	Clust®3+ MeOH	-4.02	-22.03

Table IV
Energies of Oligomerization of Methytrimethoxysilane

Reactants	Products	ΔE/(kcal/mol) VWN	BP
2MTMS + H_2O	$MTMS_2$ + 2MeOH	-2.45	-2.12
$MTMS_2$ + MTMS + H_2O	$MTMS_3$ + 2MeOH	-3.08	1.94

Figure Captions

Figure 1: Hydrated alumina model cluster used to represent the surface of alumina.

Figure 2: The product of the reaction of one methoxy group of methyltrimethoxysilane with the ψ-C_{3v} site of the cluster shown in Fig. 1. This structure is denoted Clust®1 in the tables.

Figure3: Methyldimethoxysilane adduct of the cluster formed with loss of a single methanol. This structure represents the reaction of the silane with a hydroxyl located at an Al edge site on the hydrated alumina surface. Denoted Edge®1 in Tables I and II.

Figure 4: Methylsilane adduct of the cluster shown in Fig. 1. This corresponds to Clust®3 in the tables. The reaction of methyltrimethoxysilane with the cluster in Fig. 1 proceeds with loss of three molecules of methanol.

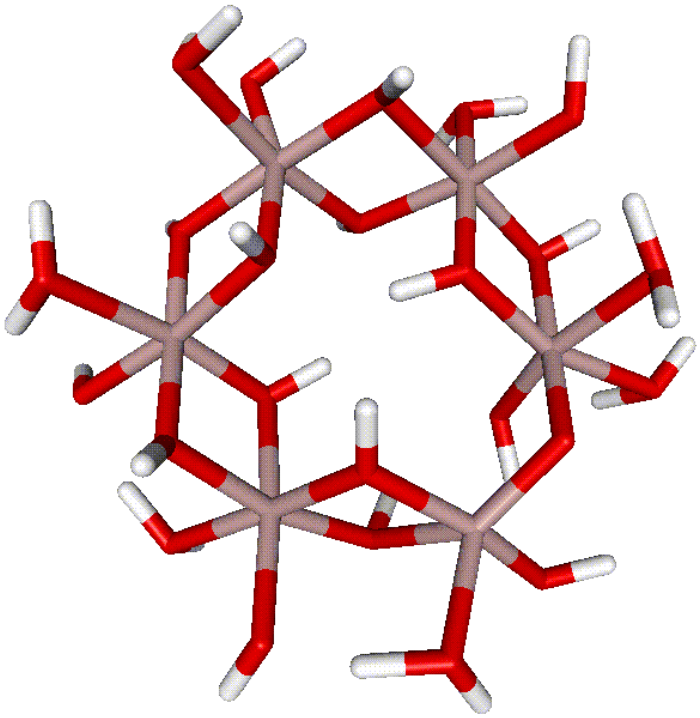


Figure 1: Eichinger and Stein

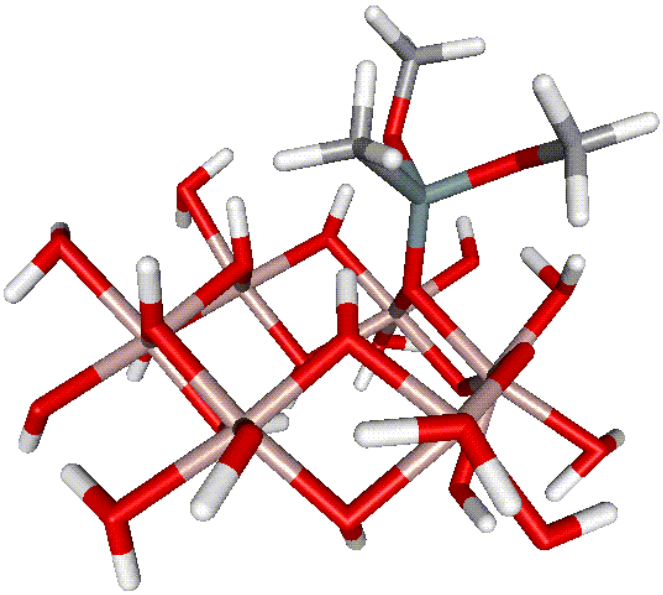


Figure 2: Eichinger and Stein

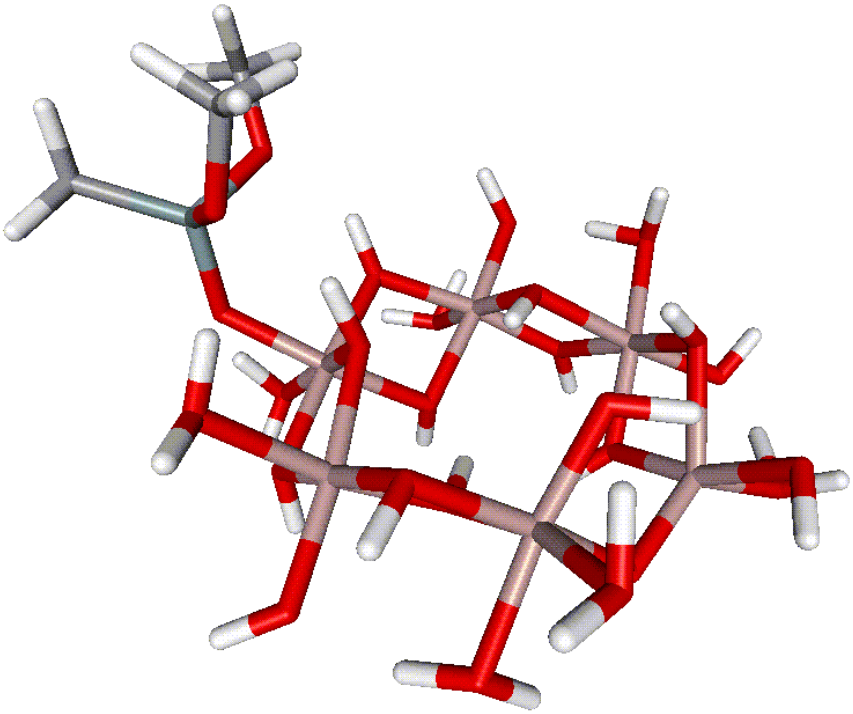


Figure3: Eichinger and Stein

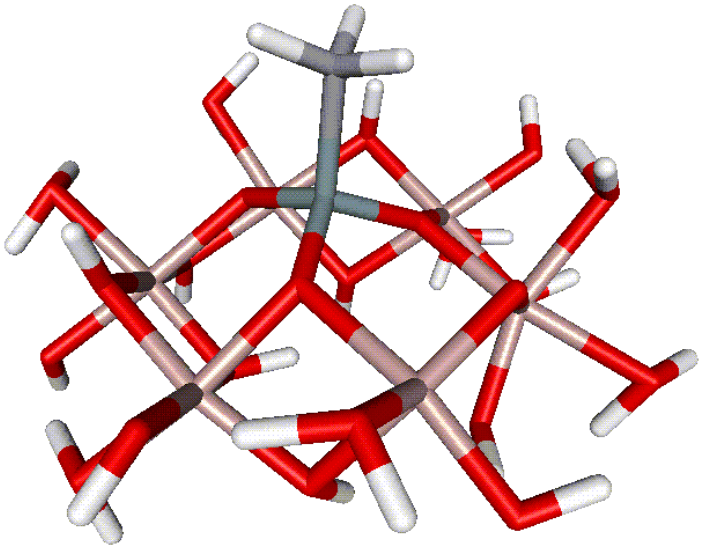


Figure 4: Eichinger and Stein

Appendix G

Cohesive Properties of Ultem and Related Molecules from Simulations

Polymer, 43, 599 (2002)

B. E. Eichinger and **David Rigby**
Molecular Simulations Inc.
9685 Scranton Road
San Diego, CA 92121-3752
Judith Stein
General Electric-CRD
1 Research Circle
Niskayuna, NY 12309

Abstract

The cohesive properties of many engineering plastics are difficult to determine experimentally, as the polymers are frequently insoluble, have high T_g's, and are sometimes poorly characterized. For difficult polymers such as these, molecular modeling can provide useful information of higher quality than might be obtained by other methods. Ultem® is a polyether imide having a very large and relatively stiff repeat unit. We have performed a series of simulations on Ultem and related molecules so as to evaluate the cohesive energy density of the polymer. Small molecular fragments (N-phenylphthalimide, 2,2-diphenylpropane, and diphenylether) of the repeat unit were studied to get approximate bounds to be expected for values of the solubility parameter for the polymer. Oligomers up to 4-mers were directly simulated, and the results were used to estimate the properties of the high polymer. These methods yield a value near 22.0$(Mpa)^{1/2}$ for the solubility parameter of the polymer, lower than has been estimated from group additivity. The interfacial interactions between Ultem and a variety of low molecular liquids have also been evaluated in an effort to identify functional groups that might interact most favorably with the polymer for adhesive applications. These calculations are in good agreement with expectations from solubility parameters. Most significantly, the calculations are fully compatible with experimental observations.

Introduction

Molecular modeling of bulk materials has advanced to the point where several properties can be reliably computed with an accuracy that rivals experiment.[1] This is especially helpful for those systems that are inherently difficult to study experimentally, and for which experimental data is therefore not available or is of uncertain quality. Foremost amongst difficult systems are the engineering plastics, which are often only soluble in extremely aggressive solvents, have high

T_g's, and may be poorly characterized. While these systems are difficult to study experimentally, they also pose challenges to simulations. The structural complexity and rigidity of this class of molecules causes them to relax very slowly, which makes them very difficult to equilibrate in the computer. However, by study of oligomers and related small molecules, with extrapolation to high MW,[2] one can partially circumvent many of these problems.

To execute this plan clearly requires a high quality force field that has been validated for molecules that are structurally homologous to the polymer of interest. We use COMPASS for this purpose, as it has been specifically optimized to provide accurate condensed phase equation of state and cohesive properties for molecules containing a wide range of functional groups.[1]

The primary purpose of this research has been to identify potential adhesives or adhesion promoters that might be used with Ultem®. On building a structural model of the surface of the polyether imide polymer, it appeared that the best opportunity for strong physisorption would be provided by H-bond or electrostatic interactions with the imide groups. Structural homology recommended benzyl alcohol as a candidate group that might fulfill these requirements. Furthermore, the published solubility parameters for the polymer[3] [23.7(Mpa)$^{1/2}$] and benzyl alcohol[4] [24.8(Mpa)$^{1/2}$] are very similar, suggesting that they should be compatible. To determine whether or not simulations might shed further light on these considerations, we have undertaken a study of the interactions of a range of low molecular liquids with a model for the surface of Ultem. If correct, benzyl alcohol should have the most favorable interactions, while molecules with solubility parameters either higher or lower than benzyl alcohol should be less attracted to the polymer.

The strategy that we chose to adopt for these calculations avoids the direct computation of surface tensions as required by the Dupré equation. This was done to avoid having to calculate the surface tension for the polymer directly, which we considered to be extremely difficult. Instead, we opted to use software to calculate the energy of interaction between the polymer and fluid phases directly, without having to subtract out the polymer-polymer and fluid-fluid contributions. A part of what we will show here is that the method is relatively simple yet very informative.

Methods

Simulations were performed with the *Discover* molecular mechanics and dynamics simulation module from MSI. Periodic cells containing from about 1500 to 5000 atoms were built with *Amorphous Cell*. The constructs were subsequently refined to provide input for production runs.

The smaller cells were used for homogeneous systems and the larger for the heterogeneous (interfacial) systems. The homogeneous systems were built with 3D periodicity, and were equilibrated in the NPT ensemble at 298K and zero applied pressure using the Berendsen[5] barostat. This equilibration was usually done for 5ps with dynamics, and this was followed by a data accumulation run lasting at least 100ps, with configurations being saved every 5ps. Sun and Rigby[6] have shown that this gives statistically independent energies for systems of small molecules.

Group-based cutoffs were used (the molecules having been subdivided into neutral charge groups), with explicit atom sums being calculated out to 9.5Å. A "tail correction" was applied to evaluate the compressive effect on the cell arising from the dispersion interaction between molecules in the cell and all others in the shell from 9.5Å to infinity. The temperature in all of the simulations was equilibrated with the Andersen algorithm,[7] with the velocities being randomized to a Boltzmann distribution every 400-800fs, depending on the size of the system. The velocity Verlet algorithm[8] was used for integration of the equations of motion. The forces were calculated with the COMPASS forcefield, using parameters given in the Appendix.

Pristine surfaces of organic materials are readily studied with simulations. Methods for contructing polymer surfaces have been described by Mansfield and Theodorou[9] as well as by Mattice and coworkers.[10-12] The method used in the *Amorphous Cell* module of *Materials Studio*[13] is similar to the Mansfield and Theodorou method. A "glass wall" potential is applied to two plane faces [conventionally taken to be orthogonal to the *c*-axis of the cell] separated by a specified distance of an otherwise periodic box containing the growing polymer. A segment of any molecule that approaches either wall experiences a strong inverse power repulsive force with a singularity outside the box, and this biases the Metropolis ballot criterion encouraging the growing molecule to stay within the box. These slabs or films are then equilibrated to the point where their energy is within the bounds that minimizers can easily handle when the potential is removed or the cells are assembled with other surfaces.

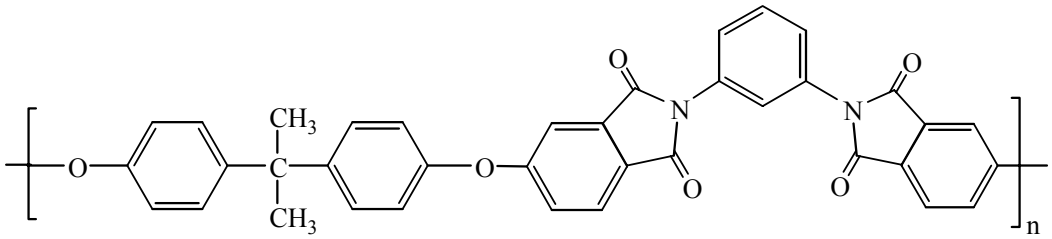
For our studies, 2D boxes of the small molecules were also built using the algorithm described above, whereupon the two slabs were merged and the box extended by 100Å in the *c*-direction. The fluids were constructed with 1500-2000 atoms each. The glass wall potential between the two interfaces was removed and the surfaces allowed to equilibrate naturally against the vacuum for approximately 2ps, following which 250ps production runs were executed. Neutral charge group cut-offs of 9.5Å were used for propagating the dynamics, with a tail correction being applied to the films in an effort to mimic bulk conditions, as described in more detail below.

This super-cell was treated as a 3D periodic system for the dynamics simulations (overall dimensions *ca.* 37Å ×37Å ×150Å). The same initial polymer configuration was used for all solvents, and no attempt was made to average over polymer configurations apart from what is realized during the run for any one of the solvents. The thickness of the polymer layer in the equilibrated systems was about 28Å. The repeat unit is about 21Å long. If one makes use of results of Mattice[10-12] on more flexible systems, one concludes that this cell is too thin, relative to the repeat unit length, to have an accurate representation of the configuration statistics of the polymer at the interface. However, to make a good sample of the configuration space of the polymer, or to better represent the surface structure by building a cell with a thickness of several persistence lengths, would have been prohibitively costly. We believe that by using the same initial structure, albeit relatively thin for the polymer, relative differences between the various solvents are meaningful. A representative structure (Ultem plus benzyl alcohol) is shown in Fig. 1.

Simulations on the heterogeneous systems were run in the NVT ensemble at 298K, with a tail correction applied outside the cutoff of 9.5Å. This is not an accurate procedure, but was used to ensure that the relatively thin fluid layer would feel an effective pressure equivalent to that in the bulk. Because the system contains a vacuum space, the polymer and solvent are free to expand even though the ensemble is one at constant volume. Every 500fs the energy of interaction between A (polymer) and B (fluid) layers was evaluated using an 18Å cutoff without tail correction. Exploration of the dependence of computed interaction energies on this cutoff distance showed that there was no advantage to using a larger cutoff, but a smaller one would have omitted significant contributions to the energy evaluation. This gives a consistent and reasonably accurate measure of the total energy of interaction of the two layers. One run with 225 ethylene glycol molecules gave results essentially identical to that obtained with 150 molecules. A total of 500 energy evaluations were performed for each system (250ps total simulation time). Visual inspection of the energy as a function of time generally revealed plateaus where the energy fluctuated about a reasonably stationary mean value, and averages over these time intervals were taken. Relatively large excursions of the energy were often seen, and these are associated with diffusion of one or two solvent molecules into the polymer. The polymer film was usually very rough when equilibrated against each of the fluids, and probably had significant voids that allowed diffusion. (This is another aspect of the difficulty in relaxing a bulky molecule below its T_g.) No attempt was made to correct for molecules that had diffused into the polymer matrix; they were included in the calculation of the interactions between polymer and solvent. Since each solvent diffused to some extent, it is probable that the trends in the results are not significantly influenced by this phenomenon.

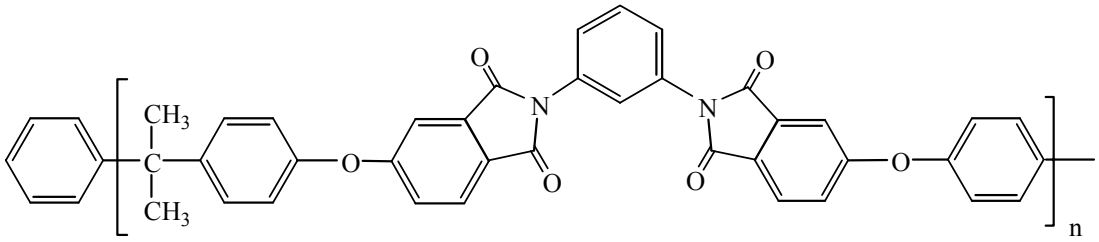
Results

The repeat unit[3] of Ultem is shown in structure I. Rather than leave a phenolic group at



I

the chain end, the oligomers used in calculations were terminated with phenyl groups. That is, oligomers with the structure II were used in the simulations. Neutral charge groups for the phenyl terminated chains were easily assigned.



II

Owing to the cited difficulties in equilibrating the polymers, it was deemed essential to survey smaller fragments of the repeat unit to establish bounds to be expected for the polymer. To this end, bulk amorphous phases of N-phenylphthalimide, 2,2-diphenylpropane, and diphenyl ether were studied. The results are given in Table I along with the results for the Ultem oligomers. The solubility parameter for N-phenyl-phthalimide, 23.78$(Mpa)^{1/2}$, provides an upper bound on the solubility parameter for the polymer. This is expected since the less polar units in the backbone will surely cause the solubility parameter to decrease. This contention is verified in Table I, where it is seen that the 2,2-diphenylpropane unit has a solubility parameter approximately 5 units smaller that the imide moiety. Similarly, the solubility parameter for the diphenyl ether group is smaller by about 2.6 units. A crude estimate for the solubility parameter for the polymer is provided by a weighted average of the values for the two imide and ether groups and one

diphenylpropane: $\delta \approx \left[2\left(23.78+21.13\right)+18.82\right]/5 = 21.7$ (Mpa)^{½}. However, the polymer is denser than the average of these structural units, and an additional correction to increase the solubility parameter by about 10% to account for this effect makes the solubility parameter very near the literature value 23.7 (Mpa)^{½}. The values computed for the Ultem oligomers can be likewise corrected to the experimental density; this gives values of approximately 21.5 for the 1-mer, 21.9 for the 2-mer, and 19.7 for the 4-mer. The average over the oligomers is about 21.0(Mpa)^{½}. We conclude that the best estimate of the solubility parameter for the polymer is about 22.0(Mpa)^{½}.

Sorption Studies

Solubility parameters of the small molecules used in these studies—*iso*-amyl acetate, *n*-amyl acetate, toluene, benzyl alcohol, and ethylene glycol—were evaluated so as to validate the COMPASS force field. The results of these simulations are shown in Table 2. The table also contains data allowing comparison of densities of the fluids obtained from the NPT simulations with the available literature values. On average, densities agree with the literature to slightly better than 1%, with the largest deviation being for *iso*-amyl acetate. However, there is some doubt as to the reliability of the literature value for this compound, as it is reported to be the same as for the unbranched isomer. Solubility parameters agree with the literature values to within an average of about 1.8%, with the largest deviations (for *iso*-amyl acetate and ethylene glycol) being for fluids having the most uncertain literature values. As previously pointed out by us,[2] the experimental values for ethylene glycol are highly scattered. For the other three liquids, solubility parameters from simulations are on average within 0.3% of the reported experimental values.

The interaction energies of the 5 fluids with the Ultem surface model are contained in the last column of Table 2. A plot of the energies against the solubility parameters of the fluids is shown in Fig. 1. It is seen that the energy appears to have a minimum near $\delta = 24(\mathrm{MPa})^{1/2}$, i.e., near the value for benzyl alcohol. Qualitative experiments show that benzyl alcohol wets the surface of an Ultem sample, as do the other solvents reported here that have solubility parameters smaller than benzyl alcohol. However, using the same experimental protocols, ethylene glycol is found not to wet Ultem. The simulations are compatible with the experiments.

Conclusions

Simulations on Ultem and related compounds suggest that the solubility parameter for the polymer is approximately 22.0(Mpa)$^{1/2}$, a value that is slightly lower than that estimated from group additivity methods. Models of interfaces of Ultem in interaction with a variety of low molecular liquids having a range of solubility parameters show that the relatively simple

determination of the molecular interaction energies advocated here suffices to identify molecules that interact most favorably with the polymer surface. A good correlation is obtained between the solubility parameters for the liquids and the interface interaction energy, showing that this energy is approximately quadratic in the difference between the solubility parameters for the polymer and the fluids. Simple experiments confirm that all the solvents except ethylene glycol will spread on Ultem. From the range of solvents considered here, simulations suggest that there is a respectably wide window of solubility parameters that are consistent with interfacial compatibility with Ultem. Densities and solubility parameters for a range of low molecular liquids have been obtained from simulations with use of the COMPASS force field, and these are shown to compare very favorably with literature data.

Acknowledgement

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References

1. Sun H. *J. Phys. Chem. B* 1998; 102: 7338-64.
2. Rigby D, Sun H, Eichinger BE *Polymer Int.* 1997; 44:311-30.
3. Bicerano J. "Prediction of Polymer Properties," Dekker, New York, 1993, p. 157.
4. Bandrup J, Immergut EH, Grulke EA, Eds, "Polymer Handbook, 4th Ed.," John Wiley &
5. Sons, Inc., New York, 1999.
6. Berendsen HJC, Postma JPM, van Gunsteren WF, DiNola A, Haak JR *J. Chem. Phys.* 1984; 81: 3684-90.
7. Sun H, Rigby D. *Spectro. Acta* 1997; A153; 1301-23.
8. Andersen HC. *J. Chem. Phys*. 1980; 72:2384-93.
9. Verlet L. *Phys. Rev.* 1967; 159: 98-103.
10. Mansfield KF, Theodorou DN. *Macromolecules* 1990; 23: 4430-45.
11. Zhan Y, Mattice WL. *Macromolecules* 1994; 27:7056-62.
12. Misra S, Fleming PD III, Mattice WL. *J. Comput.-Aided Mat. Des*. 1994; 2:101-12.
13. Natarajan U, Tanaka G, Mattice WL. *J. Comput.-Aided Mat. Des.* 1997; 4: 193-205.
14. *Materials Studio* is available from Molecular Simulations Inc., San Diego, CA.
15. Frenkel M, Gadalla NM, Marsh KN, Wilhoit RC, Eds, "TRC Thermochemical Tables, Hydrocarbons," Thermodynamics Research Center, College Station, TX, 1996.
16. Frenkel M, Gadalla NM, Marsh KN, Wilhoit RC, Eds, "TRC Thermochemical Tables, Non-Hydrocarbons," Thermodynamics Research Center, College Station, TX, 1996.
17. "The Merck Index" Eleventh Ed., Merck & Co., Inc. 1989.
18. Barton AFM. "CRC Handbook of Solubility Parameters and Other Cohesion Parameters," 2nd Ed., CRC Press, Boca Raton, FL, 1991.
19. B. Delley, *J. Chem. Phys*., **92,** 508-517 (1990). $Dmol^3$ documentation available from Molecular Simulations Inc.

Table 1
Densities and Solubility Parameters for Ultem® Oligomers and Related Molecules

Molecule	ρ/(g/cm^3) *Sim.*	ρ/(g/cm^3) *Lit.*	δ/(Mpa)$^{1/2}$ *Sim.*
N-phenylphthalimide	1.213(0.041)[a]	—	23.78(0.10)
2,2-diphenylpropane	0.984(0.010)	0.9943[b]	18.82(0.16)
diphenyl ether	1.093(0.006)	1.075[c]	21.13(0.13)
Ultem 1-mer	1.177(0.013)	—	20.7(0.3)
Ultem 2-mer	1.201(0.006)	—	21.3(0.1)
Ultem 4-mer	1.182(0.008)	1.27[d]	19.0(0.1)

[a] Standard deviations in parentheses.
[b] Ref. 14, p. a-3420; this value is for the under-cooled liquid.
[c] Ref. 16, p. 1158. Density at 20°C.
[d] Value for Ultem® 1000 from General Electric website: http://www.geplastics.com/ products/□ltem.html

Table 2
Densities and Solubility Parameters for Solvents and Their Interactions with Ultem®

Solvent	ρ/(g/cm^3) *Sim.*	ρ/(g/cm^3) *Lit.*	δ/(Mpa)$^{1/2}$ *Sim.*	δ/(Mpa)$^{1/2}$ *Lit.*	$E\times10^5$/(J/cm^2)
iso-Amyl Acetate	0.856(0.009)	0.8719[a]	16.88(0.20)	16.0[e]	-2.10(0.03)
n-Amyl Acetate	0.865(0.008)	0.8719[a]	17.63(0.22)	17.6[f],17.1[g]	-2.23(0.01)
Toluene	0.870(0.008)	0.8622[b]	18.35(0.19)	18.23[h]	-2.36(0.02)
Benzyl alcohol	1.035(0.008)	1.0416[c]	24.81(0.19)	24.8[e]	-2.66(0.02)
Ethylene glycol	1.103(0.010)	1.1100[d]	35.00(0.20)	33.89[i],29.9[j]	-1.49(0.01)

[a] Ref. 15, p. a-5560
[b] Ref. 15, p. a-3290
[c] Ref. 16, p. 176
[d] Ref. 15, p. a-5180
[e] Ref. 4, p. VII/688
[f] Ref. 15, p. m-5550
[g] Ref. 17, p. 135
[h] Ref. 14, p. m-3290
[i] Ref. 15 p. m-5230
[j] Ref. 17, p. 253

Figure Captions

Fig. 1: A representative structure of Ultem interacting with benzyl alcohol. The figure on the left shows the parent molecules superimposed on the cell, while on the right the molecules are packed into the cell with their periodic images.

Fig. 2: The energy of interaction between an Ultem® model surface and several low molecular liquids plotted as a function of the solubility parameter. Tabulated results are contained in Table 2.

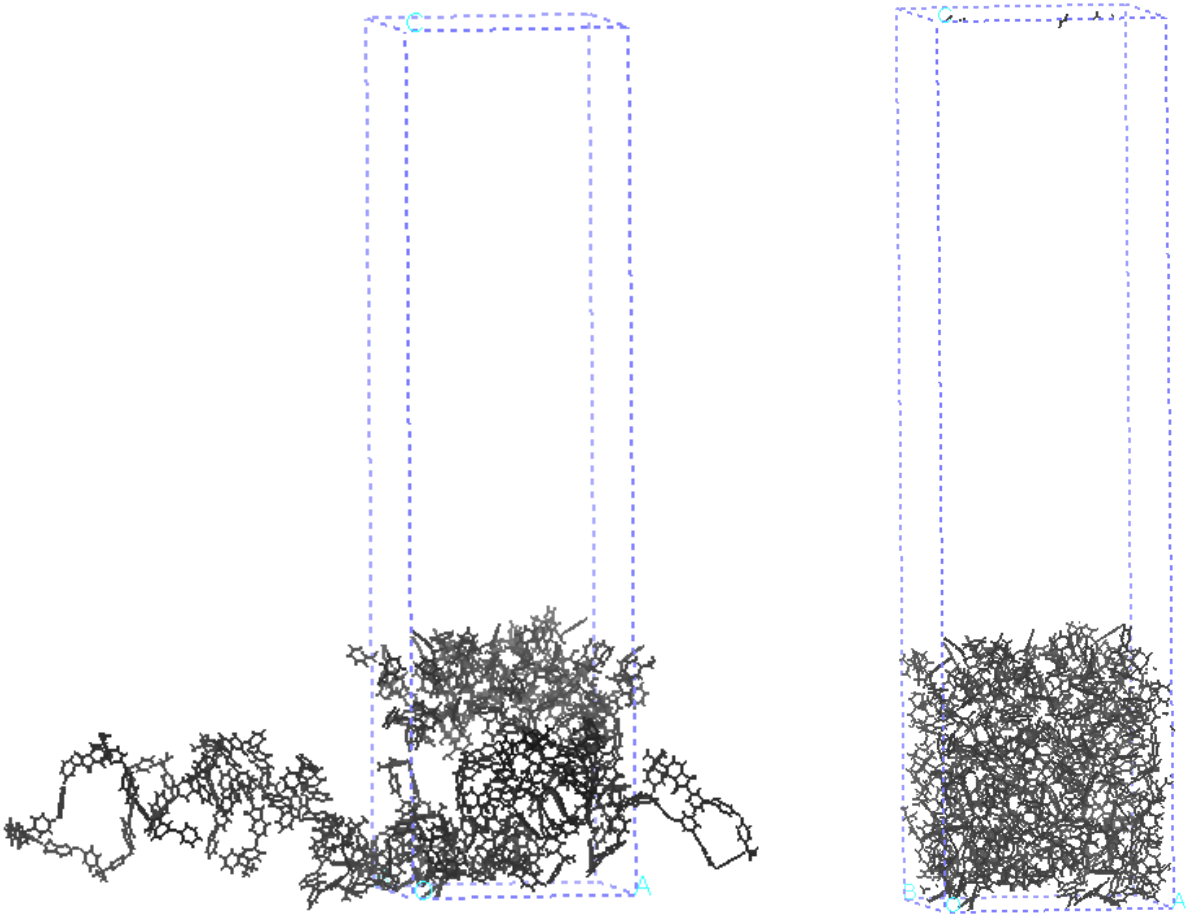


Figure 1: Eichinger, Rigby, and Stein

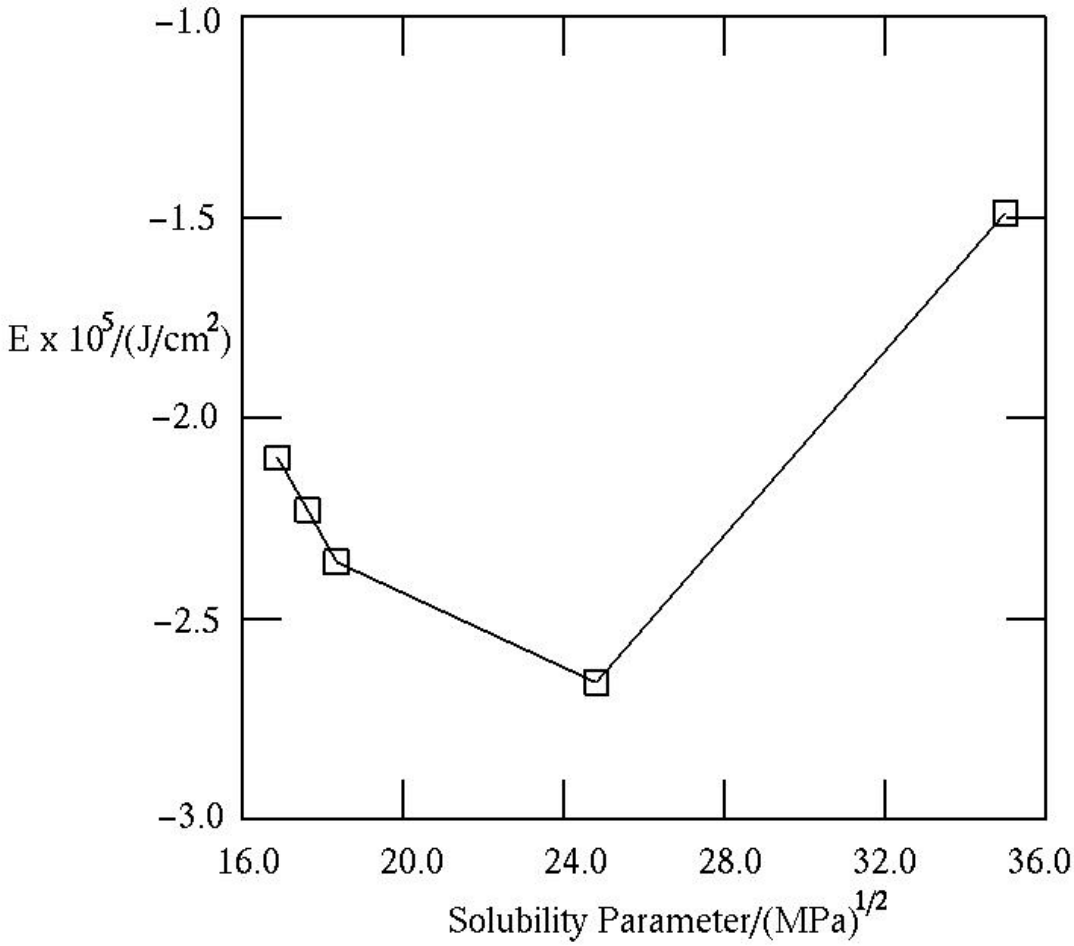


Figure 2: Eichinger, Rigby, and Stein

Appendix

The parameters from the COMPASS force field that have been assigned to the molecules studied here are provided in this appendix. Parameters not listed in these tables will be found elsewhere.[1,2] The nomenclature is consistent with the cited references. The paper of H. Sun[1] describes the function that is used to quantify the potential energy.

Definitions of atom types and equivalences

		Equivalences, if any				
Type	Definition	Non-bond	Bond	Angle	Torsion	Out-of-plane
c3'	Carbonyl carbon	c3'	c3'	c3'	c3'	c3'
c3a	Aromatic carbon with 3 bonds	c3a	c3a	c3a	c3a	c3a
c4	Generic sp3 carbon with 4 bonds	c4	c4	c4	c4	c4
c43	sp3 carbon with 3 attached heavy atoms	c43	c4	c4	c4	c4
c44	sp3 carbon with 4 attached heavy atoms	c44	c4	c4	c4	c4
c4o	sp3 carbon bonded to oxygen	c4o	c4o	c4	c4	c4
h1	generic hydrogen	h1	h1	h1	h1	h1
h1o	strongly polar hydrogen bonded to O, F	h1o	h1	h1	h1	h1
n3m	sp3 nitrogen in amides without hydrogen	n3m	n3m	n3m	n3m	n3m
o1=	sp2 oxygen in carbonyl group	o1=	o1=	o1=	o1=	o1=
o2e	ether oxygen	o2e	o2e	o2	o2	o2
o2h	hydroxyl oxygen	o2h	o2h	o2	o2	o2
o2s	ester oxygen	o2s	o2e	o2	o2	o2

Parameters

(Units: bond lengths in Å; angles in grad, except t_0 in deg; energies in kcal mol^{-1})

Bond dipole increments (in fractions of the charge on the electron)

atom I	atom j	charge
c3'	o2e	0.112
c3'	c4	0.000
c3'	o1=	0.450
c3'	c3a	0.035
c3'	n3m	0.000
c4o	h1	-0.053
c4o	o2h	0.160
c4o	o2e	0.160
c4o	c4	0.000
c3a	c4o	0.000
c3a	n3m	0.095

Quartic bond stretch

I	j	r_0	k_2	k_3	k_4
c3'	o2e	1.3750	368.7309	-832.4784	1274.0231
c3'	c4	1.5140	312.3719	-465.8290	473.8300

c3’	o1=	1.2160	823.7948	-1878.7939	2303.5310
c3’	c3a	1.4890	339.3574	-655.7236	670.2362
c3’	n3m	1.3850	359.1591	-558.4730	1146.3810
c4o	h1	1.1010	345.0000	-691.8900	844.6000
c4o	o2h	1.4200	400.3954	-835.1951	1313.0142
c4o	o2e	1.4200	400.3954	-835.1951	1313.0142
c4o	c4	1.5300	299.6700	-501.7700	679.8100
c3a	c4o	1.5010	321.9021	-521.8208	572.1628
c3a	n3m	1.3950	344.0452	-652.1208	1022.2242

Quartic angle bend

I	j	k	t_0	k_2	k_3	k_4
c3’	o2	c4	109.0000	38.9739	-6.2595	-8.1710
c3’	c4	h1	107.8594	38.0833	-17.5074	0.0000
c3’	n3m	c3’	121.9556	76.3105	-26.3166	-17.6944
c3a	c4	o2	109.5000	60.0000	0.0000	0.0000†
c3a	c4	h1	111.0000	44.3234	-9.4454	0.0000
c3a	c3a	c4	120.0500	44.7148	-22.7352	0.0000
c3a	o2	c3a	109.5000	60.0000	0.0000	0.0000†,‡
c3a	c3a	c3’	116.0640	71.2598	-15.8273	2.0506
c3a	c3’	n3m	108.4400	84.8377	-19.9640	2.7405
c3a	c3’	o1=	125.5320	72.3167	-16.0650	2.0818
c3a	c3a	n3m	120.7640	73.2738	-27.4033	13.3920
c3a	n3m	c3’	120.0700	47.1131	-32.5592	13.1257
o1=	c3’	o2	118.9855	98.6813	-22.2485	10.3673
o1=	c3’	c4	119.3000	65.1016	-17.9766	0.0000
o2	c3’	c4	100.3182	88.8631	-3.8323	-7.9802
n3m	c3’	o1=	121.5420	92.5720	-34.4800	-11.1871

† These are so-called “automatic” or generic parameters that have not been explicitly parameterized for the COMPASS force field.
‡ To investigate the sensitivity of computed properties to this bond angle, the optimized geometry of diphenyl ether was obtained with use of Dmol[3] with the VWN functional,[18] yielding a c3a-o2-c3a angle of 115.5°. The fluid phase of diphenyl ether was re-equilibrated with the angle parameter set to 113° (the difference between this angle and that from the quantum calculation being approximately compensated by non-bond interactions). The changes in density and solubility parameter were negligible.

Torsion

I	j	k	l	k_1	k_2	k_3
c3’	c3a	c3a	c3’	0.0000	0.0000	0.0000†
c3’	c3a	c3a	c3a	0.0000	4.6282	0.0000
c3’	c3a	c3a	h1	0.0000	2.1670	0.0000
c3’	n3m	c3a	c3a	0.0000	0.6500	0.0000
c3’	n3m	c3’	c3a	0.0000	0.0000	0.0000†
c3’	n3m	c3’	o1	-0.4066	1.2513	-0.7507
c3’	o2	c4	h1	0.1302	-0.3250	0.1134
c3’	o2	c4	h1	0.9513	0.1155	-0.0000
c3a	c4	o2	h1	0.0000	0.0000	0.0000†
c3a	c3a	c4	o2	0.0000	0.3000	0.0000†
c3a	c3a	o2	c3a	0.0000	0.5000	0.0000†
c3a	c3a	c3’	o1=	0.0000	0.7800	0.0000

c3a	c3a	c3a	n3m	0.0000	3.4040	0.0000
c3a	c3a	c3’	n3m	0.0000	0.0000	0.0000†
c3a	n3m	c3’	o1=	0.0000	2.0521	0.0000
c3a	n3m	c3’	c3a	0.0000	0.0000	0.0000†
c4	o2	c3’	c4	-2.5594	2.2013	0.0325
c4	o2	c3’	o1=	0.8905	3.2644	0.2646
o1=	c3’	c4	h1	0.0000	0.0000	0.0000
o2	c3’	c4	h1	0.0000	0.0000	0.0000
n3m	c3a	c3a	h1	0.0000	3.4040	0.0000

† These are so-called “automatic” or generic parameters that have not been explicitly parameterized for the COMPASS force field. Since all combinations of quartets of atoms contribute to the total torsional energy for a given bond, the null entries are compensated by contributions from other combinations of atoms.

Out-of-plane

I	j	k	l	k_2	a_0
c3’	c3’	n3m	c3a	0.0000	0.0000
c3’	c3a	c3a	c3a	17.0526	0.0000
c3’	n3m	c3’	c3a	0.0000	0.0000
c3a	c3a	c3a	h1	4.8912	0.0000
c3a	c3a	c4	c3a	7.8153	0.0000
c3a	c3a	h1	c3a	4.8912	0.0000
c3a	c3a	n3m	c3a	17.0526	0.0000
c3a	c3a	c3a	n3m	17.0526	0.0000
c3a	c3’	n3m	o1=	30.0000	0.0000
c3a	c3a	c3’	c3a	17.0526	0.0000
c3a	c3a	o2	c3a	13.0421	0.0000
c3a	c3’	o1=	n3m	30.0000	0.0000
c3a	o1=	c3’	n3m	30.0000	0.0000
c4	c3’	o2	o1=	46.9264	0.0000

Non-bond (9-6)

I	r_0	e_0
c3’	3.9000	0.06400
c3a	3.9150	0.06800
c4	3.8540	0.06200
c43	3.8540	0.04000
c44	3.8540	0.02000
c4o	3.8150	0.06800
h1	2.8780	0.02300
h1o	1.0870	0.00800
n3m	3.7200	0.15000
o1=	3.4300	0.19200
o2e	3.3000	0.12000
o2h	3.5800	0.09600
o2s	3.3000	0.09600

Bond-bond cross terms

I	j	k	ij/jk k
c3’	o2	c3a	69.5999
c3’	c4	h1	2.2522
c3’	n3m	c3’	25.9530
c3a	c4	o2	0.0000
c3a	c4	h1	2.9168
c3a	c3a	c4	12.0676
c3a	o2	c3a	0.0000
c3’	c3a	c3a	37.8749
c3a	c3’	n3m	0.0000
c3a	c3’	o1=	116.9445
c3a	c3a	n3m	37.8749
c3a	n3m	c3’	0.0000
o1=	c3’	o2	210.1813
c4	c3’	o1=	77.5201
c4	c3’	o2	19.1069
n3m	c3’	o1=	138.4954

Bond-angle cross terms

I	j	k	ij/ijk k	jk/ijk k
c3’	o2	c4	21.5366	-16.6748
c3’	c4	h1	15.5988	14.6287
c3’	n3m	c3’	20.0533	0.0000
c3a	c4	h1	26.4608	11.7717
c3a	c3a	c4	31.0771	47.0579
c3’	c3a	c3a	23.6977	45.8865
c3a	c3a	n3m	35.8865	53.6977
c3a	c3’	o1=	72.8758	76.1093
c3a	c3a	n3m	35.8865	53.6977
o1=	c3’	o2	79.4497	57.0987
c4	c3’	o1=	31.8455	46.6613
c4	c3’	o2	1.3435	4.6978
n3m	c3’	o1=	62.7124	52.4045

Angle-angle cross terms

I	j	k	l	ijk/jkl k
c3a	c3a	o2	c3a	0.0000
h1	c4	c3’	o2	4.7955

End bond-torsion cross terms

I	j	k	l	ij/ijkl			kl/ijkl		
				k_1	k_2	k_3	k_1	k_2	k_3
o1=	c3’	n3m	c3’	-0.7019	0.8305	-0.6874	0.1726	-0.4823	0.2666
h1	c4	o2	c3’	0.9589	0.9190	-0.6015	0.2282	2.2998	-0.4473
c3a	c3a	c4	h1	-0.5835	1.1220	0.3978	1.3997	0.7756	0.0000
c4	c3’	o2	c4	0.1928	1.3187	0.8599	0.0004	-1.0975	0.4831
o1=	c3’	o2	c4	-4.2421	10.1102	1.6824	0.0882	-2.4309	-0.7426
o1=	c3’	c4	h1	0.0536	0.0354	0.3853	2.9036	0.5307	0.1439
o2	c3’	c4	h1	0.4160	-0.1140	0.7099	0.7800	1.3339	0.3268

Middle bond-torsion cross terms

I	j	k	l	jk/ijkl		
				k_1	k_2	k_3
c3’	c3a	c3a	c3a	0.0000	3.8762	0.0000
o1=	c3’	n3m	c3’	-0.1118	-1.1990	0.6784
c4	c4	o2	c3’	9.9416	2.6421	2.2333
h1	c4	o2	c3’	7.7147	4.2557	-1.0118
c3a	c3a	c4	h1	-5.5679	1.4083	0.3010
o1=	c3’	c3a	c3a	0.0000	2.4002	0.0000
c3a	c3a	c3a	n3m	0.0000	5.2012	0.0000
c4	c3’	o2	c4	1.3445	3.5515	-4.9202
o1=	c3’	o2	c4	0.4552	7.3091	0.2842
o1=	c3’	c4	h1	0.0000	0.0000	-1.0000
o2	c3’	c4	h1	-13.7686	-2.5959	1.1934
h1	c3a	c3a	n3m	0.0000	5.2012	0.0000

Angle-torsion cross terms

I	j	k	l	ijk/ijkl			jkl/ijkl		
				k_1	k_2	k_3	k_1	k_2	k_3
o1=	c3’	n3m	c3’	-1.5747	2.3997	-0.2851	-0.3038	-0.0548	-0.3188
c4	c4	o2	c3’	-0.4620	1.4492	-0.6765	-0.0890	-0.9159	0.7229
h1	c4	o2	c3’	-0.4990	2.8061	-0.0401	-0.3142	-0.8699	0.0971
c3a	c3a	c4	h1	0.2251	0.6548	0.1237	4.6266	0.1632	0.0461
c4	c3’	o2	c4	0.9701	-2.5169	1.7195	0.8831	-0.8203	0.2405
o1=	c3’	o2	c4	5.9732	2.7261	1.9052	2.3573	1.0059	-0.0327
o1=	c3’	c4	h1	-2.0667	0.7308	-0.2083	14.4728	0.3339	0.0800
o2	c3’	c4	h1	-0.0241	1.4427	0.1212	13.2959	0.8005	-0.0071

Angle-angle-torsion 1

I	j	k	l	ijk/jkl/ijkl k
o1=	c3’	n3m	c3’	-3.3556
c4	c4	o2	c3’	-15.7082
h1	c4	o2	c3’	-13.1500
c3a	c3a	c4	h1	-5.8888
c4	c3’	o2	c4	-12.2070
o1=	c3’	o2	c4	-32.9368
o1=	c3’	c4	h1	-23.1923
o2	c3’	c4	h1	-13.9734

Appendix H

Virginia Polytechnic Institute (VPI) Wedge Test Data and Figures for RTV 630 Baseline and Primerless PLS100-630

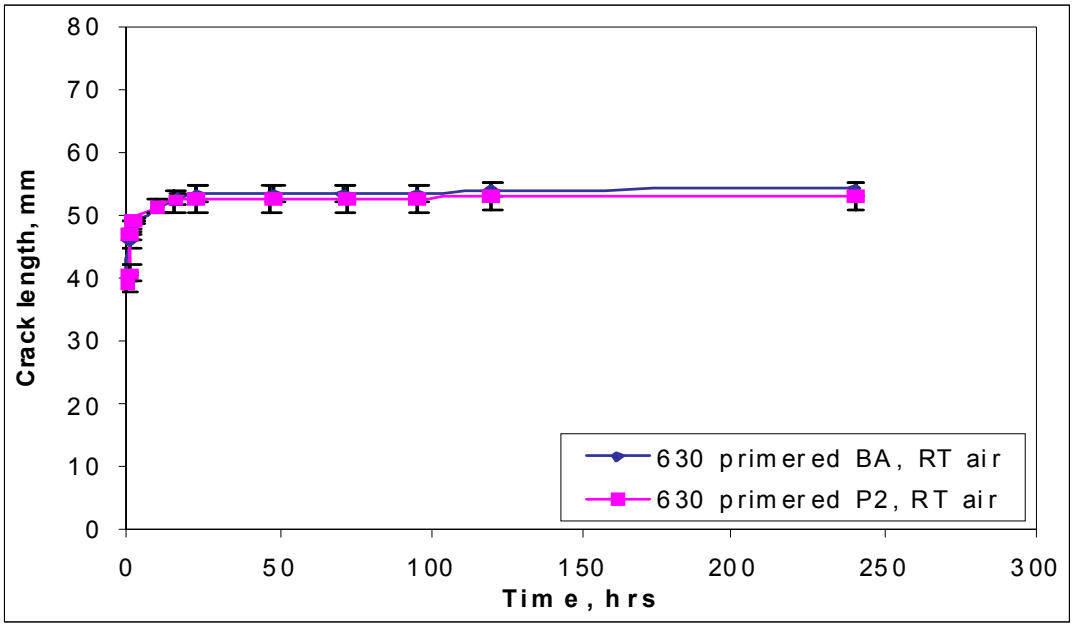


Figure H1: Crack Length versus Time for RTV 630 with GE SS-4155 Primer for Base-Acid and P2 Treated Substrates in Room-Temperature Air

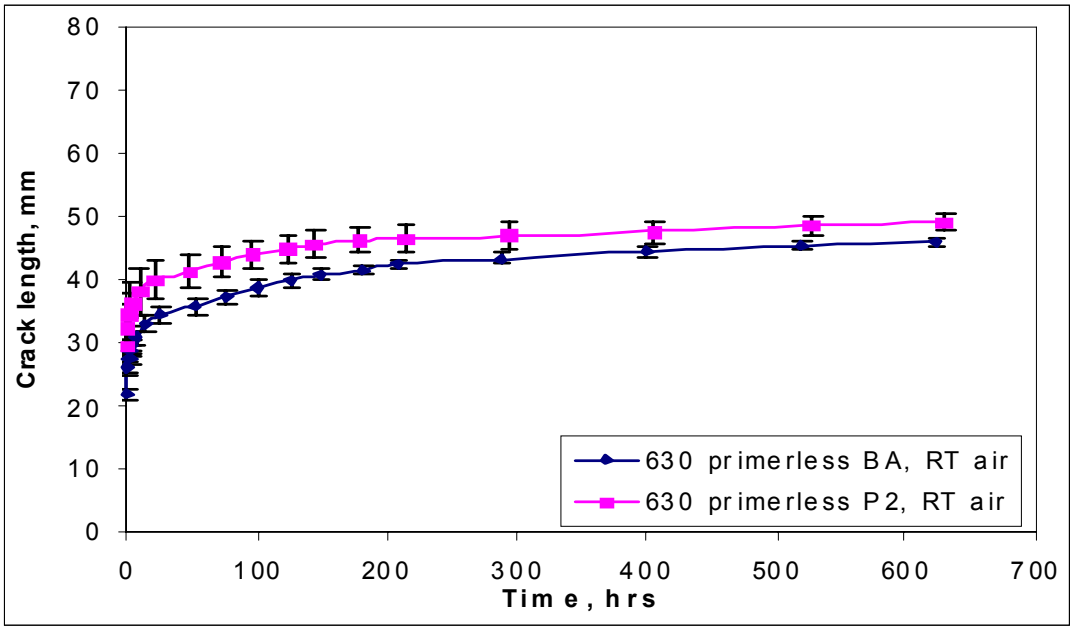


Figure H2: Crack Length versus Time for First-Generation Formulation for Base-Acid and P2 Treated Substrates in Room-Temperature Air

Appendix H

Virginia Polytechnic Institute (VPI) Wedge Test Data and Figures for RTV 630 Baseline and Primerless PLS100-630 (continued)

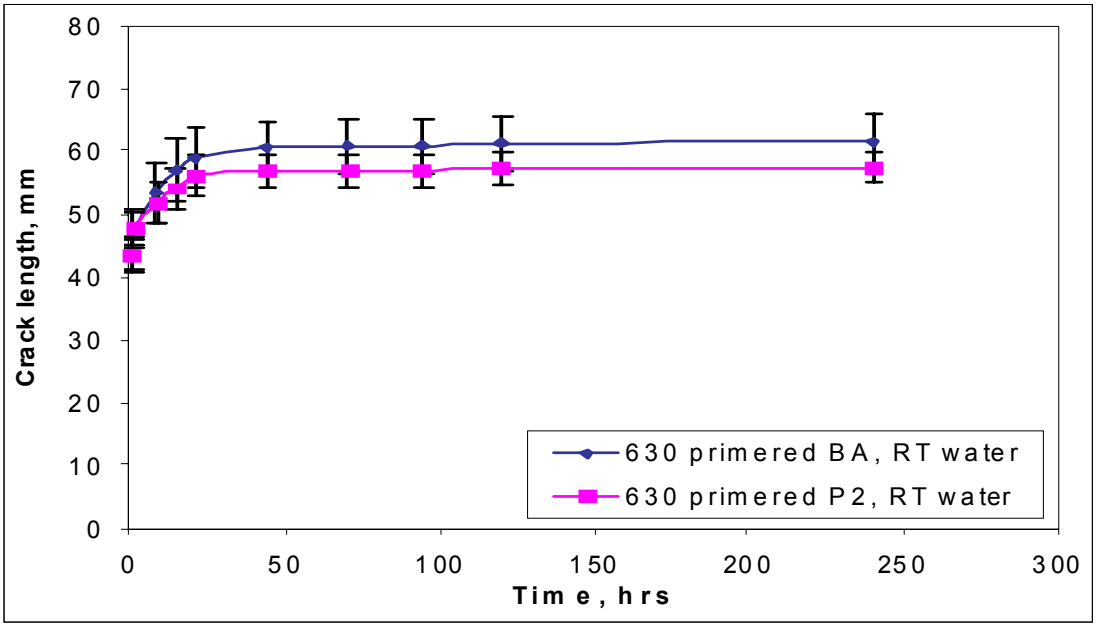


Figure H3: Crack Length versus Time for RTV 630 with GE SS-4155 Primer for Base-Acid and P2 Treated Substrates in Room-Temperature Water

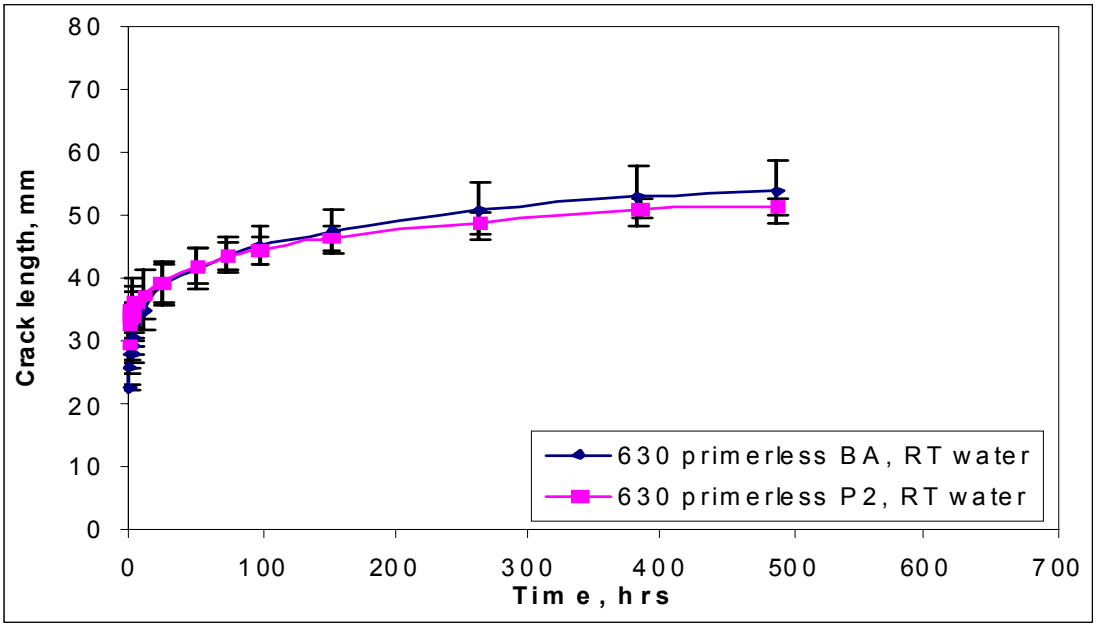


Figure H4: Crack Length versus Time for First-Generation Formulation for Base-Acid and P2 Treated Substrates in Room-Temperature Water

Appendix I

Adhesion Promoters Screened for the Second-Generation RTV 866 Formulation

Adhesion promoters full name	Shorthand
bis(trimethoxysilylpropyl) hydromuconate	hydromuconate
the reaction product of 88104 with methacryloxypropyltrimethoxysilane and allylglycidyl ether	AMU
bis(trimethoxysilylpropyl)succinate	succinate
bis(trimethoxysilylpropyl)phthalate	phthalate
bis(trimethoxysilylpropoxy)pyridine	pyridine
bis(trimethoxysilylpropyl)pyridine 1, 5 dicarboxylate	pyridine-ester
bis(trimethoxysilylpropyl)sebacate	sebacate
bis(trimethoxysilyl-propyl)adipate	adipate
bis(trimethoxysilylpropyl)-γ-aminoacrylate	aminoacrylate
glycidoxypropyltrimethoxysilane/methacryloxypropyltrimethoxy silane	Glymo/maptms
Hyperbranched-silicone ($M_{0.7}Q$),	

Adhesion promoter specific results can be found in the team's quarterly reports

Appendix J

Virginia Polytechnic Institute (VPI) Wedge Test Data and Figures for RTV 866 Baseline and Primerless PLS200-866

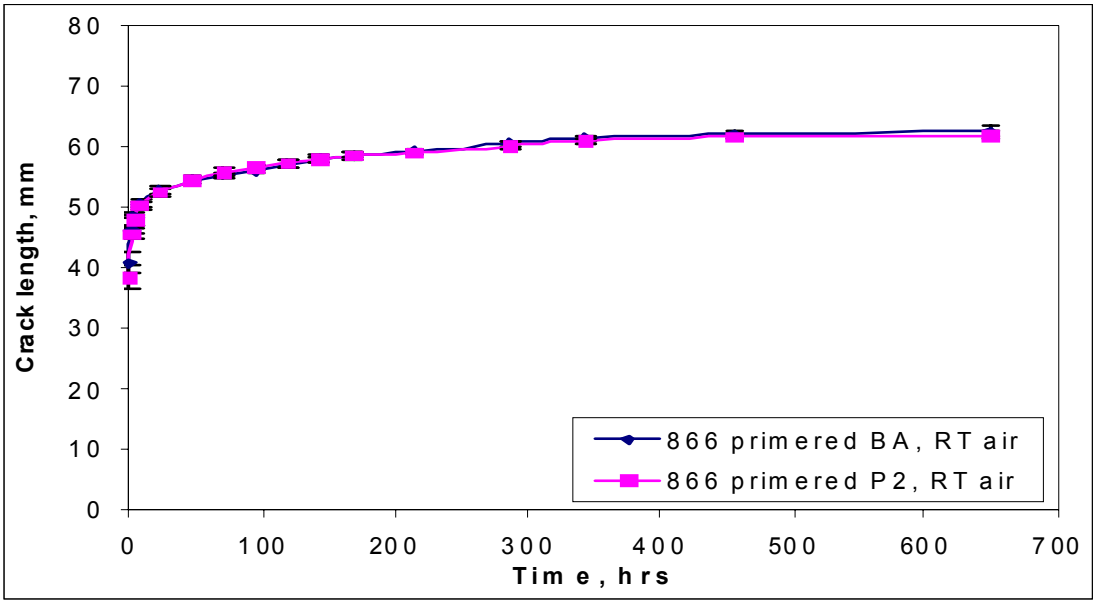


Figure J1: Crack Length versus Time for RTV 866 with GE SS-4155 Primer for Base-Acid and P2 Treated Substrates in Room-Temperature Air

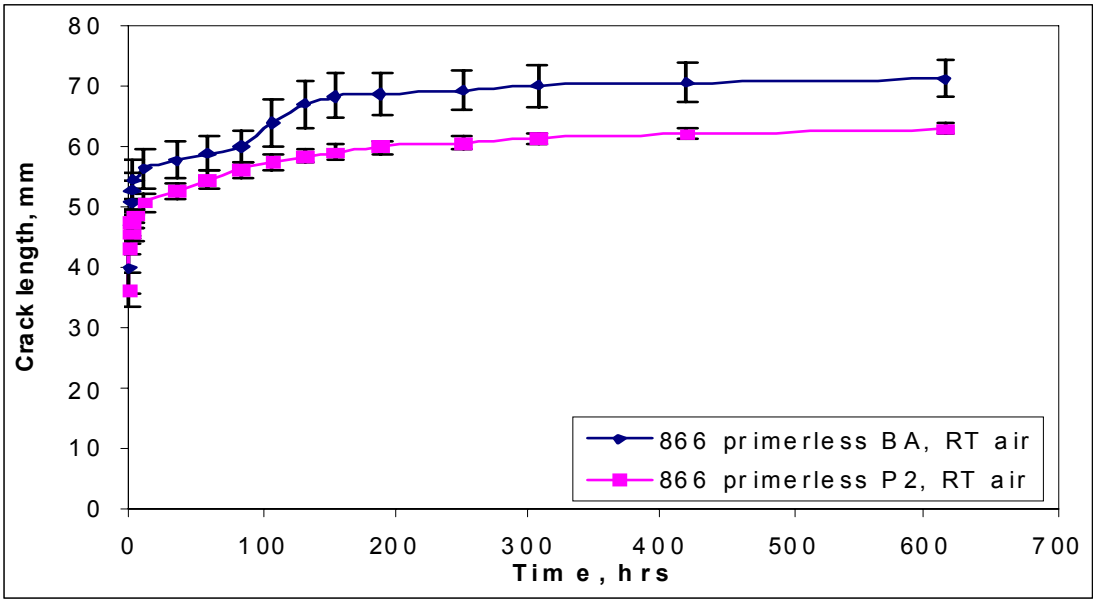


Figure J2: Crack Length versus Time for Second-Generation Formulation for Base-Acid and P2 Treated Substrates in Room-Temperature Air

Appendix J

Virginia Polytechnic Institute (VPI) Wedge Test Data and Figures for RTV 866 Baseline and Primerless PLS200-866 (continued)

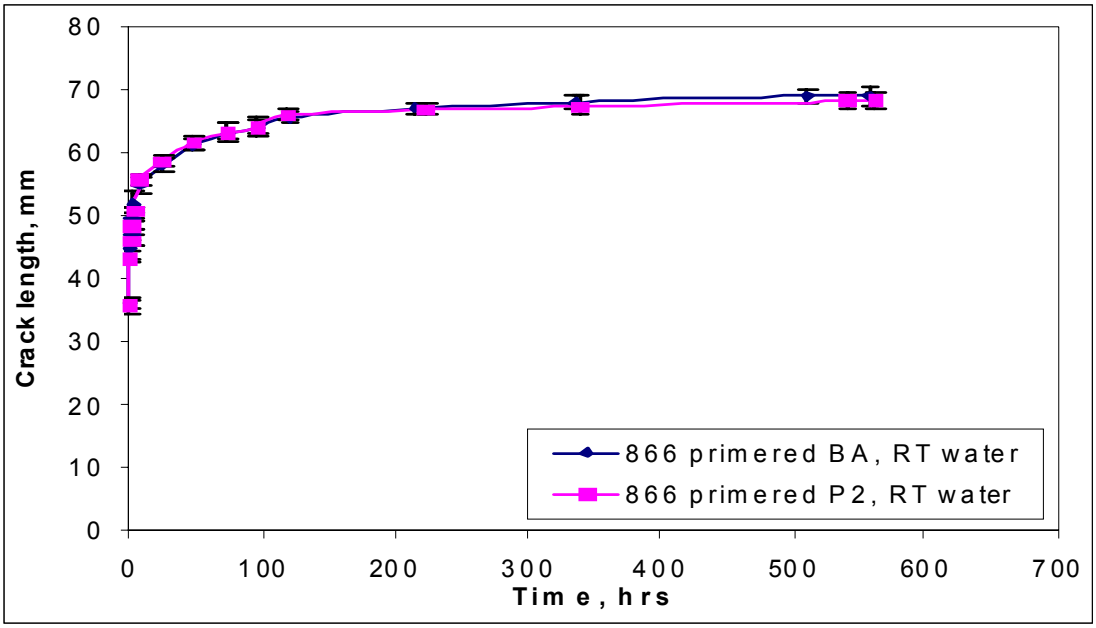


Figure J3. Crack Length versus Time for RTV 866 with GE SS-4155 Primer for Base-Acid and P2 Treated Substrates in Room-Temperature Water

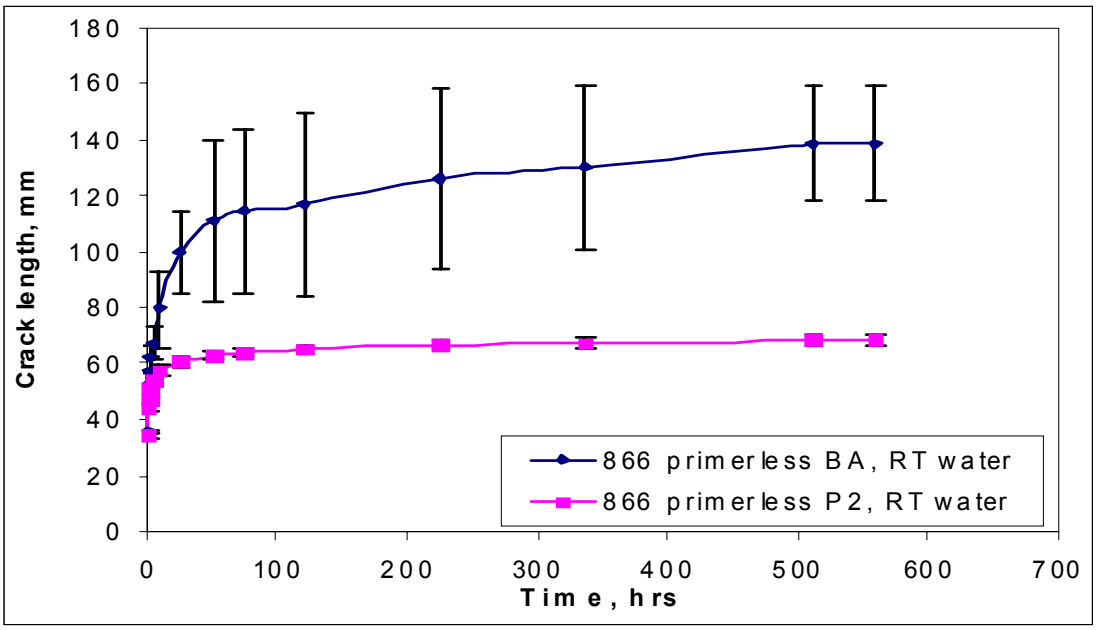
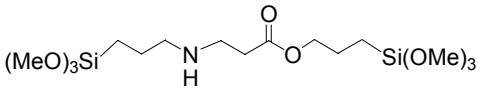
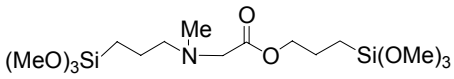
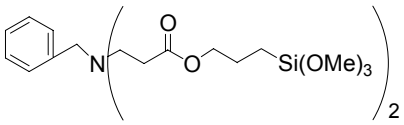
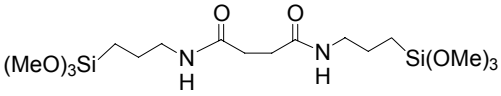
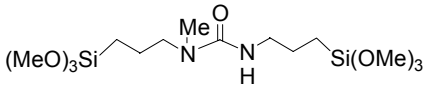
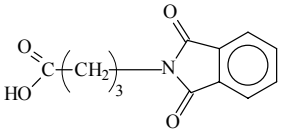
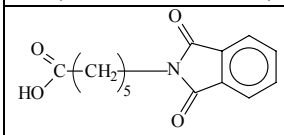
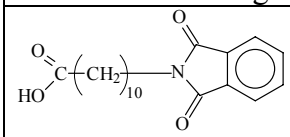
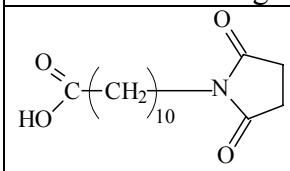


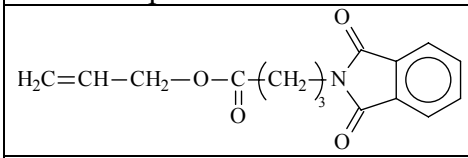
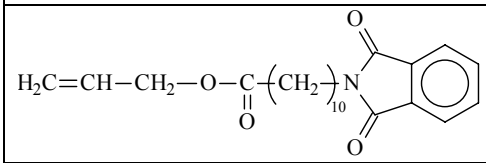
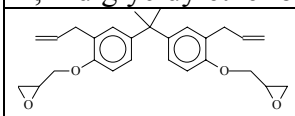
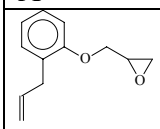
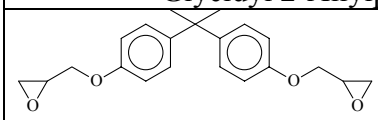
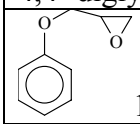
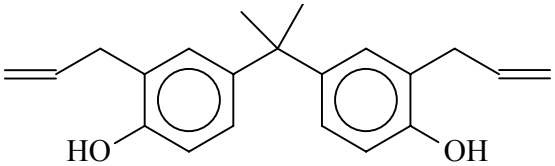
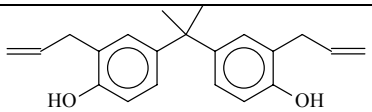
Figure J4: Crack Length versus Time for Second-Generation Formulation for Base-Acid and P2 Treated Substrates in Room-Temperature Water

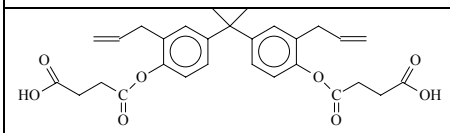
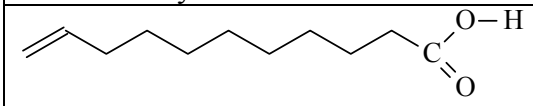
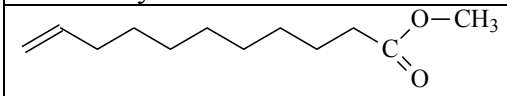
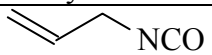
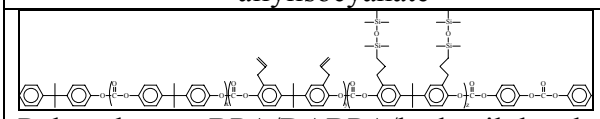
Appendix K.

Adhesion Promoters Screened for the Third-Generation Formulation

Adhesion promoter specific results can be found in the team's quarterly reports

Adhesion promoters full name	Shorthand	Substrates
bis(trimethoxysilylpropyl)succinate	succinate	Lexan, Ultem, Nylon
bis(trimethoxysilylpropyl) hydromuconate	hydromuconate	Lexan
	silyl functionalized aminoesters	Lexan, Ultem, Nylon
	silyl functionalized aminoesters	Lexan, Ultem, Nylon
	silyl functionalized aminoesters	Lexan, Ultem, Nylon
	silyl functionalized amides	Lexan, Ultem, Nylon
	silyl functionalized amides	Lexan, Ultem, Nylon
 N-(□-alkanoic acid) phthalimide	Acid terminated	Lexan, Ultem, Nylon
 N-(□-alkanoic acid) phthalimide different chain length	Acid terminated	Lexan, Ultem, Nylon
 N-(□-alkanoic acid) phthalimide different chain length	Acid terminated	Lexan, Ultem, Nylon
 N-(11-undecanoic acid) maleimide	Acid terminated	Lexan, Ultem, Nylon

Adhesion promoters full name	Shorthand	Substrates
	Double bond terminated	Lexan, Ultem, Nylon
	Double bond terminated	Lexan, Ultem, Nylon
4,4' diglycidylether of bisphenol A *		Lexan, Ultem, Nylon
 2,2' diallyl 4,4' diglycidylether of bisphenol A	AP1	Lexan, Ultem, Nylon
 Glycidyl 2-Allylphenyl ether	AP2	Lexan, Nylon
 4,4' diglycidylether of bisphenol A	AP3	Lexan, Nylon
 1,2-Epoxy 3-phenoxypropane	AP4	Nylon
 2,2' diallyl bisphenol A (purified)	AP5	Nylon, Alclad and bare aluminum, Steel, Lexan®, Ultem®, diallylphtalate, polymethylpentene (TPX), polyetheretherketone (PEEK), ABS, epoxyglass laminate, polyphenylenesulfide, phenolic, epoxy.
 2,2' diallyl bisphenol A (as received 85% pure		Nylon

Adhesion promoters full name	Shorthand	Substrates
 2,2'-diallylbisphenolA esterified with succinic anhydride		Ultem, Lexan
 11-undecylenic acid		Ultem, Lexan
 methyl ester of 11-undecylenic acid		Ultem, Lexan
 allylisocyanate		Ultem, Lexan
 Polycarbonate BPA/DABPA/hydrosilylated DABPA		Lexan

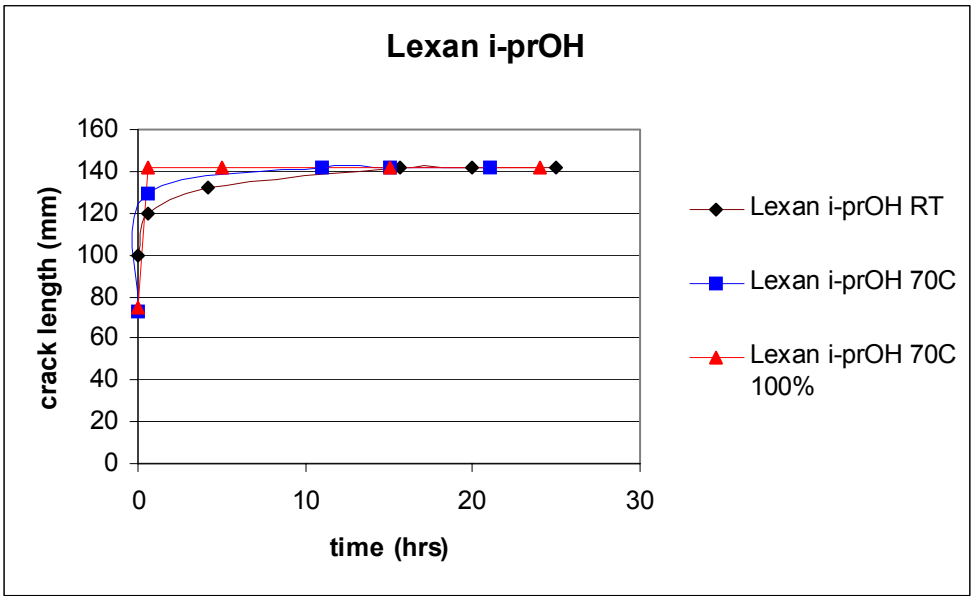
- with diallyldiglycidylether of BPA

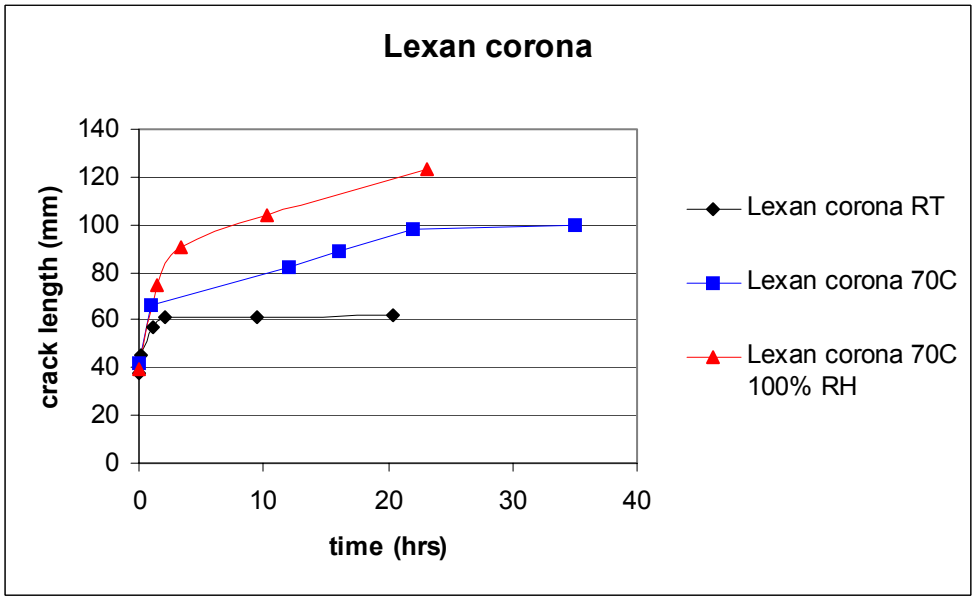
Catalyst	**Results / Comments**
$BF_3.Et_2O$	Adhesion but does not meet toxicity requirements
tripropylborate	No adhesion
triphenylphosphoranylidene acetaldhehyde	No cure
tris(pentafluorophenyl)borane	Adhesion but bubble in the RTV
$(Acac)_2Ti(OiPr)$	No adhesion
2,4,6-tris(dimethylaminomethyl)phenol	No cure
Acid salycilique	No adhesion
pTSA	No adhesion
trimethylaluminum	Adhesion but does not meet toxicity requirements
trimethoxyboroxine	Good Adhesion

APPENDIX L

Durability Curves for PLS 300A-630 and Lexan or Nylon 6,6 Samples

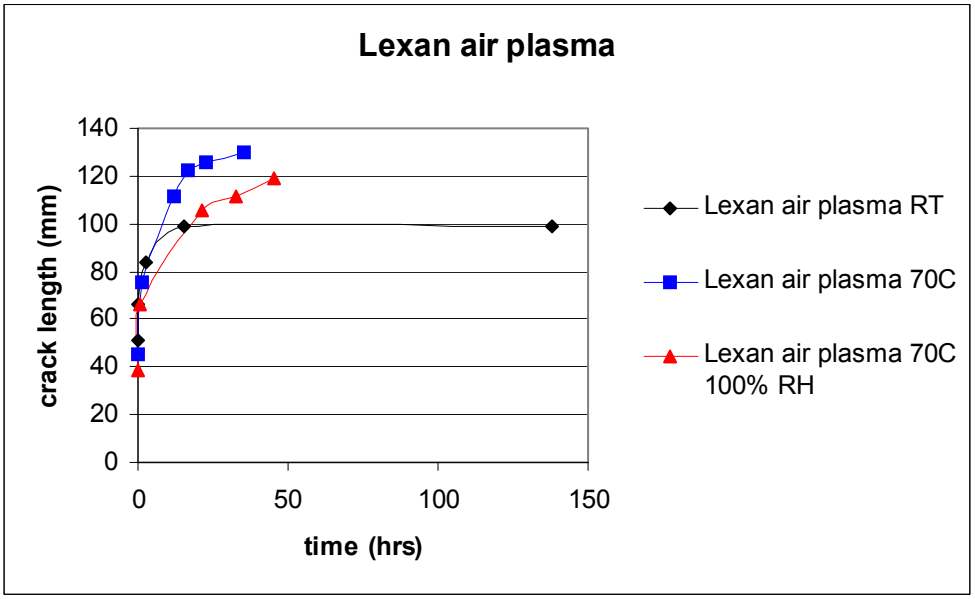
Rather than discussing every durability performance curve, only those situations giving the most promising results were discussed in the body of this report. Following are the graphs of durability performance for all systems studied. The curves are given in the order Lexan then Nylon and according to the specific surface preparation; isopropanol, corona, air plasma, and 3-aminopropyl silane, respectively. Each graph includes the results for tests at room temperature, 70°C and 70°C and 100% RH. .

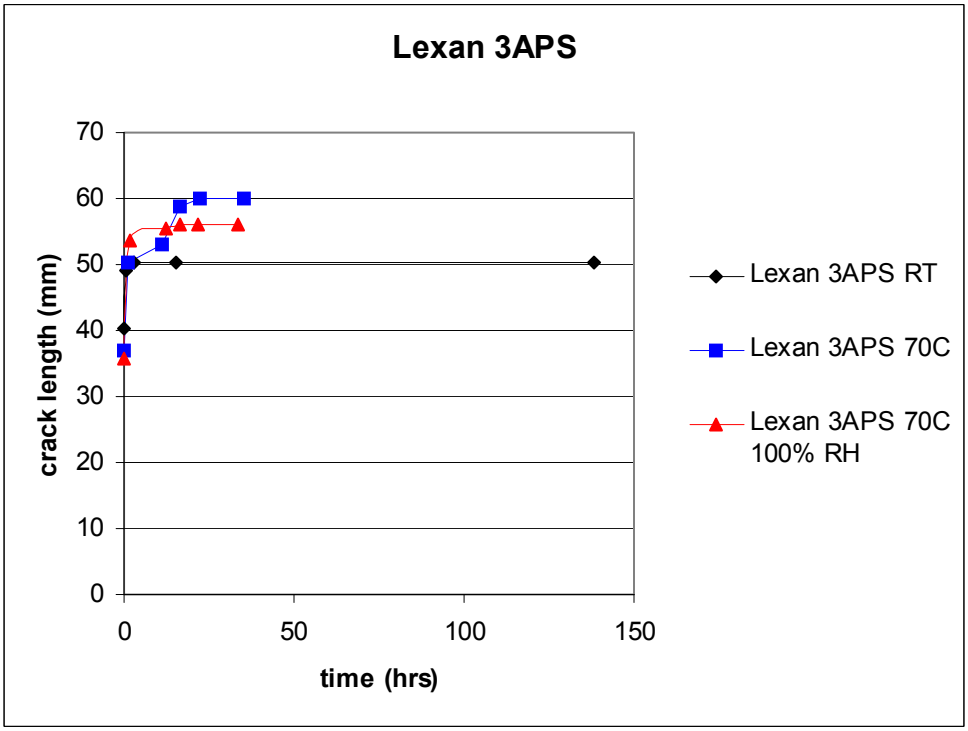




APPENDIX L

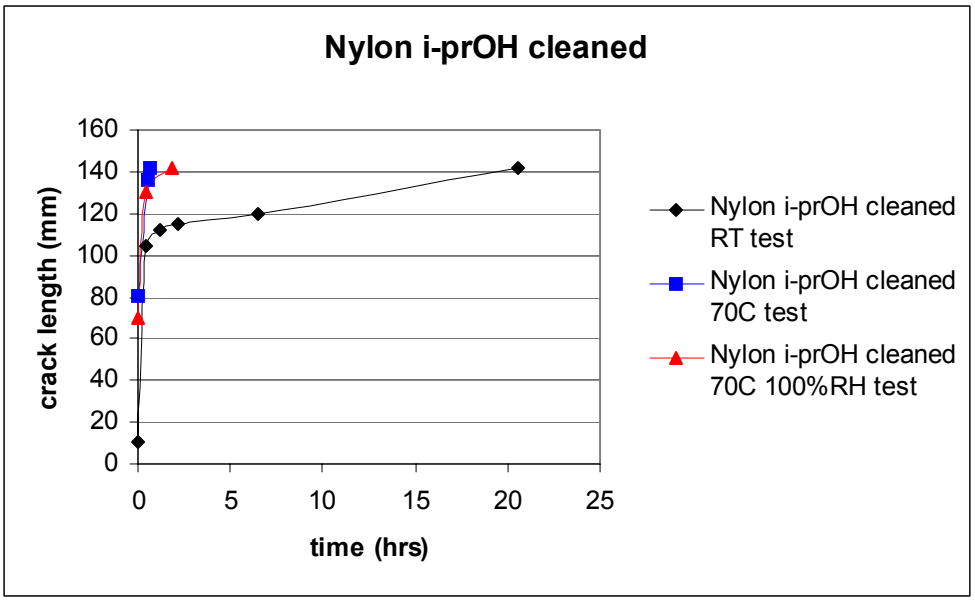
Durability Curves for PLS 300A-630 and Lexan or Nylon 6,6 Samples (continued)

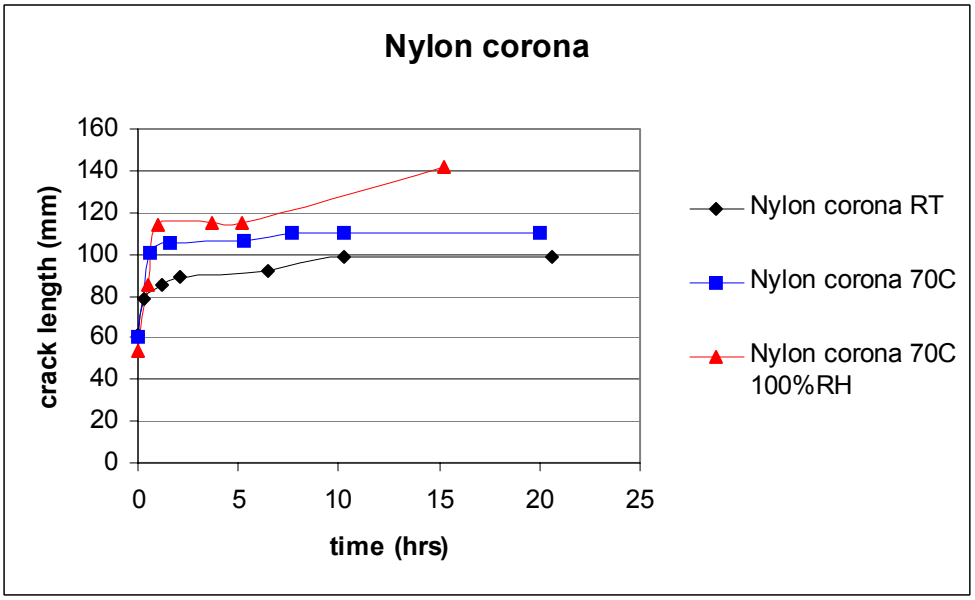




APPENDIX L

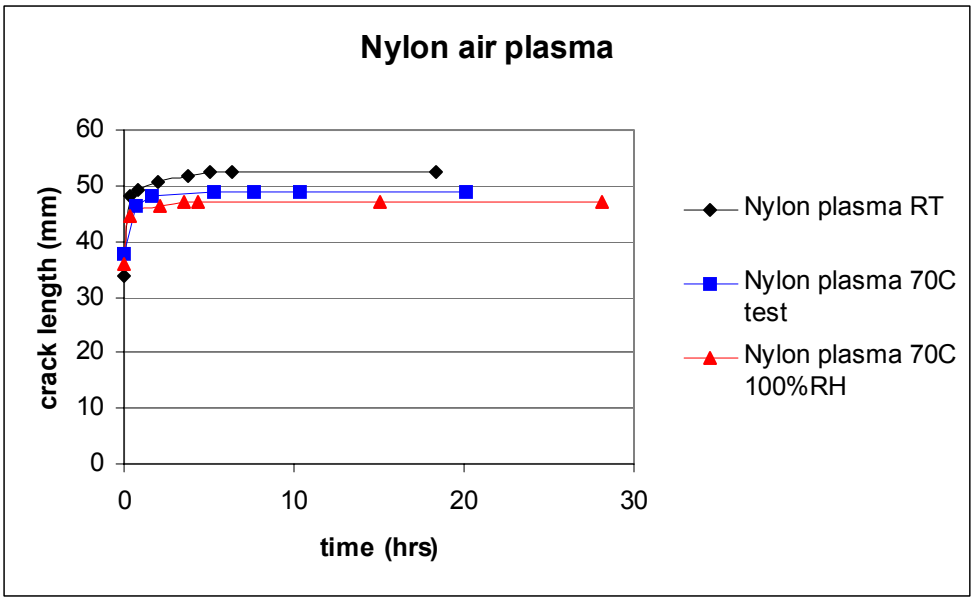
Durability Curves for PLS 300A-630 and Lexan or Nylon 6,6 Samples (continued)

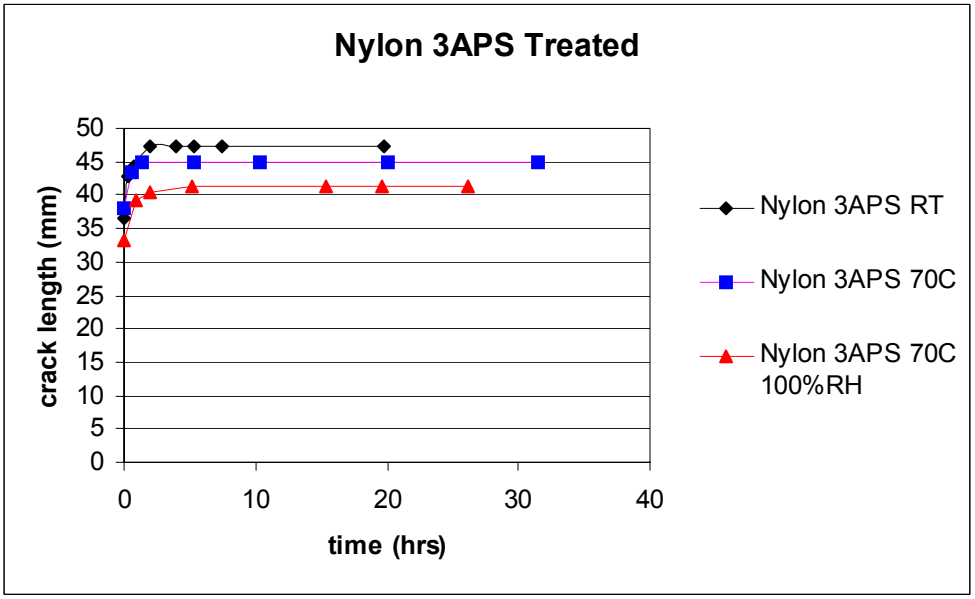




APPENDIX L

Durability Curves for PLS 300A-630 and Lexan or Nylon 6,6 Samples (continued)





APPENDIX M

Air Force Comparison of Lap Shear Properties of Base Line RTV630 + Primer & Baseline RTV 866 + Primer With First & Third-Generation (PLS100-630 and PLS300-866) Primerless RTV.

RTV 630 and PLS-100-630 LAP SHEAR STRENGTH[1]

Adhesive	Adherend	Primer	Test Temperature °F/°C	Lap Shear Strength (psi)	Cohesive (%)
PLS-100-630	2024 T3	None	-65/-53	815	100
PLS-100-630	2024 T3	None	77/23	416	4
PLS-100-630	2024 T3	None	400/204	327	93
RTV-630A/630B	2024 T3	SS-4155	77/23	216	0

[1] Test Speed = 2 in./min.

RTV 866 and PLS-300-866 LAP SHEAR STRENGTH[1]

Adhesive	Adherend	Primer	Test Temperature °F/°C	Lap Shear Strength (psi)	Cohesive (%)
PLS-300-866	Nylon 6/6	None	-65/-53	1175	100
PLS-300-866	Nylon 6/6	None	77/23	530	100
PLS-300-866	Nylon 6/6	None	200/93	264	100
RTV-866A/866B	Nylon 6/6	SS-4155	-65/-53	925	100
RTV-866A/866B	Nylon 6/6	SS-4155	77/23	612	100
RTV-866A/866B	Nylon 6/6	SS-4155	200/93	268	28

[1] Test Speed = 2 in./min.

APPENDIX N

Navy Comparison of Lap Shear Properties of Base Line RTV630 + Primer With First and Third-Generation (PLS100-630 and PLS300A-630) Primerless RTV.

Bare Aluminum Lap Shear Samples

BARE ALUMINUM

Materials	*Test Temp*	*Average Strength , psi*	*StDev*	*Failure Mode*
RTV-630 w/primer	RT	529	92.8	60% Coh/40% Adh
PLS100-630	RT	399	33.5	50% Coh/50% Adh
RTV-630 w/primer	400F	367	40.0	30% Coh/70% Adh
PLS100-630	400F	322	45.0	70% Coh/30% Adh
RTV-630 w/primer	-67F	714	70.6	10% Coh/90% Adh
PLS100-630	-67F	889	116.31	75% Coh/25% Adh

Nylon 6,6 Lap Shear Samples

NYLON 6,6 SUBSTRATE

Materials	*Test Temp*	*Average Strength , psi*	*StDev*	*Failure Mode*	***COMMENTS***
RTV-630 w/primer	RT	664..36	53.17	30% Coh/70% Adh	Failure occurred within adhesion promoter/appears promoter applied too thick.
PLS-300A-630	RT	822..99	58.31	100% Coh	
RTV-630 w/primer	200F	231..87	20.27	100% Adh	Failure occurred within adhesion promoter/appears promoter applied too thick.
PLS-300A-630	200F	399..56	58.00	65% Coh/35% Adh	
RTV-630 w/primer	-67F	898..16	32.22	15% Coh/85% Adh	
PLS-300A-630	-67F	1472.075	81.80	95% Coh/5% Adh	Nylon broke at the edge of panel overlap on 2 specimens – they are not included in either lap shear or failure mode data.

Appendix O

Spot Adhesion Testing Results

Spot Adhesion Studies				
Substrate	Adhesive Performance of Formulation			
	RTV 630 + primer	*RTV 866 + primer*	*First-Generation*	*Second-Generation*
2024 T-3 Aluminum-Bare	Excellent	Excellent	Excellent	Excellent
2024 T-3 Aluminum-Aldad	Excellent	Excellent	Excellent	Excellent
2024 T-3 Aluminim-PAA (anodized)	Excellent	Excellent	Excellent	Excellent
2024 T-3 Aluminum-Bare-SolGel Treated	Excellent	Excellent	Excellent	Excellent
Steel -Phosphate Coated	Poor	Poor	Excellent	Excellent
Titanium	Excellent	Excellent	Excellent	Excellent
ABS plastic	Excellent	Excellent	Excellent	Poor
Carbon Fiber Reinforced Ultem 1000 (1)	Poor	Poor	Excellent	Excellent
Carbon Fiber Reinforced Ultem 1000 (2)	Poor	Poor	Excellent	Excellent
Diallylphthalate	Excellent	Excellent	Excellent	Excellent
Epoxy/Glass Fiber Reinforced Laminate	Excellent	Excellent	Excellent	Excellent
Epoxy/Graphite Fiber Reinforced Laminate	Excellent	Excellent	Excellent	Excellent
Humiseal 2A53 Epoxy	Excellent	Poor	Excellent	Excellent
Humiseal 2A53 Epoxy Coated Ultem 1000	Poor	Poor	Excellent	Excellent
Loctite 362 Epoxy	Excellent	Excellent	Excellent	Excellent
Mylar	Excellent	Excellent	Excellent	Excellent
Nylon 6.6	Poor	Poor	Excellent	Poor
Nylon 6.6 -Corona Treated	Poor	Poor	Excellent	Excellent
Glass Fiber Reinforced Phenolic -Fiberite MX 2641	Excellent	Excellent	Excellent	Excellent
Polycarbonate	Excellent	Excellent	Excellent	Poor
Polyetheretherketone	Excellent	Excellent	Excellent	Poor
Polyethersulfone (Vitrex)	Poor	Poor	Excellent	Poor
Polyethersulfone (Vitrex) -corona treated	Poor	Excellent	Excellent	Poor
Polymethylpentene	Excellent	Excellent	Excellent	Poor
Poly-Ond	Poor	Poor	Poor	Poor
Polyphehylene Sulfide	Excellent	Excellent	Excellent	Poor
Santoprene®	Poor	Poor	Poor	Poor
Santoprene®-Corona Treated	Poor	Poor	Poor	Fair
Sapphire	Poor	Poor	Excellent	Excellent

APPENDIX P

Army Comparison of Lap Shear Properties of Base Line RTV630 + Primer With First and Third- Generation (PLS100-630 and PLS300A-630) Primerless RTV.

TENSILE LAP SHEAR DATA

RTV 630 AND ALCLAD 2024 – T3*

SET	Material	TEMP °F	CROSSHEAD SPEED in/min	$\bar{X}$ Psi	σ Psi	$\bar{X}$ - 3σ Psi	Cohesive Failure
I	630 + Primer	70	2.00	606.3	53.1	447.0	100 %
II	PLS100 630	70	2.00	656.3	23.6	585.5	100%
III	PLS100 630	- 25	2.00	910.0	62.2	723.5	100%
IV	PLS100 630	+ 145	2.00	530.0	45.5	393.6	100%

* SET I is Baseline RTV 630 + SS 4155 Primer
SETS II thru IV are PLS 100 630

TENSILE LAP SHEAR DATA
RTV 630 AND Nylon 6,6 *

SET	Material	TEMP °F	CROSSHEAD SPEED in/min	$\bar{X}$ Psi	σ Psi	$\bar{X}$ - 3σ Psi	Cohesive Failure
V	630 + Primer	70	2.00	620.0	38.7	503.9	50 – 70%
VI	PLS300A-630	70	2.00	768.0	64.3	575.1	100%
VII	PLS300A-630	- 25	2.00	1,008.0	80.4	766.8	100%
VIII	PLS300A-630	+ 145	2.00	549.0	43.1	419.7	100%

* SET V is Baseline RTV 630 + SS 4155 Primer
SETS VI thru VIII are PLS300A- 630

APPENDIX Q

Army Comparison of Lap Shear Properties of Base Line RTV866 + Primer With Third- Generation (PLS300-866) Primerless RTV.

TENSILE LAP SHEAR DATA (continued)

TENSILE LAP SHEAR DATA
RTV 866 AND Nylon 6,6 *

SET	Material	TEMP °F	CROSSHEAD SPEED in/min	$\bar{X}$ Psi	σ Psi	$\bar{X} - 3\sigma$ Psi	Cohesive Failure
IX	866 + Primer	70	2.00	495.0	38.4	379.8	55 - 70 %
X	PLS 300 866	70	2.00	633.0	15.7	585.9	100%
XI	PLS 300 866	- 25	2.00	888.0	30.8	795.6	100%
XII	PLS 300 866	+ 145	2.00	411.0	8.9	384.3	100%

*** SET IX is Baseline RTV866 + SS 4155 Primer**
SETS X thru XII are PLS300 866