MODIFICATION OF DIGLYCIDYL ETHER OF BISPHENOL-A EPOXY PRIMER FOR MULTI-SUBSTRATE APPLICATION

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

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ABSTRACT

Traditional vehicles and aircraft have consisted primarily of steel and aluminum alloys which due to their density, has resulted in various logistic problems including transportation, maneuverability, fuel efficiency. These hindrances have led to a major increase in the incorporation of composites material into this equipment. As the use of these composite increases, multi-substrate coating systems that can provide adequate corrosion protection to metal components, as well as superior adhesion and flexibility to the composites, are needed.

The goal of this work is the modification of diglycidyl ether of bisphenol-A epoxy coating systems for improved flexibility and adhesion for the development of multi-substrate primer. For this purpose, commercial additives of various chemistry (liquid rubber, polysulfide, novolac phenolic resins, silane coupling agents, and polyethers) were incorporated into a model epoxy-polyamine coating and their effect on flexibility and adhesion was investigated. Based on their performance, the top-performing additives were incorporated into a fully pigmented modified primer. Overall, the studies in this dissertation not only demonstrated improved flexibility and adhesion to metal and composites but also improved overall corrosion protection compared to an unmodified primer.

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DEDICATION

I dedicate my dissertation to the village of stranger and friends who got me here today.

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CHAPTER 1. STATEMENT OF OBJECTIVE

The purpose of this research is to examine the effect of various commercial additives on the flexibility and adhesion of epoxy-amine coating systems in hopes of developing a bisphenol-A-based epoxy primer for multiple substrate applications. Ideally, a noticeable improvement in the flexibility and adhesion performance of the modified coating to multiple substrates including metallic and composite is to be achieved. There is currently a knowledge gap within the literature about the adhesion performance of traditional epoxy amine primer on composite substrates such as carbon fiber reinforced plastic and fiberglass reinforced polymer. Thus, this work hopes to narrow that gap by investigating key structure-property relationships for improving adhesion.

To achieve the objective of this research, several approaches were considered. The effect of liquid rubbers, polyethers, silane coupling agents, polysulfides, phenol epoxy resins, and aminobenzoic on flexibility and adhesion performance of the epoxy amine system was investigated. Three types of liquid rubber were studied, amine-terminated poly (butadiene-acrylonitrile (ATBN), polybutadiene, hydroxyl-terminated (HTPB), and polybutadiene, epoxy functionalized, hydroxy-terminated (EHTPB). These liquid rubbers have previously demonstrated improved flexibility in several epoxy-polyamine systems however their effect on DGEBA -Epikure 3164 coatings has not been studied. The crosslinking of DGEBA with Epikure 3164 produces one of the most flexible commercially available epoxy coatings; thus Epikure 3164 was selected for this project. Furthermore, unlike carboxyl-terminated copolymer of butadiene and acrylonitrile (CTBN), the mechanism of flexiblizing of these liquid rubbers in the epoxy system has not been heavily studied. Additionally, the adhesive effect of these liquid rubbers has not been explored on metallic and composite substrates.

Polyethers are extensively used as a hardener for the preparation of flexible epoxy resins. These polyethers either have diols or amine functionality. Polyether diols contain primary hydroxyl groups. These groups react with the epoxy groups in the presence of a suitable catalyst (e.g., a tertiary amine) to form ether linkage. Without the use of catalysts, the etherification is extremely slow and must be conducted at an elevated temperature (>170° C). Polyetheramines are comprised of primary amines, which react with the epoxy group to form a secondary amine and secondary alcohol. The secondary amine produced from this reaction reacts with another epoxy group producing a tertiary amine and another secondary alcohol. The tertiary amine and alcohol can have a catalytic effect allowing for a faster reaction than the etherification; however steric hindrance makes curing at lower temperature challenging. Moreover, the use of polyether can result in decreased thermal stability and barrier performance. To mitigate these problems while utilizing their flexibilizing capabilities, aliphatic polyether can be used in additive amounts with other amine crosslinking agents. Thus, in this work, polyether diols and polyetheramine were incorporated in a DGEBA -Epikure 3164 system, and their effect on flexibility was investigated. Polytetrahydrofuran (pTHF) and Jeffamine pTHF-170 (ApTHF-170) were selected as the polyether diol and polyetheramine, respectively. These two types of polyether were selected because in contrast to Jeffamine D-230, D-2000, and T-5000 they are not heavily studied within the literature. Furthermore, according to the manufacturer, crosslinkers based on polytetrahydrofuran are effective in promoting adhesive peel strength in epoxy formulations, however, this claim has not been thoroughly researched in the literature. To examine the adhesive strength of these polyethers, a study was conducted where the polyethers were coupled with silane coupling agent adhesion promoters, 3-Aminopropyl-triethoxysilane (APTS) and 3-aminopropyl(diethoxy)methylsilane (ADMS) the two most common adhesion promoters used in the coatings and composite industries. It is worth noting that while Jeffamine D-2000 was not a part of this study it was used as a flexiblizing agent in another study since it is one of the most used flexibilizer for epoxy systems.

Aside from the use of silane coupling agents, another method of improving the adhesive strength of epoxy resin is the introduction of increased hydroxyl groups. Hydrogen bonding between the hydroxyl group present on the epoxy and metal oxide surface results in improved adhesion of epoxy to metallic substrates. The most effective method for increasing the amount of hydroxyl functionality within the cured epoxy coating system is the introduction of excess oxirane. As mentioned earlier, the epoxy group reacts with the amine forming secondary alcohol. Thus, a resin with higher epoxy functionality results in higher concentrations of hydroxyl groups. Hence, novolac phenolic resin, poly (phenyl glycidyl ether)-co-formaldehyde (PPGEF), was incorporated at additive levels in the DGEBA -Epikure 3164 system. The effect of novolac phenolic resin on adhesive strength to metallic services has been heavily studied in the literature, however, its effect on composite substrates has been neglected. Thus, this work hopes to fill that gap. PPGEF is the most utilized and commercially available novolac phenolic resin, therefore it was selected for this study.

Polysulfides have long been used to impart flexibility and adhesion in epoxy resin. The flexible disulfide bond of these polymers introduces soft segments within the epoxy matrix allowing for low glass transition temperature and rubbery behavior. Manufacture of commercially available polysulfide heavily advertises them as high-performance adhesives for multiple substrate applications. However, research and commercial application has primarily focused on substrates including aluminum, steel, concrete, and wood. Their effect on composites has been neglected. Hence, for this work, an aliphatic and aromatic epoxy-functional polysulfide, Thioplast EPS 25 and Thioplast EPS 80, were studied for the flexiblizing and adhesive effect on DGEBA -Epikure 3164 for metallic and composite substrates.

Based on the presence of a bulky and rigid aromatic, 1,3-propane-diol bis (4-aminobenzoate) (PBAB), appears to be a poor candidate for improved flexibilization. However, preliminary work by Cui *et al.* has demonstrated an improved flexiblizing effect in an epoxy molding compound. Furthermore, improved adhesive strength on copper and silver surfaces was observed. To further study the flexiblizing and adhesive effect, PBAB was incorporated into the studies performed in this work.

All these commercial additives were incorporated at various levels into a model DGEBA -Epikure 3164 coating system their effect on flexibility and adhesion was investigated. Analysis of Variance (ANOVA), a test used to determine if there were any statistical differences between the means of three or more independent groups, was utilized to determine if the effect observed by each additive on the flexibility and adhesive strength of the DGEBA -Epikure 3164 was statistically significant (p-value <0.1). Response variable corresponding to improved flexibility includes an increase in % elongation from the conical mandrel test, an increase in toughness from the reverse impact test, a decrease of Tg, a decrease in crosslinked density, a decrease in storage modulus, a decrease in hardness (König and nanoindentation), and a decrease in elastic modulus (nanoindentation).

Based on ANOVA results, the top-performing additives (most improved flexibility and adhesive strength) were incorporated into a fully pigmented epoxy primer using design of experiment. This approach allows for a systematic and efficient method of studying the relationship between the multiple additives and the key output variables (aka flexibility and adhesive strength). Novel epoxy primers were developed with improved flexibility (low Tg

(<62°C), hardness, and crosslink density), and higher adhesive strength on metallic and composite substrates. Of those novel primers, the two with the highest barrier performances and ease of application (sprayable) were downselected and their weatherability was investigated via accelerated weathering ASTM B117. These modified primers demonstrated superior flexibility, adhesion, and barrier performance compared to the unmodified primer.

CHAPTER 2. GENERAL INTRODUCTION

Multi-Substrate Vehicle Parts and Universal Coatings

Vehicles such as automobiles, planes, and ships are among the greatest sources of air pollution, therefore, there is a pressing need to minimize vehicular emissions. Governments across the world have set up tough regulations for CO_2 emission management for vehicles. In response, original equipment manufacturers are focusing on improving fuel efficiency by designing lightweight vehicles and, in the case of electric vehicles, longer battery life. To reduce weight and increase fuel-efficiency, composite materials are an attractive replacement for traditional heavyweight materials like steel and aluminum. The added benefits of composites include strong impact resistance, fatigue resistance, lower direct operating costs, and corrosion resistance.[1]

Fiberglass and carbon fiber reinforced plastics account for the largest share of the overall composite markets.[2–4] Carbon fiber reinforced plastics (CF), are comprised of fibers 5-10 micrometers in diameter. Approximately 90% of carbon fiber is produced from polyacrylonitrile. In the manufacturing process, acrylonitrile plastic powder is mixed with another plastic, such as methyl acrylate or methyl methacrylate, and reacts with a catalyst in a traditional suspension or solution polymerization process. The resulting polyacrylonitrile is then spun into fibers, chemical stabilized, and carbonized at elevated temperatures. After which, the fibers are then surface treated to allow for better bonding with polymeric matrix and are coated with either epoxy, polyester, nylon, urethane, or others. The process produces a rigid material with high tensile and compressive strength, and a low coefficient of thermal expansion.[5] Glass fiber are manufactured by a process called pultrusion, in which borosilicate material (feldspar, sodium sulfate, anhydrous borax, boric acid, and many others) are gradually melted at elevated temperature into a liquid form and extruded through orifices of various sizes to create filaments of varying diameters. The filaments are chopped into tiny glass pieces, coated with a chemical solution, and impregnated within a polymer resin producing glass fiber reinforced plastics (FG). GFRP results in high tensile, energy absorption, chemically and moisture resistance, and electrically insulative.[2,6]

CFRP and GFRP are typically used in boats, automotive parts, and aerospace parts. Initially, composites were used primarily in the interior of vehicles, however, there is increased use of composite for exterior applications. In 2019, the exterior applications of automotive composites represented 55% of the overall market in terms of value, and 50% of the market in terms of volume.[2] Important components of a car body, such as the bumper beam, fender, front end module, door panels, and hood, are constructed of composite materials, these exterior applications account for a substantial portion of the automotive composites market.[1] With the increased usage of mixed materials, several challenges have risen including corrosion, adhesion, and thermal expansion.[7]

Corrosion is the natural electrochemical process by which refined metals revert to their more chemically stable oxide, hydroxyl, or sulfide forms; this leads to the gradual degradation of structures. Organic coatings have been widely used to protect metals against corrosion by acting as a physical barrier between the metal surface and the surrounding corrosive environment. Thus, the use of coatings to protect the metal components in these multi-substrate systems is needed to expand the lifespan of vehicles. However, the use of multi-metal such as aluminum and steel within the same structure produces an additional challenge. When two dissimilar metals are electrically connected, the more active metal will corrode preferentially in a process known as galvanic corrosion.[8] Barrier coatings are unable to prevent galvanic corrosion; corrosive species such as oxygen, water, and chloride ions can reach the metal/coating interface through diffusion into the coating pores. Mitigation methods for addressing galvanic corrosion are heavily researched and are outside the scope of this paper. Nevertheless, in a mixed material structure consisting of metals and composite, a protective coating is required to prevent the corrosion of the metal substrates.

Adhesion is the most important property in barrier protection of substrates by organic coatings. For coatings to provide adequate barrier performance against the corrosive environment, which is imperative in the use of metals substrate, the coatings must adhere to the substrate. In mixed material structures, it is crucial that the coating adhere to all substrates. A uniform coating system across the entire body of the vehicle prevents penetration of the corrosive media at metal composite joints. An important characteristic relating to adhesion is surface free energy. High surface energy correlates with strong molecular attraction, while low surface energy means weaker attractive forces and poor adhesion.[9] As shown in Fig 2.1, the surface free energy of composites ranges from 30-50 mJ/m^2 depending on the polymer matrix comprising the composite. As a result, the surface of a composite has low adhesion, compared to metals which are 840 mJ/m^2 and 700-1100 mJ/m^2 for aluminum and steel, respectively.[10] To prevent corrosion of the metal component, organic barrier coatings are required, but these coatings must be formulated to achieve superb adhesion to multiple substrates.

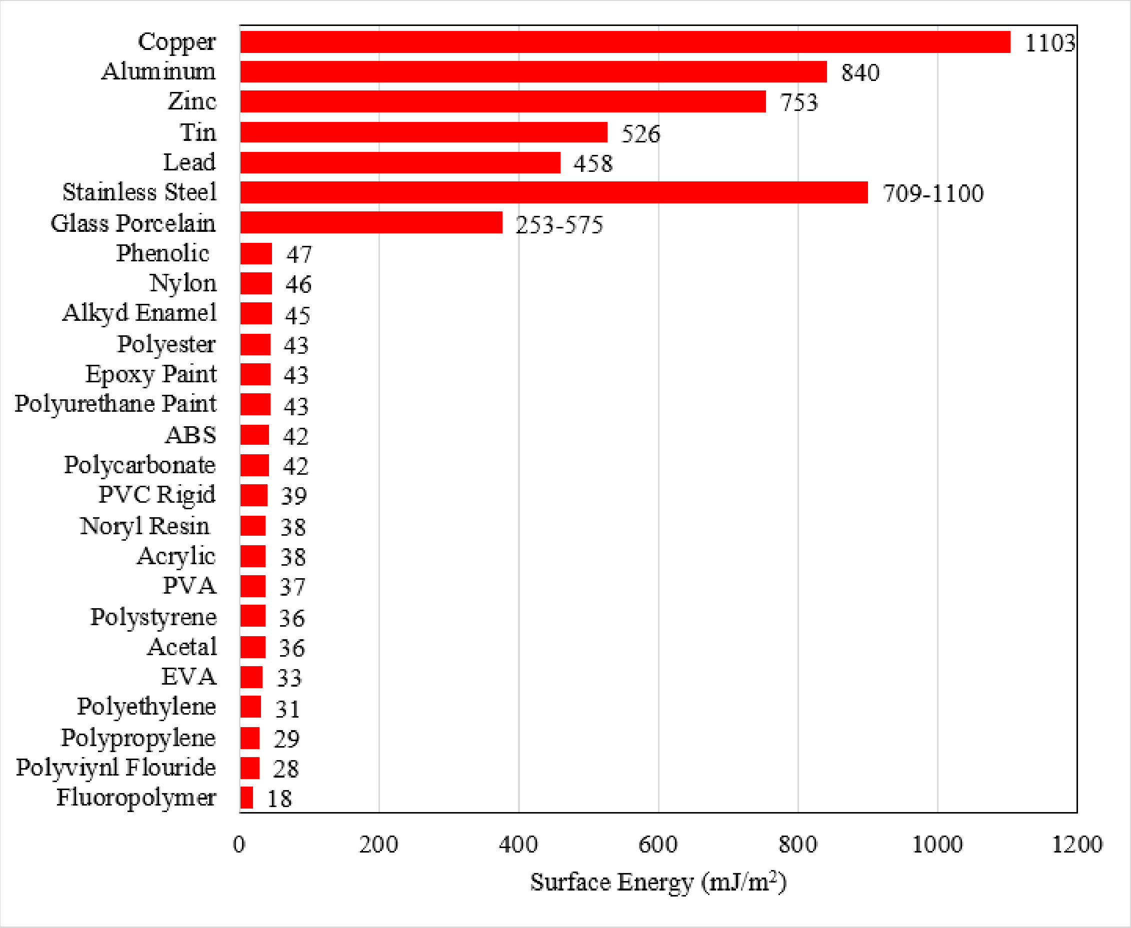

Figure 2.1. Surface Energy of Different Material[11]

Thermal expansion is the tendency of matter to alter its shape, area, and volume in response to a change in temperature under a standard pressure. The coefficient of linear thermal expansion (CLTE) measures the fractional change in size per degree change in temperature at a constant pressure. Material with lower coefficients has a lower proclivity for changes in size. While the CLTE of composite various depending on polymeric matrix, composites typically have a higher CLTE than metals meaning they have a higher propensity for dimensional change at elevated temperature.[12] This is an issue in the manufacturing of vehicles where materials are exposed to temperatures as high as 250° C. Thus, the difference in dimensional change of the mixed material bodies produces a major challenge for protective coatings. A coating must be highly flexible and durable to conform to the dimensional changes, as well capable of being applied in the standard assembly process.[13,14]

The need for lightweight, fuel-efficient, environmentally friendly vehicles has given credence to the use of composites such as CFRP and GFRP within these applications, resulting in mixed material bodies. Thus, unique challenges have arisen. Coating systems with superior barrier performance are needed to protect the metal surface from corrosion. However, to prevent corrosion and reduce the labor cost when applying these coating, the coatings need to adhere to all substrates within the system. Due to the low surface free energy of composite, traditional coatings have poor adhesion to these composites, therefore, the adhesive strength of these protective coating needs to be improved. The difference in CLTE of the various materials results in dimensional changes at elevated temperatures, thus a coating with a high degree of flexibility is needed to accommodate these structural changes. Epoxy resin primers are the perfect candidate for a multi-substrate coating system.

Epoxy Resin

Epoxy resins are characterized by the presence of one or more epoxy (oxirane) groups per molecule. Most commercially significant epoxy materials are derived by reacting epichlorohydrin with bisphenol A, to produce bisphenol A diglycidyl ether (DGEBA) as shown in Fig 2.2. Resins based on DGEBA are commercially the most important class of epoxy resins, finding extensive application in high-performance coatings, adhesives, and reinforced composites. They offer a unique combination of performance characteristics including exceptional adhesion and corrosion resistance, excellent chemical resistance, low shrinkage, high strength, good heat resistance, toughness, and excellent electrical properties.[15]

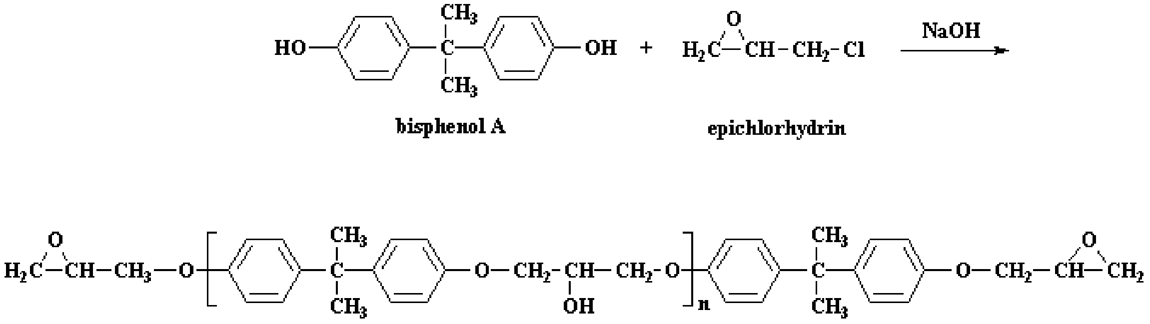

Figure 2.2. Reaction of bisphenol A with epichlorohydrin to produce DGEBA[15]

Epoxy resins by themselves are oligomeric macromolecules. To convert epoxy into a usable coating they must be reacted with a curing/crosslinking agent or hardener to produce a three-dimensional polymer network. Curing agents function by reacting with either the epoxide or hydroxyl groups on the epoxy resin to form this 3D network. Epoxy coating systems designed for ambient application typically utilize polyfunctional amines as the curing agent, either alone or in combination with other curing agents. Several classes of amine curing agents are used commercially, including aliphatic amines, amidoamine, amine adducts, Mannich bases, and polyamides. Among these curing agents, polyamides are the most desirable and important class of curing agents.[16]

Polyamides are produced from the reaction of dimerized fatty acid (dimer acid) and polyethyleneamines. These dimerized fatty acids are the product of the oligomerization of certain monomeric fatty acids. Tall oil fatty acid (TOFA) is the most common source of monomeric fatty acids; however, other vegetable acids are used as substitutes. A variety of high molecular polyethyleneamines can be used in the preparation of polyamides, such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), or pentaethylenehexamine (PEHA). However, for actual commercial practice, TETA is commonly used[16].

Polyamides are desirable as epoxy curing agents because they develop coatings with superior adhesion and demonstrate a higher degree of corrosion resistance, as well adequate retention of flexibility and impact resistance with aging. They also offer reasonable cure speeds and less of a tendency to exude to the surface resulting in surface appearance problems such as exudate, blush, and bloom compared to other hardener classes. Furthermore, due to the wide diversity of chemistry, various oligomers of varying viscosity, amine equivalent weight, and reactivity are available and can be utilized to obtain desirable performance.[17]

The oligomeric polyamine curing agent, Epikure 3164, is one of the few crosslinking agents known to impart flexibility on epoxy resin,[18,19] thus, for this work, it was chosen as the crosslinking agent.

Due to their adhesion, barrier performance, and exceptional protection against corrosive environments, thermoset epoxy is typically employed as a corrosion-resistant primer in refineries, chemical plants, marine equipment, (*i.e.*, ships and offshore platforms), automotive, aircraft, and appliances.[20]They are the current standard for corrosion resistance primers in the aerospace, automotive, and aircraft industries thus, epoxy is the ideal candidate for a universal primer for multiple substrate applications. In the formulation of a universal primer, three main properties are of greatest importance: flexibility, adhesion, and barrier performance.

The Flexibility of Coated Substrate

Flexibility, the ability of a material to be bent or flexed without cracking or undergoing other forms of failure, is one of the most important performance properties of a coating. To meet its service requirement, a coating must exhibit appropriate properties of flexibility. The flexibility of a coating applied to a substrate depends on distensibility, film thickness, and adhesion. Distensibility is the ability of the film to expand without cracking from internal pressure. As the thickness of the film increases, the flexibility of the coating tends to decrease. A similar observation for adhesion and flexibility is evident; good adhesion tends to give better flexibility than does poor adhesion. While not a direct factor influencing flexibility, toughness is an important property alongside flexibility. Toughness is the strength and resilience of a material. A tough material can withstand impact (great strain imposed over a short period) without failure (tearing, breaking, cracking, or rupturing). While flexibility and toughness are two distinct properties, they are often conflated within literature due to their dependence. A tough coating must be flexible and have adequate adhesion to not fail upon impact. Intriguingly, the toughness of an applied coating is dependent on distensibility, thickness, and adhesion as well. Other factors such as hardness, stiffness, and resiliency also relate to toughness.[21]

Flexibility depends on the viscoelastic behavior of the coating and its physical transitions and relaxation, specifically, the glass transition temperature, T_g. The T_g of a coating defines the temperature at which an amorphous material, such as a polymer, transitions from a rigid glassy state to a more flexible rubbery or leathery state. The T_g can be used as an index for flexibility. A coating with a T_g close to its temperature of operation is less susceptible to failure by cracking than if the T_g is above the operational temperature. Several factors contribute to T_g and flexibility including molecular weight and crosslinked density. Typically, as the molecular weight of a polymer increases so does flexibility. Crosslinked density and flexibility have an indirect relationship; as the crosslinked density decreases or the molecular weight between crosslinks increases, the flexibility increases.[22]

Direct flexibility measurement of a coated surface is often conducted by mandrel bend tests and falling weight impact tests. As described in ASTM D522, Standard Test Methods for Mandrel Bend Test of Attached Organic Coatings, Test Method A, the test consists of manually bending a coated metal substrate over an 8-inch-long steel cone with a diameter ranging from 1/8 inch to 1.5 inches. From this test method, a percent elongation ranging 3% to 30% can be determined for a coated surface. The falling weight impact test, as described in ASTM D6905, Standard Test Method for Impact Flexibility of Organic Coatings consists of dropping a weight from various heights onto a coated metal substrate. The appearance of the coating surfaces is visually assessed after each drop. Cracking or loss of adhesion of the coating surface constituted failure. The minimal height at which failure occurs is reported and used to calculate the absorbed energy of the specimen.

Indirect flexibility measurement is conducted by the determination of T_g and hardness. Dynamic mechanical analysis (DMA), a thermal–mechanical technique in which sinusoidal stress is applied unto a free film and the strain in the material is measured, allows for the study and characterization of the viscoelastic properties of the coating. Storage modulus (E') and loss modulus (E'') are determined from the in-phase and out-of-phase response of the materials to an applied oscillating strain over a temperature range. The storage modulus relates to the ability of materials to store energy, while the loss modulus is attributed to dissipative and viscous losses in the materials. The ratio of E'' to E' is the mechanical damping (tan δ). The maximal peak of the tan δ marks the T_g of the coating. Per the rubber elasticity theory, the crosslink density of a coating can be calculated by

$$E' = 3v_e RT \qquad \text{(Eq 1.1)}$$

where E' is the storage modulus of the thermoset in the rubbery plateau region at T_g + 50°C, R is the gas constant 8.3145 (J/mol K), and T is the absolute temperature.

Differential scanning calorimetry, DSC, can also be used to determine T_g by measuring the difference in the amount of heat required to increase the temperature of a sample, and reference material is measured as a function of temperature. However, this technique is not often used to evaluate other matrices of flexibility.

Hardness is often determined by scratch, pendulum, and penetration test methods. Pendulum and penetration are primarily utilized in this work. Pendulum hardness is measured per ASTM D4366-16, Standard Test Methods for Hardness of Organic Coatings by Pendulum Damping Tests, Test Method A. In this test, hardness is evaluated by measuring the damping time of an oscillating pendulum. The viscoelastic behavior of the coating determines the hardness. A coating with higher elasticity will cause weak damping resulting in a shorter oscillating time while a more rigid coating will have higher damping properties resulting in a longer oscillating time. Penetration hardness is another common method of measuring the elastic properties of a coating. Nanoindentation offers enhanced accuracy and capabilities not allowed by other penetration hardness methods. In this test method, an indenter tip of known geometry and hardness is applied directly unto the surface of the coating. A load is placed on the tip increased, held constant at a predetermined maximum force, and then removed during the unloading phase. The loading-hold-unloading phase occurs at specific time intervals. During the unloading phase, the area of the residual indentation in the sample is used to measure the hardness per

$$H = \frac{P_{max}}{A} \qquad \text{(Eq 1.2)}$$

Where H is hardness, P_{max} is maximum load and A is the area of indentation.

Reduced Elastic or Young’s modulus is also calculated from the indentation test per

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_p(h_c)}} \qquad \text{(Eq. 1.3)}$$

Where β is a geometric constant, S is stiffness which is obtained from the unloading curve, A_p is the project area of the indentation at the contact depth h_c.

Adhesion

Adhesion is defined as the state in which two dissimilar particles or surfaces are held together by interfacial forces consisting of either valence forces or interlocking action or both. These bonding forces can be van der Waals' forces, electrostatic forces, or chemical-bonding forces. The summation of all interfacial and intermolecular forces between the two bodies is the maximum force per unit area and is referred to as basic or theoretical adhesion. For practical purposes, basic adhesion is never obtained. Thus, the experimental or practical adhesion which represents the forces of work needed to disrupt adhering systems is utilized.[23,24]

Practical adhesion can be measured either in terms of force or work (energy). In terms of forces, adhesion is the maximum force per unit area exerted when two materials are separated. In terms of work or energy, adhesion is the work exerted to separate or detach two materials from one another. Regarding coatings, the bonding between polymeric coatings and substrates can be viewed as a union of two connecting phases, one a solid and the other a liquid that solidifies to form a thin film. The separation of the two phases is expressed by the work of adhesion

$$W_a = Y_1 + Y_2 - Y_{1,2} \qquad \text{(Eq 1.4)}$$

where W_a is the reversible work of adhesion, and Y_1 and Y_2 are the surface tensions or specific surface free energies of the two phases, *i.e.*, coating, and substrate.

The total force of adhesion F_{12} can be related to the work of adhesion W_a, by

$$W_a = \int F_{12}\,(x)dx \qquad \text{(Eq. 1.5)}$$

Equation 1.5 relies on assumptions about the changes in force with separation x, where the distance x is molecular dimensions. If the break occurs at the interface 1 and 2 then it is termed adhesive failure and if it occurs within 1 or 2 then it is a cohesive failure.[25]

Since adhesion relies on the formation of specific bonds at the phase boundary of two bodies, it is essential to ensure good wetting of the coating to the substrate. For optimum wetting to occur the surface free energy of the coating material must be lower than the surface free energy of the substrate.[23]

Adhesion measurement is performed using a battery of different test methods. However, due to the complexities of the adhesion process, no test exists that can precisely assess the actual physical strength of an adhesive bond. For an adhesion test to warrant large-scale acceptance, a few criteria must be met, including the use of a straightforward and unambiguous procedure, relevance to its intended application, reproducibility, and quantifiability, including a meaningful rating scale for assessing performance.[20] Within the paint and coating industry, several testing methods meet test criteria, including, ASTM D3359, Standard Test Methods for Measuring Adhesion by Tape Test; ASTM D2197, Test Methods for Adhesion of Organic Coatings by Scrape Adhesion; ASTM D6677, Test Method for Evaluating Adhesion by Knife; ASTM D5179-16, Standard Test Method for Measuring Adhesion of Organic Coatings in the Laboratory by Direct Tensile Method, and ASTM D4541-17 Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Tester.

For this work, ASTM D4541-17 Standard Test Method for Pull-Off Strength of Coatings Using Portable Adhesion Tester will be the primary adhesion evaluation method utilized. ASTM D4541-17 contains procedures for assessing the pull-off strength/adhesion of coating systems to metal substrates. Using this method, two factors can be determined: i) the maximum normal force (tension) that the surface area can withstand before the material can be detached from the substrates, and ii) whether the surface is intact at a given force (pass/fail). Failure will occur along the weakest plane in the system and is exposed from the fracture surface. The materials needed for this test are a test fixture (aluminum dolly), an adhesive (2K epoxy), a coating system, and a substrate. Measurements are limited by the strength of the adhesive bond between the loading dolly and the sample surface or the cohesive strength of the substrate. The test is performed by attaching the dolly perpendicularly to the surface of the coating with an adhesive. After the adhesive is fully crosslinked, the test equipment is attached to the loading fixtured and oriented to apply tension perpendicular to the test surface. The force is then gradually increased and monitored until either failure occurs, or the predetermined value is reached. The nature of the failure is evaluated as the percentage of adhesive or cohesive failure. The actual interfaces and layers involved in the failure are identified. Pull-off strength is calculated based on the indicated maximum load, instrument calibration data, and the original surface area stress. The pull of strength is recorded, and each sample is evaluated as follows: A = Adhesive failure of the coating from the substrate, C = Cohesive failure in the coating, AC = Combination of adhesive failure at the coating/substrate interface and cohesive failure in the coating, S = Adhesive failure at the stud, and CS = Combination of adhesive failure at the stud and cohesive failure in the coating.[26]

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CHAPTER 3. LITERATURE REVIEW

In the development of a multi-substrate primer, the primer must have superior adhesion to multiple substrates as well as flexibility and toughness; thus, the traditional spray epoxy primer would need to be modified and improved upon to meet required specifications.

The mechanical and physical properties of coatings affect their performance. A coated substrate is regularly exposed to several types of mechanical or physical stressors caused by impact, harsh environment, or changes in substrate dimensions. These stresses can damage the film and reduce its service life. Therefore, it is important that the coating has a desirable balance of mechanical properties including impact strength, flexibility, hardness, adhesion, and toughness to meet the service requirements of a particular application. For a primer to be utilized for multi-substrate surfaces, the coating must be flexible enough to compensate for dimensional changes of various substrates due to temperature and humidity fluctuations and must adhere to said substrate to provide adequate barrier performance.[20,27,28]

Flexibility and toughness represent the coating's ability to withstand a variety of loads. Flexibility is the ability of the coating to bend and flex without cracks or undergoing other forms of failure. Flexibility is resistance to damage to the coating when the substrate and coating are deformed. Toughness is the ability of a coating to withstand large loads in a short period without cracking, breaking, or shearing. A multi-substrate primer must be flexible and elastic enough to bend a high amount of stress but tough enough to withstand a great amount of strain in a short time frame. Flexibility, toughness, and other mechanical properties are inconsequential without proper adhesion.

Adhesion, the bond between two dissimilar bodies, is the most essential property of a coating. It is imperative that the coating remains intact and adhered to the surface for extended periods especially under harsh conditions to provide protection. The quality of adhesion is related to the durability and quality of the coating. To serve as a universal primer for multi-substrate application a primer must adhere to the various substrates of interest.[20]

Strategies for Improving Flexibility and Toughness

Modification of polymeric coating systems can be accomplished by a variety of methods. The most common method is the introduction of additives. Historically, liquid rubbers are the most common class of additives utilized the improve the flexibility of epoxide coatings. Before reviewing the literature, it is worth noting that the bulk of the work done on improving the flexibility of epoxy resin focuses primarily on composite and adhesive end usage as opposed to coating. Thus, toughening of the resin was a greater priority compared to flexibility; however, the two properties are so intertwined that they are used interchangeably within the literature. As mentioned earlier, crosslinked epoxy tends to be brittle due to its high crosslink density and rigid network formation. As the functionality of epoxy resin increases properties such as hardness and barrier performance increase. However, the brittleness of the resulting polymer network rapidly decreases toughness and flexibility. In contrast, as the crosslink density is reduced, the molecular weight between crosslinks increases, thereby increasing the overall network mobility and flexibility.

Liquid Rubbers

Frist initiated at the B.F. Goodrich Company and reported by McGarry[29], the addition of liquid rubber is one of the most successful and well-established methods of toughening and improving the flexibility of epoxy resin. Several classes of liquid rubber have been investigated; however, butadiene-acrylonitrile-based rubbers remain the primary toughening agent for epoxies, among which carboxyl-terminated butadiene-acrylonitrile (CTBN) has been most widely used.

Other common members of the butadiene-acrylonitrile-class include amino-terminated butadiene-acrylonitrile (ATBN), epoxy-terminated butadiene-acrylonitrile (ETBN), and vinyl-terminated butadiene-acrylonitrile (VTBN)[30].

In the early 1970s, McGarry *et al.* conducted a series of experiments utilizing CTBN copolymer to modify DGEBA epoxy cured with 2,4,6-tri(diethylaminomethyl) phenol (DMP). They were able to demonstrate that the incorporation of CTBN resulted in an eight-fold increase in fracture toughness of modified epoxy at the optimum rubber content (about 10 parts per resin. In a typical preparation process, CTBN is added to the epoxy resin to create a homogenous solution[29]. After the addition of the curing agent, as crosslinking occurs, and the molecular weight starts the increase, the rubbery phase precipitates out of the matrix forming particles within the epoxy network. During this phase separation, the carboxyl acid on the CTBN reacts with the oxirane rings of the epoxy resulting in a strong covalent bond between the two phases. The interfacial bond between the particles and the matrix is necessary to achieve improved toughness.[31–33,34]

Several factors influence the toughening performance of CTBN including miscibility with the epoxy resin, epoxy type, molecular weight of epoxy, and concentration of acrylonitrile on CTBN.[35] CTBN is more miscible with epoxy having similar solubility parameters. For optimum toughening, the solubility parameter of the liquid rubber and epoxy resin should be similar enough for ease of dispersion of the rubber but different enough to ensure phase separation occurs.[36] Changes in the molecular weight of the epoxy and lower acrylonitrile concentration led to changes in solubility parameters and miscibility gap. A lower concentration of acrylonitrile (AN) leads to poor miscibility while a higher concentration yields better miscibility and performance. However, optimum toughening was observed for CTBN containing

12% to 18% by weight acrylonitrile which led to a particle size between 1.5μ and 2 μ. Increasing the AN content beyond this range usually resulted in rubber particles too small for toughening purposes. As the concentration, miscibility, and the AN content increase, the morphology of the rubber-epoxy matrix transitions from bimodal to a single-phase, at which point the rubber transitions from a plasticizing (or toughening agent) to a flexibilizer.[37] It has been suggested that in rubber-toughened epoxies small rubber particles promote shear banding whereas large particles are responsible for crazing.[29,33,38,39] Cavitation of the rubber particles produce microviods during ductile stable crack growth. These voids are then filled with rubber.[39,40]

After the initial success of CTBN, other acrylonitrile liquid rubbers with amine and epoxy functionality were investigated for their toughening effect. Limited work had been conducted on the effect of ATBN starting in 1987 by Kunz *et. al* in which they investigated and compare the toughening effect of ATBN and CTBN as well as their morphology; disperse phase composition, size distribution, and particle/matrix interface. CTBN and ATBN produces identical toughness values at similar concentrations, however, rubbery particles were not as distinct in ATBN-modified epoxies compared to the sharp boundaries of CTBN particle interfaces. The ATBN particle appears to diffuse within the matrix of the epoxy, especially at higher concentrations (*i.e.*, 15 pwb.) This phenomenon was attributed to the irregular shape of the ATBN particles compare to the spherical CTBN particles. In 2000 Wise *et al.* compared the effects of CTBN and ATBN on the curing carboxyl end groups of CTBN strongly enhanced the curing rate while ATBN impeded the reaction.[41] Chikhi *et al.* used liquid ATBN containing 16% AN to toughen DGEBA epoxy cured by polyaminoimidazoline. They found that the addition of ATBN led to an increase in the elongation at break and Izod impact strength. The tensile modulus however decreased slightly with increasing ATBN content.[42] The morphology of

ATBN modified epoxy is strongly influenced by the cure temperature, and either single or double phase morphology can be obtained displaying different mechanical behavior. The cure conditions are more important than the amount of rubber.[43] ATBN contributes to adhesive strength.14,[44] Unfortunately, Unlike CTBN, the toughening effect of ATBN has not been studied as well in the epoxy system, thus, the body of literature is sparse.

ETBN is another liquid rubber of great interest. Manson *et al.* showed that epoxies toughened with ETBN with acrylonitrile content of 26% resulted in a threefold increase in impact strength, but only a 60% improvement in fracture toughness. Furthermore, ETBN demonstrated better compatibility with the epoxy resin. Due to the improved compatibility, the rubber particles formed were too small (0.16-0.3 pm) to promote toughening mechanism on par with CTBN; however, improved flexibility is expected. Verchere *et al.* further expanded on the ETBN mechanism by incorporating within a DGEBA-based epoxy system cured with a cycloaliphatic diamine. They were able to demonstrate the inclusion of ETBN in gelation and that phase separation takes place well before gelation and vitrification resulting in rubber remaining in the continuous phase of the polymer matrix rather than completely phase separating.[45] Due to their homogenous mixture with epoxy resin, ETBN can impart more flexibility without sacrificing toughness as demonstrated by Zhao *et al.* when they observed 2.3 and 1.6 times increases in impact strength and tensile strength, respectively, and z 4 times increase in elongation at break compared to neat epoxy.[46–48]

Another series of liquid rubber that are of interest are functionalized polybutadiene rubber. HTPB (Hydroxyl-terminated polybutadiene) is a liquid polybutadiene rubber with hydroxyl end groups, which could be used to improve the toughness of epoxy resins. However, HTPB has poor compatibility with epoxy resins.[49,50] To improve compatibility with epoxy resin, both HTPB and epoxy resin should be chemically bonded to each other. Functionalization of HTPB via epoxidation is an effective method of improving compatibility as the introduction of epoxy groups into the double bonds of HTPB increases the miscibility with epoxy resin, thereby leading to phase separation of rubber domains in the epoxy matrix resulting in toughening and flexibility effect.[51,52] Kaynak *et al.* performed a series of experiments utilized a silane coupling agent to enhance the interaction between HTPB and epoxy resin resulting in increased tensile strength, plastic deformation, and a Charpy impact tests result of 44% increase in impact strength with the addition of 2% SCA and 1% HTPB.[53–55] Functionalization of HTPB has been another successful method of increasing compatibility with epoxy.

Epoxidized hydroxyl-terminated polybutadiene (EHTPB) was utilized by Latha *et al.* to improve the compatibility and mechanical properties of epoxy resin. Lap shear strength and T-peel strength were observed to increase with increasing EHTPB content, indicating both an increase in toughness and flexibility as well as adhesion. Maximum lap shear strength and peel strength occurred at EHTPB content of about 10 parts per 100 parts epoxy resin (phr). At higher EHTPB content, a decrease in toughness and an increase in flexibility were noted due to the rubber phase becoming continuous;[51] Zhou *et al*. corroborated these results.[56] Barcia *et al.* prepared an epoxide end capped HTPB by first reacting HTPB with an appropriate amount of toluene diisocyanate (TDI). The isocyanate end capped HTPB (ITPB) was then reacted with the epoxy resin to form a block copolymer. This method is known to improve the miscibility and achieve more stable dispersed particles of diol compounds during the preparation of polymer networks. The addition of these rubber components leads to improve flexibility, impact performance, lower T_g, at a proportion up to 10 wt % when compared to the neat, cured resin.[30,49] Carboxyl-terminated polybutadiene (CTPB) liquid rubber was shown to improve the toughness of epoxy rubber at 20 phr, above that level, a fall in the strength and modulus was observed.[57,58] Amine-terminated polybutadiene have also shown great flexibility and toughening effect a up to 15 phr.[59,60]

Other rubbers including liquid rubber obtained from pyrolysis of scrap rubber,[61,62] hydroxyl-terminated liquid nitrile rubber,[63,64] liquid natural rubber,[65–67] recycled car tire rubber particles,[68] and acrylate liquid rubber,[34,69,70] have also shown promise as potential toughening and flexibilizing agents. The incorporation of nano and micro fillers in conjunction with liquid rubber particularly ABTN and CTBN has also been investigated and shown great promises as potential candidates for improved toughness,[71–79] however are not known to impart flexibility and, thus, the use of inorganic filler goes beyond the scope of this paper.[80–82]

Thermodynamics and chemistry aid in determining the final properties of the rubber-epoxy blends. The balance between phase separation and polymerization establishes whether dilution, phase separation, or even phase inversion will occur. The toughening effect and mechanism of all liquid rubber are depended on particle size and particle size distribution. Determining the optimum liquid rubber and particle size for a particular epoxy and crosslinker system is challenging because changing one parameter of the systems heavily influences the phase separation mechanism which affects the toughening mechanism. This balance is primarily affected by the degree of compatibility between the rubber and the epoxy, the amount of rubber present in the sample, and the epoxy resin curing cycle.[83–85]

Toughening and flexibilization are interrelated processes. When rubber modifiers remain fully miscible within the polymer resin, they act as flexibilizer rather than a toughening agent. The dissolved rubber increases the matrix ductility but reduces the level of stress at which shear bands initiate. Since the rubber modifiers do not phase separate when the flexibilization effect is observed, the process of energy dissipation and crack propagation of the modified epoxy is different. However, toughening and flexibilization effects can occur simultaneously as noted above in systems where phase separation did not occur, but impact strength and modulus were increased.[86,87] This phenomenon normally takes place when the reactivity of the functional groups is too high.[49,84,85]

Thermoplastics Modifiers

Blends of ductile thermoplastics have widely been used with thermoset resin to improve flexibility and toughness. Several types of thermoplastics, such as poly (ether sulfone) (PES), polysulfone (PSu), poly (ether imide) (PEI), and poly (ether ether ketone), have been explored for the modification of epoxy resins.[88]

Poly (ether sulfone) resins possess excellent mechanical properties, high thermal stability, and high T_g. It is expected that the inclusion of a reactive end group (*i.e.*, hydroxyl end group) to polyethersulfone will lead to a chemical reaction during the curing of epoxy resin and thus modify the system by copolymerization of two components. Thereby, providing excellent toughness and flexibility for epoxy resins. In contrast, Raghava *et al.* found that the addition of low molecular weight hydroxyl-terminated PES into a trifunctional epoxy-anhydride system resulted in a two-phase bimodal particle distribution morphology, but low elongation and low fracture toughness.[89] Bucknall *et al.* corroborated the findings of Raghava, however, they observed both single and double phase morphology depending on the hardener.[90]

It was hypothesized that PES might decrease the cross-link density of cured resin by blocking reaction sites on epoxy resulting in increased flexibility at the expense of toughness. Too much flexibility can reduce shear banding within the polymer matrix leading to an elastomeric type of material.[90] Hedrick *et al.* were able to improve toughness with the addition of poly (arylene ether sulphone) however, minimal changes in flexibility parameters were observed.[91] Jiang *et al.* were able to produce a highly flexible but tough polymer by using hydroxyl-terminated PES as a crosslinking agent for epoxy resins.[92] Amine-terminated poly(arylene ether sulfone)–carboxylic-terminated butadiene-acrylonitrile–poly(arylene ether sulfone) (PES-CTBN-PES) tri block copolymers with molecular weight of 15,000 or 20,000 g/mol were synthesized and incorporated into a epoxy4 ,4-diaminodiphenylsulfone system at loading of 5-40 wt%. High fractural toughness and flexural modulus was observed compared to samples modified by PES/CTBN blends, PES oligomer, or CTBN. The performance of the copolymer was ascribed to ductile fracture of the continuous PES-rich phases, as well as the cavitation of the rubber-rich phases.[93]

Polysulfone was also investigated as a modifier for epoxy due to its high toughness, modulus, T_g, thermal, and chemical resistance.[94] Huang *et al.* incorporated a bisphenol-A functional PSu into DGEBA epoxy-diaminodiphenylmethane (DDM) system. Scanning Electron Microscope (SEM) observation revealed that the modified matrix was homogeneous. Both tensile and flexural properties of were slightly improved compared to those of the unmodified resin. Fracture toughness (K_{IC}) and fracture energy (G_{IC}) were increased by 20%.[94] Jin *et al.* observed an increased toughness but decreased flexural strength by incorporation of polysulfone.[95]

Blends consisting of PEI and trifunctional epoxy cured in the presence of 4,4'-diaminodiphenylsulphone resulted in two-phase morphology as well as improved flexibility (flexural strength, flexural modulus, and strain at break) and fracture toughness properties (K_{IC} and G_{IC}). Phase inversion did occur at PEI content above 15 wt.% of 30 phr, however, no significant correlation between fracture properties and the morphological changes was observed.

However, a substantial increase in toughness was observed when PEI forms the continuous phase.[38,90,96] Similar performance was observed with phenylmaleimide (PMI)-styrene (St) alternating copolymers.

A range of microstructures could be obtained by controlling the cure temperature, thermoplastic content, molecular weights of the epoxy resins, as well as curative. It is frequently observed that at high enough thermoplastic content, the morphologies of the epoxy matrix change from bimodal to phase inversion to co-continuous phase. Toughening is achieved by the absorption of fractural energy due to ductile drawing and tearing of the thermoplastic continuous phase. Furthermore, flexibility parameters such as flexural strength and modulus can be increased along with thermoplastic concentration and toughness.[88,97–99]

Polysiloxane

Polysiloxanes are a great candidate for flexibility modifiers for epoxy resin due to their highly flexible backbone of Si-O-Si, low glass transition temperature, excellent thermo-oxidative stability as well as low surface tension, and good weathering ability. However, due to the chemically inert nature of pure PDMS, there is extremely poor compatibility between the soft segment of the PDMS and the polar hard segment of the epoxy resin. To overcome the thermodynamic incompatibility of polysiloxane with epoxy resins by conventional mixing method, various methods have been developed, including using silane coupling agents as well as the introduction of functional groups, such as hydroxyl, amino, epoxy, and isocyanate onto PDMS to form an interpenetrating network (IPN).[100] Epoxy-miscible compounds were grafted into polysiloxane to improve miscibility. Block polymer has also been used as well as the sol-gel method to bridge the polysiloxane and epoxy phases.[101–103]

Unfortunately, the inclusion of pure low molecular weight silane coupling agents into an epoxy amine polymer network as flexibilizing agents has demonstrated unfavorable results, higher glass transition temperature and higher cross-linked density have been observed signifying a reduction in flexibility.[104] The deficient performance of these silane compounds is attributed to small molecular weight. Morita *et al.* showed that the flexibility of polymer increases with the presence of increasing siloxane chain length after preparing difunctional epoxy siloxane monomers containing disiloxane, trisiloxane, and tetrasiloxane by hydrosilylation of an α, ω-difunctional Si-H-terminated siloxane with a vinyl-functional epoxide.[105]

A favorable improvement in flexibility was also observed by the introduction of the epoxy miscible functional group onto polysiloxane additives. To investigate the effect of siloxane/epoxy coating systems Ahmad *et al.* modified DGEBA epoxy with hydroxyl-terminated poly dimethyl siloxane (HPDMS) through ring-opening addition polymerization reaction in presence of catalytic phosphoric acid. The modified resin was crosslinked with a polyamide curative and formulated with TiO_2, Fe_2O_3, and lemon chrome pigments. A tremendous increase in the impact resistance values of the siloxane-modified paints (350 lbs/in) compared to that of net paint (126 lbs/in) was noted. The unusually high flexibility (higher impact resistance) and bending ability of the modified coatings are due to the presence of Si-O-Si.[106] Ma *et al.* were also able to demonstrate enhanced impact resistance by the introduction of a novel polyether-grafted epoxide polysiloxane (FEPMS) to epoxy resin. FEPMS was synthesis via hydrosilylation. SEM micrographs indicated that FEPMS-modified epoxy resins formed a phase-separated fine structure morphology, which correlated well with the changes of the impact resistance.[101] An epoxypropoxypropyl terminated polydimethylsiloxane (DMS-E09) blended with a commercial DGEBA epoxy resin, using methyl tetrahydrophthalic anhydride as a curing agent in the presence of the accelerator N, N-dimethyl benzylamine demonstrated lower T_g implying increase elasticity and flexibility. Hanoosh *et al.* prepared a novel interpenetrating network between the epoxy resin and different weight percentages of PDMS in the presence of tetraethoxysilane (TEOS) and triethylenetetra amine (TETA). Optimum toughness performance was achieved at 5 wt% PDMS as shown by tensile strength. Flexibility increased proportionally with PDMS content.[107]

Copolymerization of epoxy and siloxane has shown great promise in improved flexibility. Bregstrom *et al.* developed an amino-functional silicone resin to toughen epoxies which, when preerected with the epoxy at elevated temperature, undergoes in-situ phase separation during final epoxy curing. The silicone modified epoxy resulted in improve fracture toughness of 250-400% and T_g of the modified epoxy.[108] A series of epoxy-silicone copolymers were prepared from methyl phenyl silicone intermediates (PMPS) with a bisphenol A type epoxy resin (E-51) by condensation with dilaurate dibutyltin acting as catalyst showed increased impact resistance with PMPS content and phase-separated morphology.[109] A novel imide ring and siloxane-containing cycloaliphatic epoxy compound 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido)propyl]tetramethyldisiloxane (BISE) synthesized by Tao *et al.* exhibited good mechanical properties with the flexural strengths of 63–82 MPa and tensile strengths of 31–33 MPa. The flexibility of the polymer system was credited to the low glass transition temperatures due to the presence of flexible propyl and siloxane segments in the epoxy backbone.[110] Silicone-modified polyurethane-epoxy resulted in a singular T_g signifying homogenous phase morphology. The flexible urethane linkages and free rotation of the Si–O–Si linkages resulted in reduced T_g values.[111] A siloxane-containing curing agent was synthesized from epoxy-terminated siloxane oligomer (ETSO) and 4,4′-diaminodiphenyl methane (DDM) with a hot-melt method. The flexibility impact strength was increased with increasing ETSO context however, flexural modulus was compromised.[112]

Overall, polysiloxane demonstrates great promise as a modification method for improved flexibility of epoxy resin system, however, compatibility is still a great challenge. Ensuring that the silicone additives are miscible within the epoxy system either requires the synthesis of novel compounds or modification of the epoxy or silicone resin and additives. The use of novel compounds, as well as the need for energy and time-consuming chemical reactions for improved miscibility, makes most method of incorporation of siloxane compounds to epoxy resin system unfeasible for commercial application.

Other Additive Classes

Rubber

Utilizing conventional epoxidation reaction and Rh(I)-catalyzed hydrosilylation Januszewski *et al.* were able to successfully modify epoxy resin with reactive epoxidized polybutadiene-based functionalizing agents. Microscopic techniques, thermogravimetric analysis, differential scanning calorimetry, and nanomechanical analysis were used to examine the synthesized material. It was shown that the type of modifier along with content heavily influenced the microstructure of the resins, and subsequently mechanical performance. A decrease in hardness and modulus was observed compared to neat epoxy. However, thermal stability was not impacted, implying that the viscoelastic properties of the resin can be modulated without affecting its thermal stability.[113]

Polysulfide

Polysulfide oligomers are great candidates for flexibilization for epoxy resins. These polymers are mercaptan-terminated saturated elastomeric chains prepared from bis(2-

chloroethyl)-formal and crosslinked with trichloropropane. Excess epichlorohydrin is often employed in the reaction resulting in epoxide terminated groups. The flexible disulfide bond of these polymers introduces soft segments within the epoxy matrix allowing for low glass transition temperature and rubbery behavior. The mechanism by which polysulfide improves the flexibility or toughening of epoxy depends on the mixing sequences. In one-step mixing process, the polysulfide additive, epoxy and crosslinker are mixed in a noticeably brief time leading to the formation of block copolymer consisting of soft polysulfide and hard epoxy segments. The phase morphology leads to more of a toughening effect as observed with liquid rubber. In contrast, in a two-step mixing process, the polysulfide and epoxy are premixed followed by the addition of the curing agent leading to the forming an intermediate oxirane-terminated flexible polyether. This prepolymer is later cross-linked with the hardener forming a continuous phase morphology resulting in moderate strength but high elongation and flexibility.[114–116] Other factors such as polysulfide type, molecular weight, curative type, curative amount, and curative schedule all influence the mechanism of polysulfide/epoxy systems thus it is imperative to investigate the effect of each system.[117] Nano and micro inorganic fillers have also been incorporated in epoxy polysulfide modified system to improve flexibility and toughness with varying degrees of success.[82,118,119] Thiokol has also shown promise as flexibilizing agent for epoxy system.[120–123]

Polyether

Modification of epoxy with polyether has gained traction over the years. Polyethylene glycol diamine (PEG-amine) and polypropylene glycol diamine (PPG-amine) also known as Jeffamines® represent the most industrially produced Polyetheramines. [124,125] Notable work includes that of Yang *et al.*, in which diethyl toluene diamine cured DGEBA epoxy resin was modified with two flexible diamines (Jeffamine D-230 and D-400), and the cryogenic mechanical behaviors of the modified epoxy resins were studied at cryogenic (77 K) and room temperature (RT). The results show that the addition of flexible diamines improves the elongation at break and impact strength at both RT and 77 K. The addition of the lower molecular polyetheramine, D-230, required between 21-78 wt% to show simultaneous improvement in strengthening and toughening DGEBA epoxy resins at both RT and 77 K, while the higher molecular weight additive D-400 requires only 21 wt% to show similar enhancement. As expected with the improvement in flexibility, differential scanning calorimetry (DSC) analysis shows a decrease in T_g with an increase in polyetheramine content. Interestingly, unlike the liquid rubber, both SEM and the presence of a signal T_g peak showed that the modified resin had a homogeneous phase structure.[126] McAninch *et al*. observed similar pattern.[127] A DGEBA/diethylenetriamine system was modified with polyetheramine, polyethylene glycol diamine, and polypropylene glycol diamine (PPG- amine) at two different molecular weights (*i.e.*, 200 and 400 g mol^{-1}). The higher molecular weight PEG-amine has the best performance on critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}) of the epoxy, which have an increase up to 82 and 294%, respectively. The overall performance of the higher PEG is due to a high flexibility index, longer change length, and higher secondary interactions. SEM was utilized to demonstrate that the polyetheramine has a homogenous structure.[124]

Lou *et al.* synthesized a series of imidazole (MI) blocked 2,4-toluene diisocyanate (TDI) with polyethylene glycol (PEG-400) as soft segment (PEG-MI-*b*-TDI). An optimum content of PEG (molar ratio of OH was 1% of NCO) into the epoxy resin offered higher toughening and impact strength than those of the neat MI and MI-*b*-TDI cured epoxy resins. Toughness was improved without sacrificing the tensile shear strength. Furthermore, the long soft chains of the PEG resulted in lower T_g denoting better flexibility.[128]

Shao explored hydroxyl functional polytetrahydrofuran (pTHF) as a toughening modifier in the epoxy-cured methyl tetrahydro phthalic anhydride system. DMA data showed that pTHF reduce the T_g of the cured material while increasing toughness and flexibility as suggested by the increase in impact strength, flexural strength, and flexural modulus. At 8 wt % epoxy resins, pTHF resulted in the maximum tensile modulus of 201.3 MPa compared to the 71.1 MPA of the neat epoxy. The maximum flexural strength of 125.6 was reached by the incorporation of 16 wt % pTHF compared to 92.5 MPa of the neat epoxy.[129] Carboxyl terminated pTHF have been investigated and show great promise as flexibilizing agent.

The flexibilizing effect of pTHF and other polyethers as additives to epoxy-amine substrate bonded coating systems has not been fully investigated.[126]

Others

Strzelec *et al.* utilized novel mercaptan-terminated polythiourethane hardeners in the presence of diamine co-reactant to improve the flexibility, tensile strength, and impact toughness of epoxy resins. A homogeneous matrix was formed. An increase in flexibility was attributed to the presence of the aliphatic polyether chains that separated the rigid aromatic rings of the epoxy molecules and provided greater degrees of freedom for the chains. Thus, a decrease in the T_g values of the mercaptan modified resins was observed. Higher percentages of polythiourethanes resulted in extremely flexible rubber-like material. With ratios lower than 50 phr of polythiourethane, resilient impact resistant epoxy materials were prepared.[100,130]

Two types of hydroxyl-terminated polyester resin (Desmophen 800 and 1200) were used by Harani *et al.* as modifiers for epoxy resin. The impact strength increased with Desmophen content and reaches a maximum value of 7.65 J/m at 10 phr for Desmophen 800 and 9.36 J/m at 7.5 phr for Desmophen 1200, respectively. At a critical concentration (7.5 phr), Desmophen

1200 demonstrated better results with a fracture toughness of 2.41 MPa compared to 0.9 MPa of the unmodified epoxy. The intensive hydrogen bonding between the epoxy and Desmophen 1200 may contribute to the toughness performance.[131] An IPN was produced by grafting Desmophen 1200 into an epoxy-urethane prepolymer. Compared to virgin resin, the effect on the mechanical properties of the IPN was minor with a slight increase in impact strength. The incorporation of a chain extender, TDI, within the prepolymer produced a drastic improvement in toughness reaching a maximum value (seven-fold that of virgin resin) at a modifier critical concentration (40phr).[132]

Diglycidyl ether of diethylene glycol modified epoxy showed increased impact toughness and elongation of break with increasing loading. A single-phase morphology was observed.[133]

Hyperbranched

Varley *et al.* reported on the use of an epoxidized aliphatic polyester hyperbranched polymer (HBP) as a modifier for epoxy anhydride resin system. At additive level ranging from 0 to 20 wt%, the HBP can almost double the fracture toughness, with little evidence of any deleterious effects upon processing and the durability of the cured resin system.[134]

Another non-chemical method of improving flexibility has been investigated including processing method such as reactive encapsulation of solvent/drying a method in which epoxy curing was conducted in the presence of varying amounts of inert small-molecule solvent, followed by a drying/annealing process in which the solvent was removed.[135] While these techniques have been successful, they go beyond the scope of this paper, as the focus of our epoxy coating relies on traditional application techniques.

Strategies for Improving Adhesion

Adhesion is the most important property in barrier protection of substrates by organic coatings. In the development of a multi-substrate primer, it is important to enhance adhesion to improve upon the barrier properties of the coating for both metallic and nonmetallic surfaces. Adhesion promoters are materials used to form a primary bond with a substrate or a coating for the specific purpose of improving adhesion. The adhesion promoter can either be utilized as a pretreatment to the substrate, incorporated within the coating formulation or in a combination of the two methods. Historically, chromate or phosphate compounds were heavily utilized as an adhesion promoter for metallic surfaces, however, due to their toxicity, carcinogenic nature, and health risk of chromate (VI), environmental regulations have limited their use. In the search for more ecological alternatives to chromate adhesion promoter, coupling agents such as titanates, zirconates, silanes, phosphates, zircoaluminates, thiones, and thiol has emerged as a potentially valuable alternative, however, silane coupling agents remains the most promising adhesion promoter.[136–138]

Silane adhesion promoters are organic-inorganic silicone compounds that offer stable adhesion to a broad range of coating systems as well as corrosion protection of various metal substrates. Structurally, silanes are comprised of an organofunctional group (-SH, -OH, -NH), alkene linker, silicon atom, and hydrolyzable group (alkoxy or acyloxy). Organofunctional groups are selected based on the chemistry of the organic molecules, *i.e.*, coating, to be bonded to the substrate. The general mechanism to enhance adhesion involves four steps: (i) hydrolysis of alkoxy or acyloxy leading to the formation of a highly reactive silanol (-S-OH), (ii) condensation of the silanol with other silanol oligomers, (iii) hydrogen from oligomeric silanol bonds with hydroxide group on the surface of the substrate, and (iv) covalent linkage is formed with the substrate by dehydration reaction.[137,139]

Silanes have been utilized on various metallic substrates including aluminum and aluminum alloys, copper, steel, zinc, galvanized and electro-galvanized steel, and magnesium alloys.[140] As mentioned earlier, silanes can be utilized as pretreatment for adhesion and corrosion enhancements and/or incorporated into a coating system. To be effectively implemented as a pretreatment, a hydroxide group must be presence on the substrate, limiting its use on composites which are chemically inert. Thus, for this review, only the literature focusing the use of silanes as an additive within an organic coating system will be highlighted. Unfortunately, extraordinarily little has been published on the use of silane as adhesion promoters in coatings. Only amine functional silane coupling agents have consistently demonstrated improved adhesion to Al and Fe substrate. The performance of silane adhesion promoter is depended upon orientation of the alkoxysilane group onto the substrate which is difficult to achieve within a heterogeneous coating system. However even in uncontrolled orientation, the inclusion of amino functional silane can lead to a three-fold increase in adhesive strength between epoxy and metal substrate.[141]

Another method of improving the adhesive strength of polymeric material is by chemical modification. Early work by de Bruyne demonstrated the importance of hydroxyl groups in determining the adhesive strength of epoxy to metallic surfaces. Hydrogen bonding between the hydroxyl group present on the epoxy and metal oxide surface results in improved adhesion of epoxy to metallic substrate.[142] By altering the OH content or either the epoxy resin or metallic substrate, a significant increase in interfacial adhesion is observed.[143]

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CHAPTER 4. MODIFICATION OF BISPHENOL-A EPOXY WITH LIQUID RUBBER FOR IMPROVED FLEXIBILITY AND ADHESION

Introduction

Weight reduction has been a major motivator of innovation in the watercraft, aerospace, and automotive industries. As a result, the use of composite materials within these structures has risen. Usage of composites such as fiberglass reinforced polymer and carbon fiber reinforced plastics provide significant advantages including reduced fuel consumption, improved efficiency, fatigue resistance, reduced direct operating costs, and corrosion resistances.[2,144–146] Furthermore, it is easier to achieve smooth aerodynamic profiles for drag reduction and complex double-curvature parts for aircraft. Due to the plethora of advantages offered by composites, current generations of aircraft have slowly reduced the use of metal in favor of composite. For example, the Boeing 787 is comprised of 50% composite (carbon fiber reinforced plastics, fiberglass reinforced polymer), 21 % aluminum, 15% titanium, 10% steel and 5% trace material.[147] The continued use of mixed material structures has led to the need for coating systems with adequate flexibility,[7,13,148] adhesion,[9–11] and barrier performance[8] of multi-substrates, namely carbon fiber reinforced plastics, fiberglass reinforced polymer, aluminum, and steel. Epoxy resins are a prime candidate for a multi-substrate coating system.

Epoxies are a class of high-performance thermosetting polymers known for exceptional adhesion, high modulus, and barrier performance. They are also commonly used as primers for a variety of applications including automotive, aerospace and watercraft. Unfortunately, epoxy resin is quite brittle.[20] Thus, for the use as a universal coating system for multiple substrates greater adhesion and higher degree of flexibility is required. The flexibility of epoxy resins can be improved by changing the network density, specifically by increasing the molecular weight between chain junctions. This can be accomplished by the introduction of long chain molecules within the polymer matrixes.

Originally reported in the scientific literature by McGarry *et al.* in 1968, the addition of liquid rubber is one of the most successful and well-established methods of toughening and improving the flexibility of epoxy resin. Incorporation of low molecular weight carboxyl-terminated acrylonitrile-butadiene rubber (CTBN) within different DGEBA epoxies treated with piperidine (PIP) resulted a two-phase microstructure and a ten-fold increase in fracture toughness.[29,33] Following CTBN's initial success, researchers investigated alternative acrylonitrile liquid rubbers with amine and epoxy functionality for their toughening properties.

In 1982, Kunz *et al.* researched and compared the toughening impact of CTBN, and amino-terminated butadiene-acrylonitrile (ATBN) as well as their morphology, disperse phase composition, size distribution, and particle/matrix interaction. At similar concentrations, CTBN and ATBN yield similar toughness values; however, rubbery particles in ATBN-modified epoxies were not as distinguishable as sharp CTBN particle interface boundaries. The ATBN particles appears to diffuse into the epoxy matrix, particularly at greater concentrations (*i.e.*, 15 pwb.). This was credited to the ATBN particles' irregular form compared to the spherical CTBN particles.[149] Wise *et al.* examined the effects of CTBN and ATBN on the curing mechanism of epoxy and amine, finding that CTBN had a catalytic effect, accelerating the reaction rate while ATBN slowed down the reaction by either dilution effects or changes in dielectric contact of the reaction medium.[41] To toughen DGEBA epoxy cured by polyaminoimidazoline, Chikhi *et al.* employed liquid ATBN containing 16% AN. They discovered that adding ATBN to the mix increased elongation at break and Izod impact strength. However, as the ATBN content increased, the tensile modulus reduced slightly.[42]

The competition between phase separation and cure rate has a substantial impact on the morphology of ATBN modified epoxy. Single or double phase morphologies can be achieved with varied mechanical properties.[150] Unfortunately, unlike CTBN, the toughening impact of ATBN in the epoxy system has not been explored as thoroughly, resulting in a paucity of research.

Functionalized polybutadiene rubber is another type of liquid rubber of great interest. HTPB (hydroxyl-terminated polybutadiene) is a liquid polybutadiene rubber containing hydroxyl end groups that can be used to make epoxy resin toughening agents. However, HTPB has poor compatibility with epoxy resins. Both HTPB and epoxy resin should be chemically linked to each other to improve compatibility with epoxy resin. The inclusion of epoxy groups into the double bonds of HTPB enhances the miscibility of HTPB with epoxy resin, leading to phase separation of rubber domains within the epoxy matrix, resulting in toughening and flexibility effect.

With the addition of 2% silane couple agent and 1% HTPB, Kaynak *et al*. performed a series of experiments to enhance the interaction between HTPB and epoxy resin resulting in increased tensile strength, plastic deformation, and a 44% increase in impact strength.[54] Another successful way of enhancing epoxy compatibility has been the functionalization of HTPB. Latha *et al.* used epoxidized hydroxyl-terminated polybutadiene (EHTPB) to increase the compatibility and mechanical qualities of epoxy resin. With increasing EHTPB concentration, lap shear strength and T-peel strength both increased, showing increased toughness and flexibility as well as adhesion. At an EHTPB level of around 10 parts per 100 parts epoxy resin, maximum lap shear strength and peel strength were achieved (phr). Due to the rubber phase becoming continuous with greater EHTPB concentration, a decrease in toughness and an increase in flexibility were observed;[51] Zhou *et al.* agreed with similar findings.[56] By initially treating HTPB with enough toluene diisocyanate, Barcia *et al.* created an epoxide end capped HTPB (TDI). The epoxy resin was then reacted with the isocyanate end capped HTPB (ITPB) to generate a block copolymer. During the creation of polymer networks, this approach is known to increase miscibility and generate more stable dispersed particles of diol compounds. When compared to the neat resin, the addition of these rubber components improves flexibility, impact performance, and lowers T_g by up to 10%.[49] At 20 phr, carboxyl-terminated polybutadiene (CTPB) liquid rubber improved the toughness of epoxy rubber, but above that level, strength and modulus decreased.[57,58]

Other classes of liquid rubbers have been investigated; however, butadiene-acrylonitrile and polybutadiene rubbers remain the primary toughening agent for epoxies.

When liquid modifiers are incorporated within an epoxy matrix, one of two mechanisms occurs during curing. The rubber can pre-react with the epoxy resin forming an intermediate prepolymer that crosslinks with a curative, or the rubber can phase separate during the curing process forming a diphase morphology consisting of microscopic and nanoscopic rubber domains. In the homogenous mixture of rubber and epoxy, a flexibilizing effect is observed as opposed to plasticizing effect.[84,85] The polymer matrix becomes more ductile, the T_g reduces, and the crosslinked density is reduced. While the toughening and the flexibilizing effects of liquid rubbers have been heavily studied in epoxy adhesive; their influence on epoxy coating remains heavily neglected. Furthermore, the effect of liquid rubber on the adhesive strength of epoxy coating to various substrates has not been investigated or publicized.

In this work, an experimental design was used to prepare a series of liquid rubber-modified epoxy coatings using amine-terminated poly(butadiene-acrylonitrile), polybutadiene, hydroxyl terminated, and polybutadiene, epoxy functionalized, hydroxy terminated rubbers. These liquid rubbers were selected because they are readily commercially available however unlike CTBN they are not commonly used as flexibilizer in epoxy-polyamide systems. Furthermore, the adhesive impact of these liquid rubbers on metallic and composite substrates has not been investigated. The effect of epoxy modified rubber on flexibility as well as adhesion to multiple substrates, including steel, aluminum, carbon fiber reinforced plastics, and fiberglass reinforced polymer were studied. A two-step process was employed, first involving the pre-reaction of epoxy and liquid rubber, followed by the introduction of a crosslinking agent. The amount of liquid rubber was varied from 1 to 10 wt.% epoxy resin; ANOVA was utilized to determine significance of adhesive effective and flexibility.

Experiments

Materials

EPON 828, also chemically known as bisphenol-A-(epichlorohydrin), was supplied by Hexion Specialty Chemicals. The curing agent, Epikure 3164, was supplied Hexion. Sigma Aldrich (now Millipore) was used to obtain polybutadiene, hydroxyl terminated (HTPB-1200) and, hydroxy terminated epoxy functionalized polybutadiene (HTEPB-1300), as well as and xylene. Amine-terminated poly(butadiene-acrylonitrile) Cat# 517 (ATBN-4150) and Cat# 549 (ATBN-3200) were provided by Scientific Polymer. Steel (QD-35) and aluminum (A-36) panels were obtained from Q-Panel. MacMaster-Carr provide the carbon fiber reinforced plastics sheets (Ultra-Strength Lightweight 1/16” thick) and fiberglass reinforced polymer (3/16’’ thick).

Experimental Design

The study was designed using 4 types of additives at three levels (1%, 5% and 10% based on Epon 828 weight) on four different substrates (aluminum, steel, carbon fiber reinforced plastics, and fiberglass reinforced polymer). The representative chemical structures of the additives used are shown in Fig 4.1. The coatings were designed as a three-factor factorial study where type of additives, weight percent of additives, and substrate type were considered factors. Factor 1 (type of additives) had 4 levels, Factor 2 (wt % of additive) had 3 levels, Factor 3 (substrate type) had 4 levels, resulting in 12 different formulations and 48 treatment combinations (Table 4.1) The statistical analysis of response variables was calculated using Design expert 13 (Stat-Ease Inc., USA).

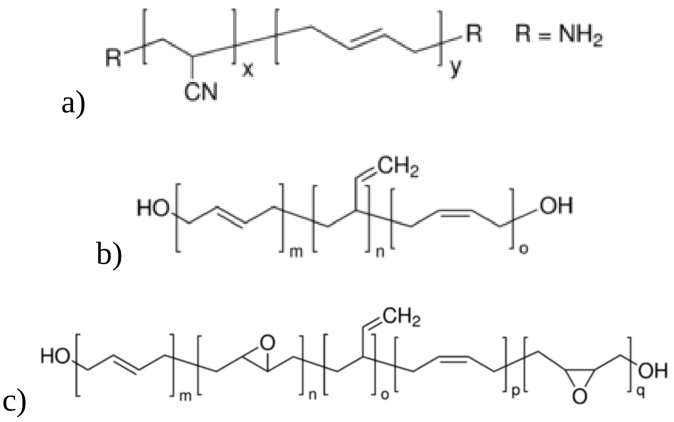

Figure 4.1. Chemical structure of liquid rubber used for the experiment. a) amine-terminated Poly(butadiene-acrylonitrile), b) polybutadiene, hydroxyl terminated, and c) polybutadiene, epoxy functionalized, hydroxy terminated

Table 4.1. Properties of liquid rubber used in the study

Additives	Description	Eq. Wt.	Amine Value	Hydroxyl value (mg)	Acrylonitrile (wt. %)	Mw (g/mol)	Tg
ATBN-4150	Amine-terminated Poly(butadiene-acrylonitrile)	900	62		16.5	8300	-51
ATBN-3200	Amine-terminated Poly(butadiene-acrylonitrile)	1,200	47		10	6400	-65
HTPB-1200	Polybutadiene, hydroxyl terminated			1.7		2400	
EHTPB-1300	Polybutadiene, epoxy functionalized, hydroxy terminated					2600	

Coating Formulation

A general formulation procedure is described as follows: an epoxy base consisting of 74 wt% Epon 828 and xylene was made by mixing the components together until a homogenous solution was formed. To create a preerected modified resin, the additives (1, 5, and 10% based on Epon 828) were added to the epoxy base and mixed for 30 minutes. After which, Epikure 3164 was added at a 1:1 equivalent (epoxy: amine) ratio. The formulation was hand mixed for a few minutes and underwent an induction period of 20 mins. A control, CLR-00, consisting of epoxy and amine crosslinker without the incorporation of additives is also made. Table 4.2 lists all the experimental coating formulations.

Table 4.2. Composition of liquid rubber modified epoxy coatings

Formulation	Additive (g)	Xylene (g)	Epon 828 (g)	Epikure 3164 (g)
ATBN-4150-1	0.41	9.83	29.75	40.13
ATBN-4150-2	1.92	8.40	29.98	38.97
ATBN-4150-3	3.69	6.56	29.75	37.61
ATBN-3200-1	0.40	9.93	29.68	40.14
ATBN-3200-2	1.92	8.42	29.68	40.05
ATBN-3200-3	3.65	6.69	29.68	37.63
HTPB-1200-1	0.41	9.96	29.65	40.16
HTPB-1200-2	1.94	8.44	29.64	38.99
HTPB-1200-3	3.66	6.72	29.65	37.62
EHTPB-1300-1	0.45	9.92	29.65	40.12
EHTPB-1300-2	1.92	8.45	29.64	38.95
EHTPB-1300-3	3.63	6.74	29.65	37.63
CLR-00		9.82	29.76	40.16

Coating Application and Curing

The formulations were applied at 8 mil wet drawdown on steel, aluminum, fiber glass, and carbon fiber reinforced plastics substrates previously cleaned with acetone. Drawdowns were also made on PTFE films to produce free standing films of the formulations. The coatings were flashed for 20 minutes at room temperature and force cured at 80°C for another 20 minutes. All formulations were air dried for 24 hours prior to testing. An average dry film thickness of 60 µm ± 5 µm was obtained using an Elcometer thickness gauge on metal substrates (Al and Fe).

Pull Off-Adhesion Testing

The adhesive strength was characterized by a PosiTests pull-off adhesion tester (DeFelsko Corporation, New York) in accordance with ASTM D4541. Dollies of 20 mm diameter were glued to the coated specimens using a two-component epoxy (3M ™ Scotch-Weld ™ Epoxy Adhesive 460) formulated to a 1:1 volume mix ratio. To ensure proper adhesion of the glue, 220-grit sandpaper was utilized to abrade the coating surface prior to the application of the glue. The glue was fully cured for 24 hours at ambient temperature. Prior to testing, the adhesive around the edges of the dolly was cut through with a 20 mm cutting tool, and any excess adhesive was removed. The dollies were then pulled vertically until failure occurred. For each sample, at least three replicates of the specimens were performed, and the arithmetic mean was reported.

Reverse Impact Resistance

The resistance of coatings to rapid deformation was determined by the reverse impact strength test. In this test, a 4 lbs steel indenter is dropped from various heights through a guide tube onto the noncoated surface of the steel and aluminum panels per ASTM D2794. The height at which cracking or other forms of failures of film is noted and the impact resistance is calculated.

Conical Mandrel

Flexibility of the coatings on the metal substrates (Al and Fe) was assessed on a conical mandrel with a roller frame of diameter 3 to 38 mm. The panels were secured in the mandrel and bent over the roller frame. The panels were inspected for cracks or delamination after bending. This test was performed in accordance with ASTM D522

Dynamic Mechanical Analysis

The mechanical properties of each specimen (measuring 10 mm x 0.5 mm x 0.10 mm) were evaluated using a TA Instruments Q-800 Dynamic Mechanical Analyzer equipped with tensile film clamps. The samples were evaluated in a dynamic temperature ramp mode from −80 °C to 150 °C at a heating rate of 5 °C/min with amplitude of 10 microns. The dynamic storage, loss moduli, and tan δ (E”/E’) were recorded as a function of temperature. The peak tan δ was utilized to determine glass transition temperature and the crosslink density was calculated from the storage modulus at 120 °C.

Differential Scanning Calorimetry

The thermal properties of the polymers were determined on a TA Instruments Q2000 Modulated Differential Scanning Calorimeter (DSC). Circular samples of approximately 10–15 mg was weighed into an aluminum pan, sealed, and heated under nitrogen. Heat flow was monitored and compared against a reference. The samples were heated from −80 to 200°C at a rate of 5°C /min follow by cooling to −80°C and heated again to 200°C at the same rate. T_g was obtained from the second heating cycle.

Nanoindentation

Nanoindentation experiments were conducted using a Hysitron Triboindenter. A 1 μm Berkovich tip was used on 1 inch x 1 inch aluminum-coated samples. The tip-area calibration was done using a standard fused quartz substrate and Quasi-static indentation mode was used to measure the hardness and elastic modulus. The indentation process consisted of a 5 s period to reach a load of 1000 μN, with a holding time of 5 s, followed by a 5 s unloading to 0 N. The elastic modulus and hardness were calculated from the load–displacement curves using Oliver–Pharr method. Nine replicates were performed on each sample.

König Pendulum Hardness

The König hardness of the coatings was measured by monitoring the damping time of the oscillations of a pendulum. In this test, two steel balls attached to pendulum rests on the film. The oscillation of the pendulum is damped over time depending on the viscoelastic properties of the coating. The time required for the pendulum to decay from the initial amplitude of 6° to the final amplitude of 3° is a measure of the hardness of coating. ASTM D 4366 is the standard utilized in this test. The hardness tester used was a Byk pendulum hardness tester. All pendulum hardness test were performed on aluminum-coated substrates. Six replicates for each formulation were performed.

Results and Discussion

Flexibility

Conical Mandrel and Reverse Impact

The flexibility of the metal coated substrates was evaluated by conical mandrel bend test. The results from all formulations applied on metal substrates assessed was 0 cm, the highest possible flexibility achievable by this test method. Since the conical mandrel was unable to provide a more nuanced and sensitive method of characterizing flexibility, other indirect characterization methods for flexibility were needed. Reverse impact, DMA, DSC, and nanoindentation were used to indirectly observe flexibility.

Reverse impact resistance was performed on the steel and aluminum-coated substrates to evaluate impact strength. All formulations evaluated on steel resulted in a reverse impact strength of <169 in-lbs., the highest possible force the instrument can output. Reverse impact is the optimum method of evaluating both adhesion and flexibility of a coating. The interfacial adhesive forces between the coating and substrates needs to be strong enough that upon impact the coating does not become detached from the substrate. But also, flexible enough that the coating does not deform or crack upon impact. The aluminum panels failed around 100 in-lbs.; substrate failure occurred before any of the coatings investigated failed.

Due to limitations of the method utilized to determine direct flexibility of a coated substrate, other indirect flexibility measurements were needed. DMA was performed to determine the T_g as well as crosslinked density of each formulation. DSC also provided T_g. Hardness measurements were performed via König Pendulum and Nanoindentation. The Indentation method also provided an elastic modulus.

DMA and DSC

Based on the DMA graph in Fig 4.2, the pre-reaction method and curing the epoxy coating at elevated temperature over a short period of time prevented the liquid rubbers from phase separating during the crosslinking stage, inhibiting the formation of a bimodal morphology. The presence of a singular tan δ peak is indicative of a homogeneous polymeric network. Work by Tripathi *et al.* has demonstrated that the formation of a homogenous matrix in rubber-modified epoxy is suggestive of a flexibilizing effect as opposed to a plasticizer effect.[151] Furthermore, Bussi *et al.* were able to demonstrate that by pre-reacting the epoxy with the liquid rubber prior to the introduction of the crosslinker, phase separation of the rubbers is prevented during the curing stage leading to a more flexibilizing effect.[84,85]

The storage modulus is a sign of a material’s ability to store deformation energy in an elastic manner. This is related to the extent of cross-linking, the higher the degree of cross-linking, the shorter the chain between crosslink, the more rigid the polymer network, the greater the storage modulus. Shown in Fig 4.2 and Table 4.3, above 5 wt%, ATBN-4150 results in a slight decrease in storage modulus at -50 °C compared to the unmodified coating. While ATBN-3200 yielded a similar decrease below 5 wt %. HTPB-1200 at 5 wt% and EHTPB-1300 at 10 wt%, demonstrated the lowest decrease in storage modulus specifying the highest amount of flexibility. ANOVA results obtained for the storage modulus are given in Table 4.4. According to the results, liquid rubbers showed statistically and physically significant effects on the storage modulus in the glassy region ($p<0.1$). However, the level at which the liquid rubbers are added is not statically significant. The interaction plot of the effect of rubber on storage modulus is given in Fig 4.3. EHTP-1300 results in the lowest storage modulus in the glassy region showing the greatest degree of flexibility.

The tan δ curves represent the ratio of the viscous to elastic response or the energy dissipation. The addition of all additives at all levels leads to a noticeable increase in the tan δ curve as well as an increase in the tan δ value when compared to the unmodified epoxy. The height and area under tan δ curve are an indication of the total amount of energy that can be absorbed by a material. A large area under the tan δ curve implies a great degree of molecular chain mobility, which translates into better damping properties, implying that the material can better absorb and dissipate energy. Increases in polymer chain segmental motion implies an increase in overall network flexibility and a more flexible material.[21,22,152]

The temperature at the peak of the tan δ curve represents the T_g, or temperature at which the material goes from the hard, rigid, glassy state to the rubbery state. The direct correlation between flexibility, crosslinked density, and glass transition temperature is well established. The more flexible a polymer network, the lower the crosslinks per unit volume or crosslink density. Since crosslinks are topological constraints, which hinder segmental mobility of the polymer chains, a decrease in crosslink density due to the introduction of flexibilizer will require lower thermal energy to enable molecular mobility of polymer segment thus a decrease in T_g will be observed. Based on the DMA results in Table 4.3, EHTPB-1300 at 10 wt.% has the lowest XLD and T_g and thus imparts the higher level of flexibility. These results agree with the DSC analysis.

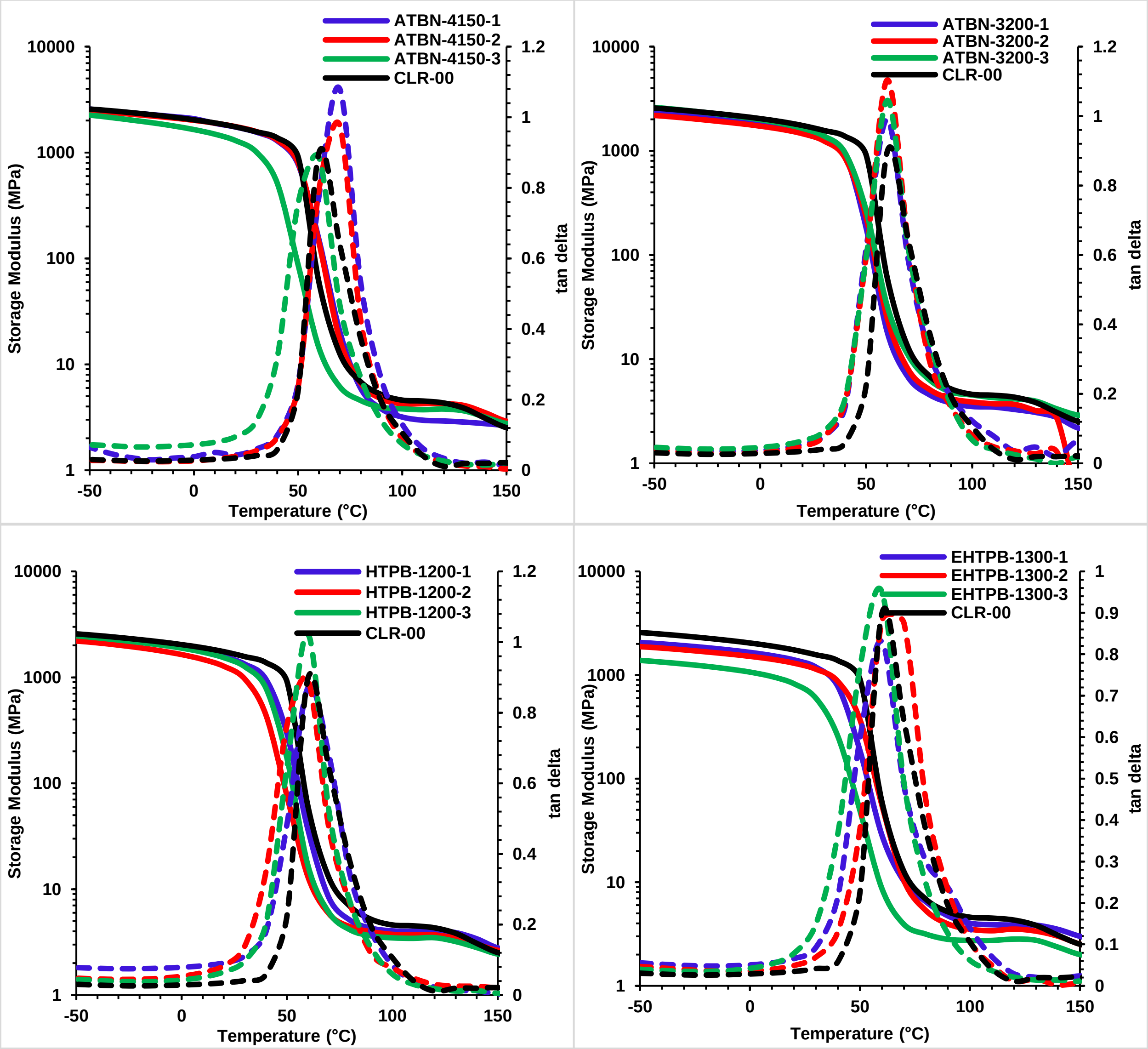

Figure 4.2. DMA results of unmodified epoxy-amine and modified coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 4.3. Characteristic of DMA for liquid rubber -modified epoxy coating: T_g, XLD, and storage modulus

Formula	E' at -50° C (MPa)	T_g (°C)	E' at T_g+50 °C (MPa)	XLD (mol m^{-3})
ATBN-4150-1	2573	66.7	2.946	0.3
ATBN-4150-2	2468	66.23	4.308	0.44
ATBN-4150-3	2255	56.96	3.721	0.38
ATBN-3200-1	2356	60.18	3.475	0.35
ATBN-3200-2	2184	58.53	3.781	0.39
ATBN-3200-3	2609	59.11	4.294	0.44
HTPB-1200-1	2520	63.04	4.02	0.41
HTPB-1200-2	2201	56.87	3.719	0.38
HTPB-1200-3	2464	58.06	3.525	0.36
EHTPB-1300-1	2060	58.66	3.925	0.4
EHTPB-1300-2	1879	65.07	3.426	0.35
EHTPB-1300-3	1384	56.83	2.737	0.28
CLR-00	2572	62.25	4.46	0.45

Table 4.4. ANOVA result of liquid rubber on storage modulus

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	9.974E+05	5	1.995E+05	3.48	0.0803
A-Additive	8.941E+05	3	2.980E+05	5.20	0.0416
B-Additive Level	1.033E+05	2	51639.08	0.9018	0.4545
Residual	3.436E+05	6	57262.75		
Cor Total	1.341E+06	11			

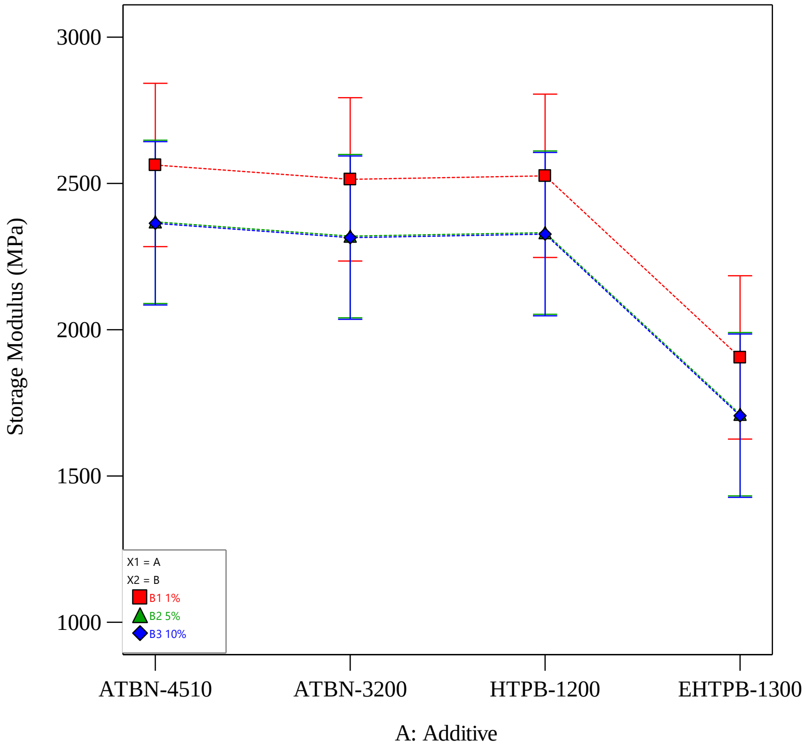

Figure 4.3. Interaction plot of elastic modulus from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

A 20-30° C difference in the T_g was observed from DMA and DSC analysis. This disparity is attributed to the different heating rate of each method. Based on the result of DSC analysis reported in Fig 4.4, the addition of liquid rubber additive to a bisphenol-A epoxy coating induced a slight decrease in T_g. The reference formulation without any additive has a T_g of 35.22 °C. As the concentration of ATBN-4150 increases from 1 to 10 wt%, the T_g decreases from 34.17 °C to 30.52 °C. The addition of ATBN-3200 at all levels reduces the T_g and thus flexibility, but there is very little change with the concentration and an influence on T_g. A similar trend is noted for EHTPB-1300. The effect of HTPB-1200 on flexibility based on T_g agrees with all other flexibility measurements. As the concentration of HTPB-1200 decreases, the T_g and, thus, flexibility increases. Overall, ATBN-4510, HTPB-1200, and EHTPB-1300 at 10 wt% has the lowest T_g. The increased flexibility imparted by ATBN-4510, HTPB-1200, and EHTPB-1300 could be ascribed to higher miscibility within the epoxy resin.

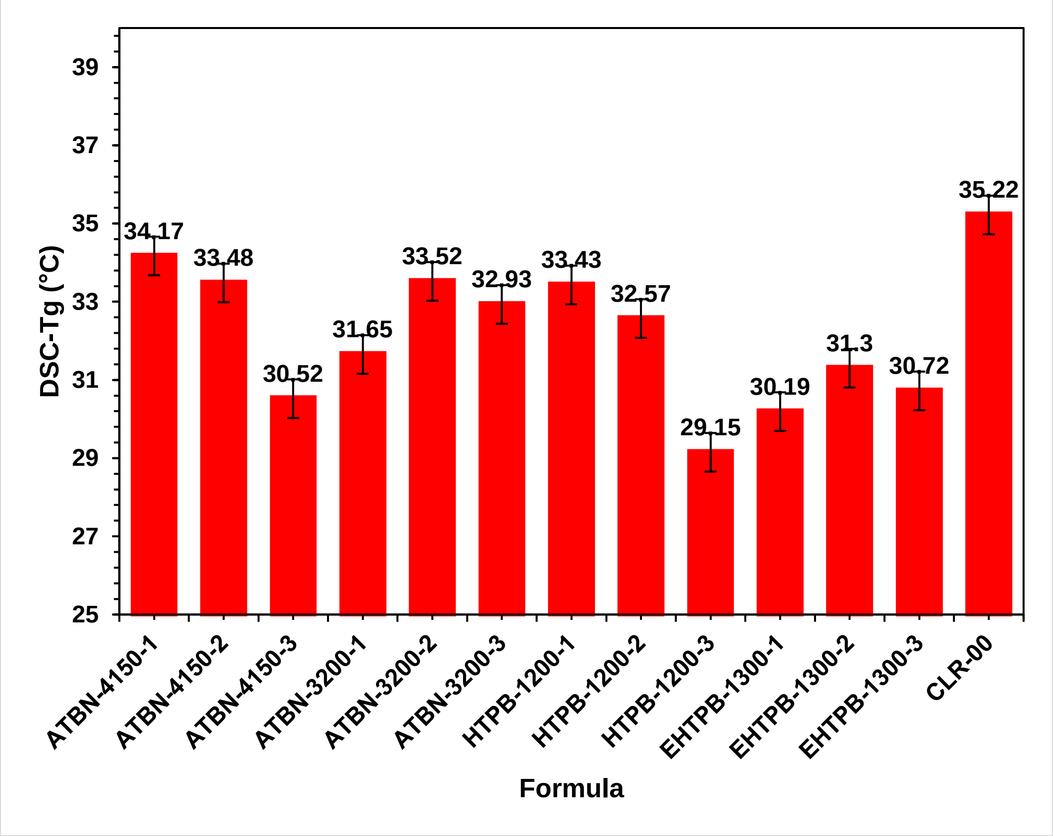

Figure 4.4. Glass Transition Temperatures from DSC of modified and unmodified epoxy-amine coatings with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

ANOVA was performed on the DMA and DSC results, however the effect of liquid rubber and additive level on the storage modulus in the glassy region (-50° C), T_g, and XLD was not found to be statistically significant at the 95% confidence level. However, the storage modulus in the glass region is statistically significant at the 90% confidence interval.

Nanoindentation

Nanoindentation techniques were used to determine the modules of elasticity and hardness of rubber modified epoxy and the result are reported in Fig 4.5 and 4.6. The elastic (or young’s) modulus is used as an indirect measurement of flexibility since it measures the resistance of a material to elastically deform under a load. A stiff or inflexible material has a high elastic modulus and undergoes a slight shape change under elastic loads (*e.g.*, diamond). A flexible material has a low elastic modulus and undergoes considerable shape change under loads.[153,154] Based on Fig 4.4, the experimental coatings showed an elastic modulus range 1277 to 3075 MPa, suggesting a wide range of flexibilities.

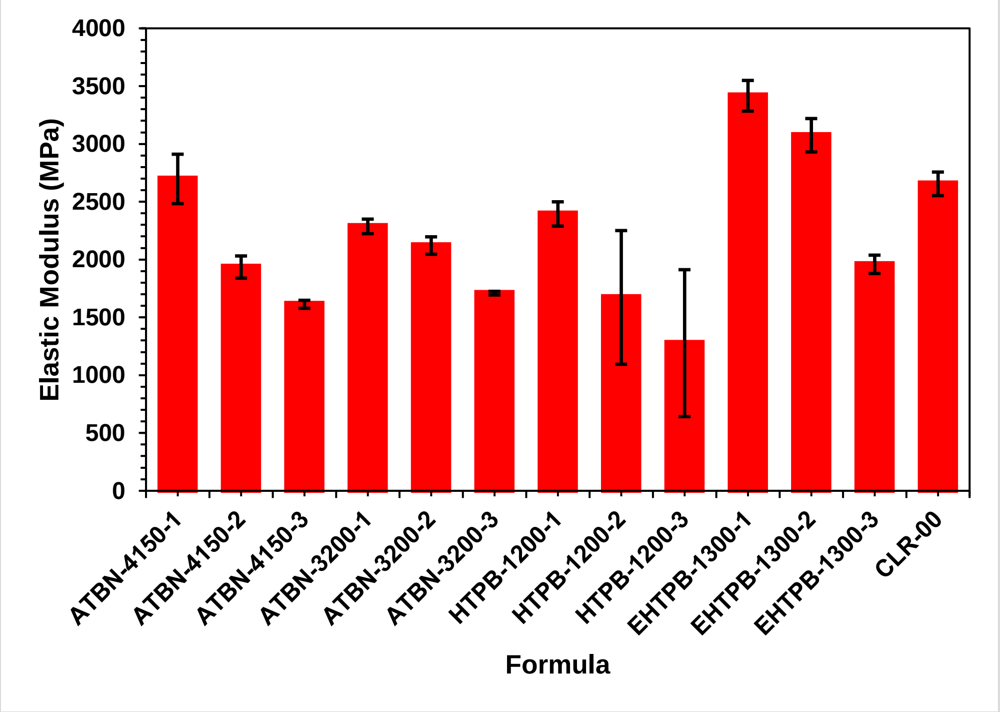

Figure 4.5. Elastic Modulus from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, HTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

ANOVA results obtained for the elastic modulus are given in Table 4.5. An F-value of 13.61 implies the model is significant; there is only a 0.32% chance that the F-value could occur due to noise. According to the results, the liquid rubbers and level at which they were added showed statistically and physically significant effects on the elastic modulus ($p < 0.05$).

Table 4.5. ANOVA result of liquid rubber on elastic modulus

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	4.028E+06	5	8.056E+05	13.61	0.0032
A-Additive	1.781E+06	3	5.938E+05	10.03	0.0094
B-Additive Level	2.246E+06	2	1.123E+06	18.98	0.0025
Residual	3.551E+05	6	59176.68		
Cor Total	4.383E+06	11			

The interaction plot of the effect of rubber on elastic modulus are given in Fig 4.6. As the additive level increases for each liquid rubber the elastic modulus decreases. These findings agree with the literature; Thomas *et al.*, observed similar trend and ascribed it to the potential increase in the relative amount of dissolved rubber as rubber content increases.[155] For the amino-terminated liquid rubber (ATBN-4510 and ATBN-3200), molecular weight does not appear to influence elastic response. The presence of the oxirane ring in the hydroxyl terminated rubber results in higher modulus of elasticity when compared to the non-epoxy functional rubbers and neat epoxy. These results are more apparent at lower additive levels as demonstrated by the elastic modulus of EHTPB -1200 at 1 wt.% is 3416 MPa, compared to the 2395 MPa and 2655 MPa for HTPB-1300 and unmodified epoxy, respectively. DMA has shown that the molecular weight between crosslinked increases with the addition of EHTPB-1300 therefore the increased in elastic modulus could be attributed to the increase in hydrogen bonding. The epoxy functional group on EHTPB-1300 is expected to react with the primary amine of the curative, thereby producing a secondary amine and hydroxyl group. The hydroxyl group can react with the epoxy resulting in etherification. However, the hydroxyl-epoxide reaction is slower than that of the epoxide-amine reaction, especially at temperature below 80°C. Thus, additional epoxy results in an increased hydroxyl bond which leads to increased hydrogen bonding.[156] Li *et al.* demonstrated via molecular dynamics simulation that an increase in hydrogen bonding reduces the free volume within a polymer matrix thereby increasing stiffness and elastic modulus. However, hydrogen bonding was found to have limited influence on T_g.[157]

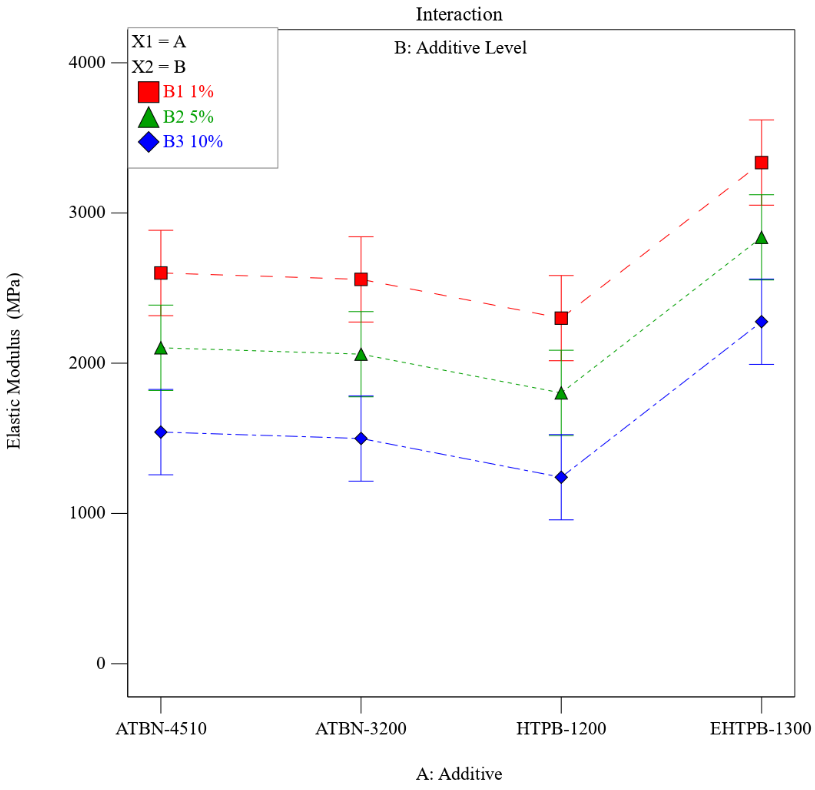

Figure 4.6. Interaction plot of elastic modulus from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

The indentation hardness results reported in Fig 4.7 parallel that of the elastic modulus. The statistical analysis of the indentation hardness is given in Table 4.6. An F-value of 5.95 implies the model is significant; there is only a 2.54 % chance that the F-value could occur due to noise. According to the findings, the liquid rubbers and level at which they were added showed statistically effects on the indentation hardness ($p < 0.05$).

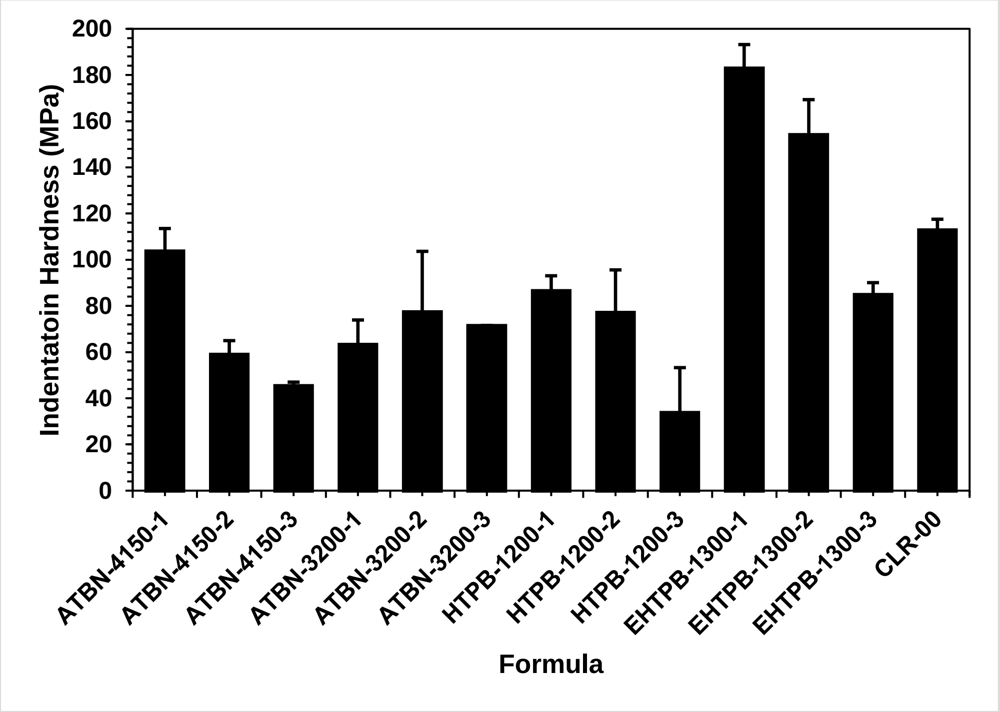

Figure 4.7. Hardness from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 4.6. ANOVA result of liquid rubbers on indentation hardness

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	16915.32	5	3383.06	5.95	0.0254
A-Additive	11698.29	3	3899.43	6.86	0.0229
B-Additive Level	5217.03	2	2608.51	4.59	0.0618
Residual	3410.66	6	568.44		
Cor Total	20325.98	11			

The interaction plot of rubbers and level at which added effects on indentation hardness is given in Fig 4.8. As the additive level increases, the indentation hardness decreases for each liquid rubber investigated indicating increase in flexibility. As observed in the elastic modulus response, ATBN-4510, ATBN-3200 and HTPB-1200 display similar effects on the indentation hardness respective to their additive levels. HTPB-1200 at 10 wt% results in the lowest hardness.

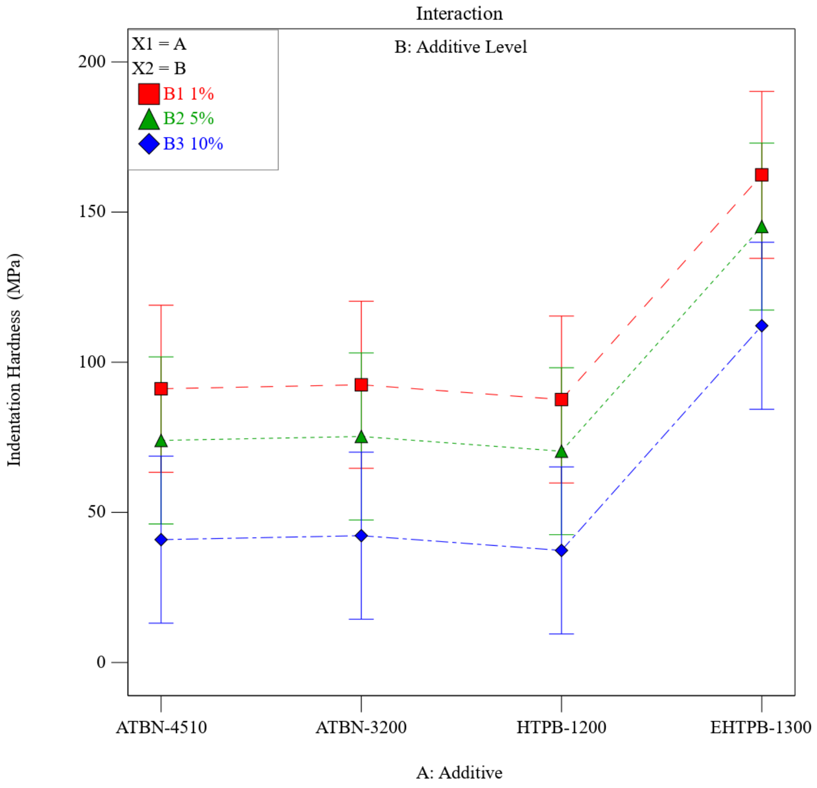

Figure 4.8. Interaction plot of hardness from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

König Pendulum Hardness

Pendulum hardness measures viscoelasticity: a property which is proportional to the reciprocal of the damping capacity or mechanical loss of the coating. The more elastic the coating, the less damping, the longer the oscillation of the pendulum, and the harder the coating. The more viscous or flexible the material, the less damping, and the softer the coating.[158] Pendulum hardness for the experimental coatings is reported in Fig 4.9. Based on the ANOVA result in Table 4.7, only the level at which the additives are added significantly effects the pendulum hardness. The pendulum hardness result agrees with the other test method; Fig 4.10 shows that HTPB-1200 and EHTPB-1300 at 10 wt.% produces the softest and most flexible coating.

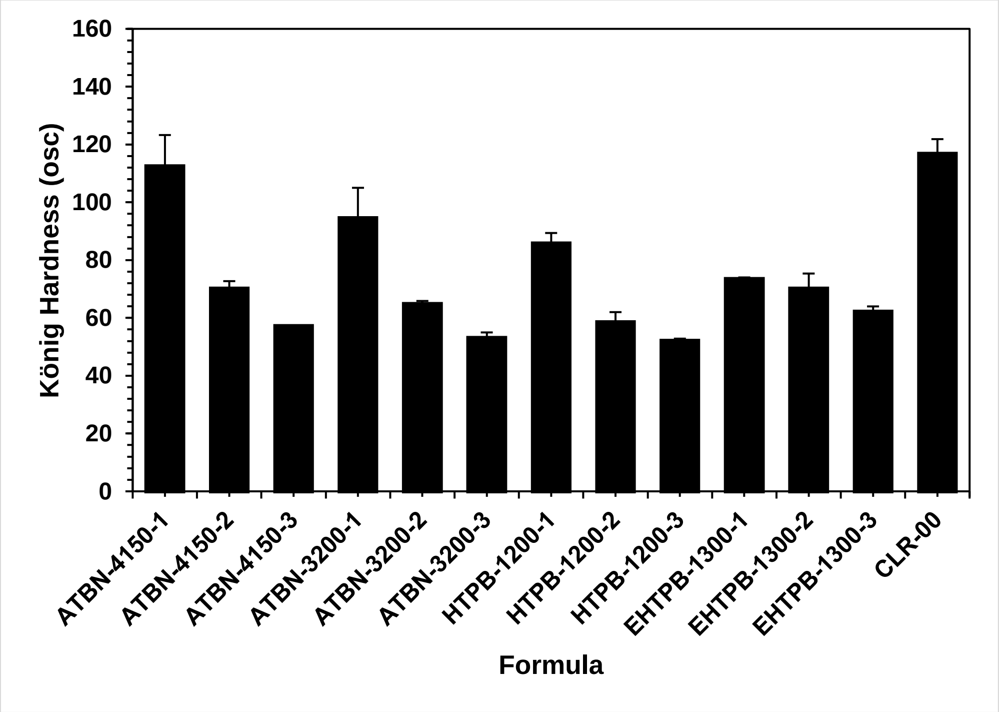

Figure 4.9. Hardness from König pendulum experiment of unmodified and modified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, HTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 4.7. ANOVA of liquid rubbers on pendulum hardness

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	3024.94	5	604.99	5.92	0.0257
A-Additive	347.37	3	115.79	1.13	0.4080
B-Additive Level	2677.57	2	1338.79	13.10	0.0065
Residual	613.02	6	102.17		
Cor Total	3637.96	11			

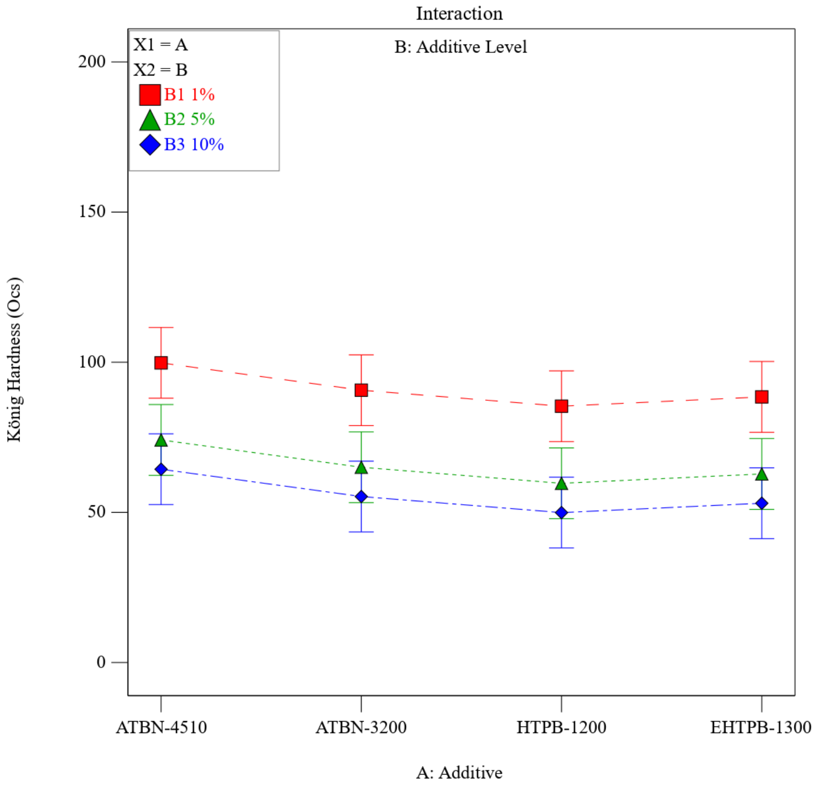

Figure 4.10. Interaction plot of König pendulum hardness from nanoindentation experiment of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Adhesion

When evaluating the pull-off adhesion result, two major factors are of importance: the adhesive strength and mode of failure. Adhesion performance on metal substrates (Fe and Al) and composites (CF and FG) were investigated and reported in Fig 4.11. To evaluate the difference between adhesive strength of the various substrates a One-way ANOVA was performed, and the results are reported in Table 4.8. The p-value corresponding to the F-statistic of one-way ANOVA is lower than 0.05, suggesting that the one or more treatments (substrate) are significantly different. Thus, a Tukey HSD test for multiple comparison was performed to identify which of the pairs of substrates are significantly different from each other.

Based on the Tukey HSD analysis reported in Table 4.9, there is no difference between the mean adhesive strength of epoxy resin on Fe and Al, Al and CF, Fe and CF. A noticeable and significant difference was observed between FG and all other substrates. These results reflected in Fig 4.10 are reflected in adhesives strength of the CLR-00 which are 358, 420, 401 and 2699 MPa for Al, Fe, CF, and FG, respectively. The adhesion strength between the coating and substrate comes from two properties, mechanical interlocking, and chemical bonding. Since the substrates had the same finish, the mechanical interlocking can be considered identical. Therefore, the increase in the adhesion strength is attributed to the stronger chemical bonds, which were developed at the coating-substrate interface during coating deposition process.[159] The difference in adhesive strength between the substrates were initially attributed to surface free energy; composites are known to have lower surface free energy making adhesion difficult,[9] however opposite behavior was observed. Surface free energy analysis demonstrated that all substrates investigated had similar free energy. Thus, a potential explanation for the enormous difference in adhesive strength between the FG and the other material could be attributed to thickness of the substrate. Both metal substrates and the carbon fiber reinforced plastics substrate were approximately 1/16 inch thick, while the FB was approximately 3/16 inch thick. The thin nature of the substrates results in more of a peel effect rather than a pull-off effect due to deformation of the surface and misalignment of the normal force, thus the pull-off adhesion strength between the substrates cannot be compared, however the effect of the additive on each individual substrate is comparable.[160]

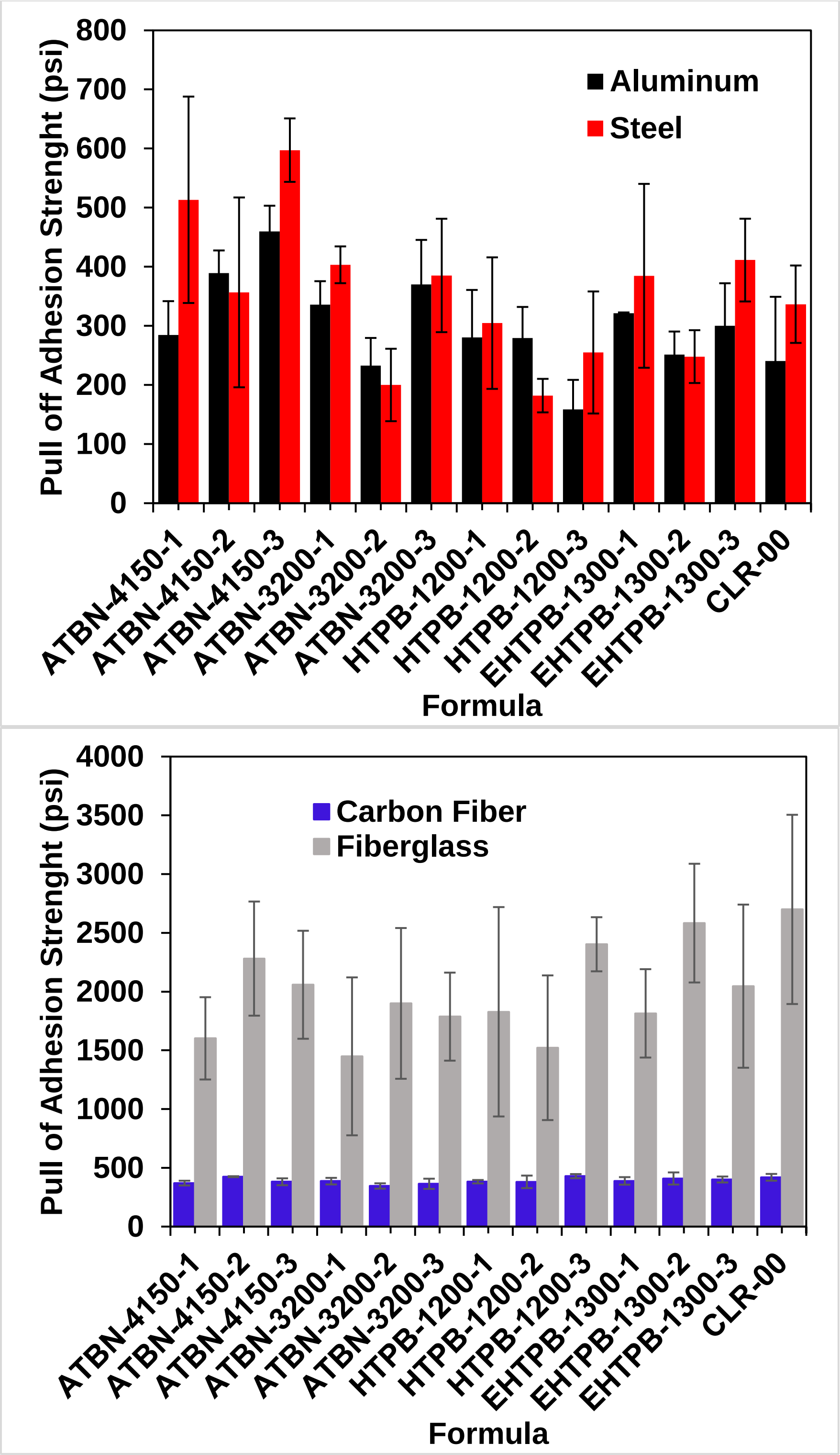

Figure 4.11. Pull-off Adhesion strength of formulation; Top: on metal substrates. Bottom: on composites.

Table 4.8. ANOVA result of substrate effect on adhesive strength

Source	Sum of Squares	df	Mean Square	F-value	p-value
Treatment-Substrate	2.66E+07	3	8.87E+06	199.535	1.11E-16
Residual	2.13E+06	48	4.44E+04		
Cor Total	2.87E+07	51			

Table 4.9. Tukey HSD result of substrate effect on adhesive strength

Treatment pairs	Tukey HSD Q statistic	Tukey HSD p value
Al vs Fe	0.8855	0.9000
Al vs CF	1.5486	0.6738
Al vs FG	29.0342	0.0010
Fe vs CF	0.6631	0.9000
Fe vs FG	28.1487	0.0010
CF vs FG	27.4856	0.0010

For the aluminum substrates, the addition of ATBN-4150 and EHTPB-1300 results in enhanced adhesive strength between coating and substrates at all levels, with ATBN-4150-3 at 460 MPa resulting in the highest adhesive strength. An association between the concentration of ATBN-4150 and adhesive strength on steel was observed, as the concentration increased from 1 to 5 to 10 wt.%, the adhesive strength increases from 285 to 389 to 460 MPa, respectively. The improved adhesion performance imparted by ATBN-4500 on the metallic substrates could be attributed to the stronger interaction between the polar cyano group and the oxide layer of the metal surface. HTPB-1200 appears to have an inverse reaction between additive concentration and adhesive strength; as the additive concentration increases from 1 to 10 wt.%, the adhesive strength decreased from 305 to 255 MPa. ATBN-3200 and EHTPB-1300 does not appear to have a direct correlation between concentration and adhesive strength, however 10 and 1 wt% respectively, shows the best improvement on adhesive strength performance.

ANOVA results for pull-off adhesion on Fe substrates are given in Table 4.10. An F-value of 20.21 implies the model is significant, there is only a 0.11% chance that an F-value this large could occur due to noise. According to the results, the liquid rubbers and level at which they were added showed statistically and physically significant effects on the pull-off adhesion on steel substrate ($p < 0.05$).

For steel, ATBN-4150-1, ATBN-4150-3, ATBN-3200-3, HTPB-1200-1, EHTPB-1300-1, and EHTPB-1300-3 showed improved adhesive strength. A defined correlation between molecular weight of liquid rubber and weight percent added was not observed for steel substrate.

Table 4.10. ANOVA result of liquid rubber on adhesion of Fe substrate

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1.595E+05	5	31908.49	20.21	0.0011
A-Additive	90866.77	3	30288.92	19.18	0.0018
B-Additive Level	68675.69	2	34337.84	21.75	0.0018
Residual	9473.43	6	1578.90		
Cor Total	1.690E+05	11			

The interaction plot of the effect of adhesion on steel are given in Fig 4.12 The addition of 1wt% and 10 wt.% of liquid rubber results in the highest adhesive strength for all additive investigated ATBN at 10 wt.% result in the highest adhesive strength between the epoxy and Fe substrate.

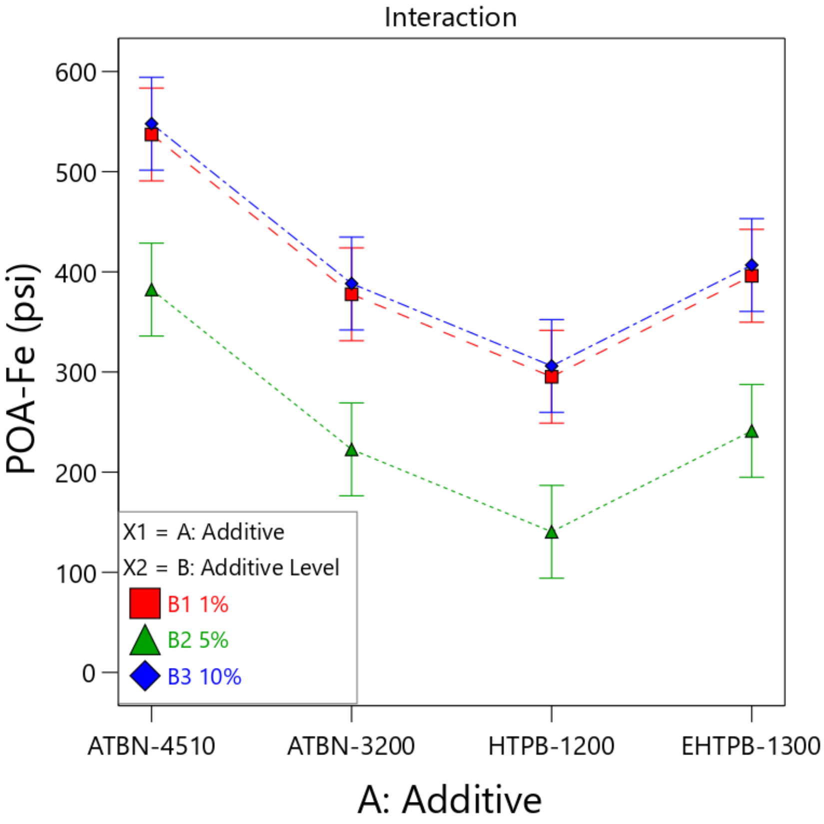

Figure 4.12. Interaction plot of pull-off adhesion of modified and unmodified epoxy-amine coating with addition of ATBN-4150, ATBN-3200, HTPB-1200, EHTPB-1300 at levels 1 (1 wt.%), 2 (5 wt.%) and 3 (10 wt.%) on Fe substrate

For the composite substrates, the addition of the liquid rubber at all levels to the epoxy resin did not appear to improve adhesive. Unfortunately, for fiberglass reinforced polymer, the liquid rubbers have a detrimental influence on adhesive strength resulting in a decrease in adhesive strength between the coating and substrate compared to the neat formulation.

An important aspect of the adhesion test is the mode of failure. A typical adhesion failure topography of each the coating on each substrate is illustrated in Fig 4.13. There are 4 different failure modes: 1) coating-substrate (c-s): the adhesion failure between the coating and substrate; 2) coating-coating (c-c): the cohesion failure which occurs between the matrix of the coating 3) coating-adhesive (c-a): the adhesive failure that happens between the adhesive and the coating, and 4) substrate-substrate (s-s) failure that happens between the matrix of the substrate. Adhesion strength measures the how strong the coating bonds with the substrate; cohesion strength measures how strong the coating itself holds together; the adhesive failure signals poor bonding between the adhesive, dolly, and top of the coating surface. Substrate failure denotes strong interfacial bonding between the coating and substrate. A mixed failure consisting of c-s, c-c, and c-a as shown for aluminum, steel, and fiberglass reinforced polymer substrates in Fig 4.13 is commonly observed. For the metal and CF substrates over 70% of the mode of failure within the tested area were c-s, suggesting that the adhesive strength reported for those tests were an adequate representation of the adhesive strength between coating and substrate. The results in Fig 4.13 are representative of all formulation assessed. The s-s failure shown for carbon fiber reinforced plastics is unusual and is a sign that the cohesive strength between the carbon fiber and the polyester resin used within the matrix of the composite is weaker than that of adhesive strength of the epoxy coating and the substrate. Thus, the addition of the rubbers did not improve the adhesion between carbon fiber reinforced plastics and the bisphenol-A resin.

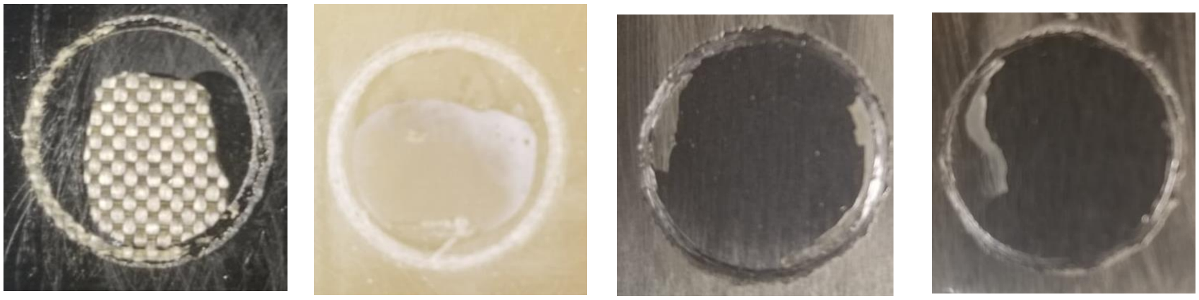

Figure 4.13. Failure mode after pull-off adhesion; a.) carbon fiber reinforced plastics, b.) fiberglass reinforced polymer, c.) steel, d.) aluminum

Conclusions

Liquid rubber modified epoxy coating with increased flexibility were prepared using a two-step process. This method allowed for the formation of a homogenous polymer network, thereby indicating a more flexiblizing effect. The hydroxyl terminated, HTPB and EHTPB rubber imparts the most flexibility without sacrificing toughness. Higher miscibility within the epoxy resin may account for the increased flexibility provided by HTPB-1200, and EHTPB-1300. However, adhesion on steel, aluminum, carbon fiber reinforced plastics and fiberglass reinforced polymer either remained either unchanged or decreased. The higher molecular weight ATBN, -4510 demonstrated improved adhesion on Al and Fe. ATBN-4500's increased adhesion performance on metallic substrates could be due to a greater interaction between the polar cyano group and the oxide layer of the metallic surface.

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CHAPTER 5. EFFECT OF SILANE COUPLING AGENT AND POLYETHER ON ADHESION AND FLEXIBILITY OF EPOXY FOR MULTIPLE SUBSTRATES

Introduction

Known for their extraordinary adhesion, high modulus, and barrier performance, epoxy resins are employed as primers for a variety of applications including automotive, watercraft, and aerospace vehicles.[15] Over the last few years, there has been an increased usage of composite materials within these structures. Composites offer great advantages including reduced fuel consumption, improved efficiency, fatigue resistance, reduced direct operating costs, and corrosion resistances[1]. The continued use of mixed material structures has led to the need for coating systems with adequate flexibility, adhesion, and barrier performance on multi-substrates, namely carbon fiber reinforced plastics, fiberglass reinforced polymer, aluminum, and steel.[7–9] Due to their current use in primers for metal substrates, epoxies are a prime candidate for a multi-substrate coating system. However, due to their brittle nature, an increase in flexibility is needed as well as adequate adhesion to a variety of substrates including aluminum, steel, carbon fiber reinforced plastics, and fiberglass reinforced polymer.

Chemical modification of polymeric coating systems can easily be accomplished by the introduction of additives. Polyetheramines are ideal candidates for flexibilizing agents since the presence of the ether chain allows for more flexibility compared to the rigid bisphenol-A chain of the epoxy. Furthermore, a higher molecular weight polyether can be utilized to increase the molecular weight between crosslinks thereby increasing the overall flexibility of the polymer matrix.[124,127]

Polyether, especially diamine terminated derivatives have been used as a curative for diglycidyl ether of bisphenol-A epoxy resins and their influence on the epoxy properties has been investigated previously. Yang *et al.* published a study in which two flexible diamines (Jeffamine D-230 and D-400) were added to a diethyl toluene diamine cured DGEBA epoxy resin and the mechanical behaviors of the modified epoxy resins were evaluated at cryogenic (77 K) and normal temperature (RT). The inclusion of flexible diamines enhanced elongation at break and impact strength at both RT and 77 K, according to the findings. The lower molecular weight additive D-230 required between 21 and 78 wt.% to exhibit simultaneous improvement in strengthening and toughening DGEBA epoxy resins at both RT and 77 K, but the higher molecular weight additive D-400 only required 21 wt.%. Differential scanning calorimetry (DSC) studies demonstrated a drop in T_g with a rise in polyetheramine content, as expected with the improvement in flexibility.[126]

Polyethylene glycol diamine (PEG- amine) and polypropylene glycol diamine (PPG-amine) at two distinct molecular weights (200 and 400 g mol^{-1}) were used to modify a DGEBA/diethylenetriamine system. The higher molecular weight PEG-amine outperforms the lower molecular weight PEG-amine in terms of critical stress intensity factor (K_{IC}) and critical strain energy release rate (G_{IC}), with increases of up to 82 and 294%, respectively. A high flexibility index, longer chain length, and stronger secondary interactions are responsible for the higher molecular weight PEG's overall performance.[124] The homogeneous structure of the polyetheramine was demonstrated by SEM. In the epoxy-cured methyl tetrahydrophthalic anhydride system, Shao *et al.* investigated hydroxyl functional polytetrahydrofuran (pTHF) as a toughening modifier.

The increase in impact strength, flexural strength, and flexural modulus revealed that pTHF reduced the T_g of the cured material while enhancing toughness and flexibility, as evidenced by DMA measurements. The maximal tensile modulus of pTHF at 8 wt% epoxy resins was 201.3 MPa, compared to 71.1 MPA for neat epoxy. The addition of 16 wt% pTHF resulted in a maximum flexural strength of 125.6 MPa, compared to 92.5 MPa for the neat epoxy.[161]

Jo *et al.* studied the effects of two flexible poly(oxypropylene) diamines, Jeffamine D-230 (D230) and Jeffamine D-400 (D400), as a secondary curing agent in epoxy shape memory polymer. It was observed that T_g increased with increasing flexible diamine content due to an increase of crosslink density as shown by a decrease in the molecular weight between chains. However, these results were not reflected in elongation of break, which decrease proportionally with diamine content. No noticeable difference in the T_g of D230 and D400 was reported due to a balancing effect between crosslink density and chain flexibility. Due to the stress relaxation properties of the diamines' flexible molecular chains, the impact strength was increased.[162]

Aside from flexibility, another important property in the development of a universal primer is adequate adhesion. Adhesion of a coating is imperative to provide protection. Adhesion promoters can improve the adhesive strength of coating; materials used to form a primary bond with a substrate or a coating. The most common class of adhesion promoters are silane coupling agents; compounds consisting of a reactive functional group and an alkoxysilane group.[139] Amino functional silane coupling agents are known to impart the most superior adhesion of metal substrate to organic resin. However, silane coupling agent (SCA)are typically incorporated as a pretreatment for metal substrates.[163] Very few publications have focused on the incorporation of these adhesion promoters as part of the coating system.

Esfandeh *et al.* investigated the effect of silane-based adhesion promoters as additives in a silicone top-coated, epoxy primed system applied on an aluminum substrate. Various SCA and three different application methods were used to improve the adhesion of silicone coating to the epoxy primer. In application method one, the SCAs were added to the epoxy hardeners at various weight percentages. The adhesion strength of the coating system increased proportionally with additive levels. A maximum adhesion strength of 1494 kN/m^2 was obtained when 5 wt.% of 3-aminopropyltriethoxysilane was added to the primer, and adhesive failure was observed. For application method two, the SCAs were added to the silicon topcoat. The best adhesion strength of 2068.8 kN/m was obtained with 1 wt.% of Bis-(gammatrimethoxysilylpropyl) amine. Cohesive failure was noted. Unfortunately, the incorporation of the SCA reduced the pot life of the topcoat to less than 3 mins, which is not feasible for application. In application method three, the SCAs were added as a unicoat consisting of epoxy/silicone/hardeners at 1 wt%. The epoxy/silicone ratio was varied. At all ratio blends, the aminosliane outperformed other SCAs. The best performance was attributed to Bis-(gammatrimethoxysilylpropyl) at 50/50 silicone/epoxy systems in 2097 kN/m^2.[141]

Fedoseev *et al.* improved the adhesion of epoxy adhesive cured with anhydride and amine hardener on aluminum by incorporation of (3-glycidoxypropyl)trimethoxysilane and 3-aminopropyltriethoxysilane promoters. They demonstrated that the addition of promoters decreased the surface free energy of adhesive, which is a required condition for good adhesion between an adhesive and a substrate[164]. Miszczyyk *et al.* demonstrated the increased adhesion of additive of (3-glycidoxypropyl)trimethoxysilane to epoxy results in improved protective behavior of the coating and is related to a large increase in the resistance in the pores of the coating.[136]

In this work, polyether diols and polyetheramine were incorporated in a DGEBA - Epikure 3164 system, and their effect on flexibility was investigated. Polytetrahydrofuran (pTHF) and Jeffamine pTHF-170 (ApTHF-170) were selected as the polyether diol and polyetheramine, respectively. These two polyethers were chosen because, unlike Jeffamine D-230, D-2000, and T-5000, they have not been extensively investigated in the literature. Furthermore, the manufacturers claim that crosslinkers based on polytetrahydrofuran are beneficial in enhancing adhesive peel strength in epoxy formulations, however, this claim has not been well investigated in the literature. For improved adhesion, the polyethers were paired with silane coupling agent adhesion promoters, 3-aminopropyl-triethoxysilane (APTS) and 3-aminopropyl(diethoxy)methylsilane (ADMS), the two most common adhesion promoters used in the coatings and composite industries. The adhesive strength of the modified epoxy was evaluated on aluminum, steel, carbon fiber reinforced plastics, and fiberglass-reinforced polymer.

Experiments

Materials

The epoxy resin used in this study was EPON 828 supplied by Hexion Specialty Chemicals, Inc. EPON 828, also chemically known as bisphenol-A-(epichlorohydrin), has a density of 1.16 g/cm3 at 298 K. The curing agent, Epikure 3164, with a density of 0.98 g/cm^3, was supplied by BASF Corporation. Jeffamine THF 170 (ApTHF-170) was provided by Huntsman. Sigma Aldrich (now Millipore) was used to obtain ~250 and ~1000 average Mn polytetrahydrofuran (pTHF-250 and pTHF-1000), as well as 3-aminopropyltriethoxy-silane (APTS), 3-aminopropyl(diethoxy)methylsilane (ADMS), and xylene. Steel (QD-35) and aluminum (A-36) panels were obtained from Q-Panel. MacMaster-Carr provided the carbon fiber reinforced plastics Sheets (Ultra-Strength Lightweight 1/16” thick) and Fiberglass reinforced polymer (3/16’’ thick).

Experimental Design

The study was designed using nine distinct types of polyether-based additives at three levels (1%, 5%, and 10% based on Epon 828 weight). Three of the additives consist solely of polyethers of various molecular weights. Another three additives are comprised of a 2:1 APTS to polyether mixtures. While the remaining three consisted of 2:1 AMDS to polyether mixtures. The weight percent of additives is based exclusively on the amount of polyether. The formulations were applied on four different substrates (aluminum, steel, carbon fiber reinforced plastics, and fiberglass reinforced polymer). The representative chemical structures of the additives used are shown in Figure 5.1. The coatings were designed as a three-factor factorial study where the type of additives, weight percent of additives, and substrate type were considered factors. Factor 1 (type of additives) had 9 levels, Factor 2 (wt % of additive) had 3 levels, Factor 3 (substrate type) had 4 levels, resulting in 27 unique formulations with 108 treatment combinations (Table 5.1). The statistical analysis of the response variable was calculated using Design expert 13 (Stat-Ease Inc., USA).

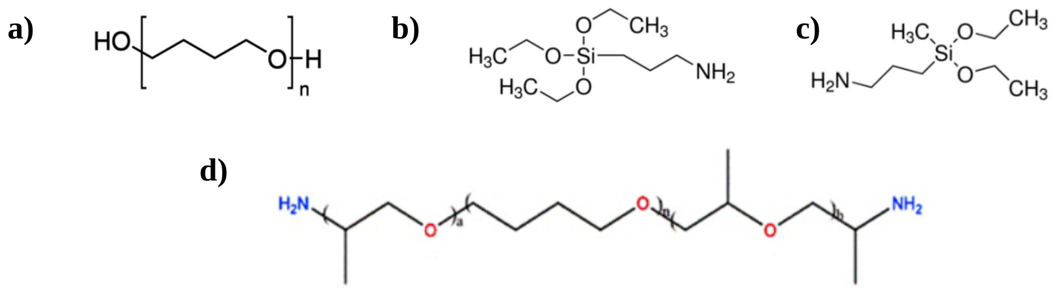

Figure 5.1. Chemical structure of polyethers and silane coupling agents used for the experiment.
a) polytetrahydrofuran, b) 3-Aminopropyl-triethoxysilane,
c) 3-aminopropyl(diethoxy)methylsilane, d) polyether amine

Table 5.1. Properties of polyether and silane coupling agent used in the study

Additives	Function	Description	AHEW	Hydroxyl Number (mgKOH/g)	Tg (°C)	MW (g/mol)
pTHF-250	Flexibilizer	Polytetrahydrofuran Mn 250	-	408.0-498.7	-98	250
pTHF-1000	Flexibilizer	Polytetrahydrofuran Mn 1000	-	109.5 –115.1	-77	1000
ApTHF-170	Flexibilizer	polyether amine	380	-	-	1700
ADMS	Adhesion Promoter	3-Aminopropyl(diethoxy) methylsilane	-	-	-	191.43
APTS	Adhesion Promoter	(3-Aminopropyl) triethoxysilane	-	-	-	221.37

Coating Formulation

A general formulation procedure is described as follows. An epoxy base consisting of 74 weights % Epon 828 and Xylene was made by mixing the components until a consistent solution was formed. The appropriate amount of polyether and silane coupling agent was added to the epoxy resin and the components were mixed for 20 mins to ensure the formation of a uniform blend. The crosslinking solution consisting of additive and Epikure 3164 was added at a 1:1 equivalent (epoxy: amine) ratio to the epoxy mixture. The formulation was hand-mixed for a few minutes and an induction period of 20 minutes was observed. A control, CLR-00, consisting of epoxy and amine crosslinker without the incorporation of additives is also made. Table 5.2 shows all the experimental coating formulations.

Table 5.2. Composition of silane coupling agent and polyether-modified epoxy coatings

Formulation	Polyether (g)	Silane Coupling Agent (g)	Xylene (g)	Epon 828 (g)	Epikure 3164 (g)
ApTHF-170-1	0.40		9.85	29.75	39.21
ApTHF-170-2	1.91		8.35	29.75	35.30
ApTHF-170-3	3.64		6.62	29.75	30.20
pTHF-250-1	0.39		9.86	29.75	40.13
pTHF-250-2	1.92		8.34	29.76	38.96
pTHF-250-3	3.66		6.59	29.75	37.64
pTHF-1000-1	0.40		9.86	29.78	40.17
pTHF-1000-2	1.91		8.35	29.75	38.97
pTHF-1000-3	3.63		6.62	29.75	37.58
ADMS/ApTHF-170-1	0.41	0.77	9.87	29.76	39.20
ADMS/ApTHF-170-2	1.91	3.48	8.51	29.75	35.30
ADMS/ApTHF-170-3	3.64	6.15	7.29	29.75	30.22
ADMS/pTHF-250-1	0.39	0.77	9.87	29.76	40.46
ADMS/pTHF-250-2	1.75	3.49	8.51	29.75	39.02
ADMS/pTHF-250-3	2.96	5.99	7.29	29.75	40.50
ADMS/pTHF-1000-1	0.39	0.78	9.87	29.76	40.15
ADMS/pTHF-1000-2	1.75	3.51	8.50	29.75	38.98
ADMS/pTHF-1000-3	2.97	5.93	7.29	29.75	37.63
APTS/ApTHF-170-1	0.39	0.77	9.87	29.75	39.20
APTS/ApTHF-170-2	1.75	3.50	8.51	29.76	35.30
APTS/ApTHF-170-3	3.00	6.00	7.29	29.75	39.63
APTS/pTHF-250-1	0.39	0.77	9.87	29.76	40.10
APTS/pTHF-250-2	1.75	3.48	8.51	29.75	38.99
APTS/pTHF-250-3	3.08	6.15	7.17	29.75	37.59
APTS/pTHF-1000-1	0.38	0.78	9.88	29.76	40.11
APTS/pTHF-1000-2	1.75	3.51	8.51	29.75	38.95
APTS/pTHF-1000-3	3.08	6.16	7.17	29.75	37.62
CLR-00			9.82	29.76	40.16

Coating Application and Curing

All formulations were applied on steel, aluminum, fiberglass reinforced polymer, and carbon fiber reinforced plastics substrates previously cleaned with acetone and Kimwipes. The coatings were applied at 8 mils wet film thickness flashed for 20 minutes at room temperature and cured at 80°C for another 20 minutes. The coatings were then allowed to air dry for 24 hours before to testing. An average dry film thickness of 60 µm ± 5 µm was obtained using an Elcometer thickness gauge on the metallic substrates (Al and Fe). Drawdowns were also made on PTFE films to produce free-standing films of the formulations for DMA and DSC tests.

Pull Off-Adhesion Testing

Pull-off adhesion testing of the coating was performed according to the procedure described in ASTM D 4541. Dollies of 20 mm diameter were cleaned by acetone and then glued to the surface of the coated panels with two components epoxy (3M ™ Scotch-Weld ™ Epoxy Adhesive 460) formulated to a 1:1 volume mix ratio. After adhesive curing for 24 hours, the area of the dollies was separated from the rest of the coating using a cutting tool, and the testing apparatus, a PosiTests pull-off adhesion tester (DeFelsko Corporation, New York), was attached to the loading fixture. A normal force was applied onto the dolly until failure occurred. For each test, three replicate samples were employed, and the arithmetic mean was calculated.

Reverse Impact Resistance

The reverse impact test, which demonstrates the resistance of coatings to rapid deformation, was measured by dropping a 4 lbs weight from various heights through a guide tube onto the metallic side of the steel and aluminum coated panels. The related height at which cracking or other failures in the coating films happened was noted and impact strength was calculated. Samples that did not fail were noted as having impact strength of >169 in.-lb. A Gardner impact tester was used per ASTM D 2794.

Conical Mandrel

The coated aluminum and steels panels were assessed for flexibility by bending over a conical mandrel per ASTM D522. The specimens were fastened and bent over the frame of the mandrel, and cracks were observed along the increasing radius of the conical mandrel.

Dynamic Mechanical Analysis

Dynamic mechanical analysis was conducted in a nitrogen atmosphere with a TA Instruments Q-800 Dynamic Mechanical Analyzer. Measurement of the shear storage modulus (E') and loss tangent (tan δ) of fully cured samples was conducted at a frequency of $\omega = 1$ Hz and working in tensile clamps with rectangular samples (10 mm × 0.5 mm × 0.10 mm). The temperature was increased from -80 to 150 °C at a constant rate of 5 °C/min. T_g was taken as the maximum in the damping peak associated with α transition (maximum of the tan δ curve).

Differential Scanning Calorimetry

A TA Instruments Q 2000 differential scanning calorimeter (DSC) was used to determine the glass transition temperature (T_g) of the coatings. The cured coatings were placed in an aluminum pan and subjected to a heat–cool–heat cycle under nitrogen. The samples were heated from -80°C to 200 °C, cooled to -80°C, and then heated again to 200°C at 5°C/min. T_g was obtained from the second heating cycle.

Nanoindentation

Hardness and elastic modulus are calculated from the load vs. displacement data obtained by nanoindentation on the aluminum-coated substrate. Nine indentations were performed using a Hysitron Triboindenter nanoindenter apparatus. This instrument monitors and records the dynamic load and displacement of a diamond Berkovich tip with a radius of about 1 µm as it penetrates the sample while increasing force from 0 to 1000 µN.

König Pendulum Hardness

König pendulum hardness of the coatings was measured following ASTM D 4366 using a Byk pendulum hardness tester from an amplitude of 6° to 3°. The hardness test results are reported in oscillations. Aluminum-coated substrates were used for hardness measurements.

Results and Discussion

Flexibility

Conical Mandrel and Reverse Impact

The flexibility and impact resistance of the metal-coated substrates was evaluated by conical mandrel bend and reverse impact test. The results of all formulations applied on metal substrates evaluated were 0 cm of cracking for the conical mandrel, the highest possible flexibility results. The reverse impact test also resulted in the highest possible impact strength possible for all formulations evaluated. The steel coated panels for all formulations assessed 169 in-lbs., while substrate failure for aluminum occurred around 100 in-lbs. Since the conical mandrel and impact resistance was unable to provide a more nuanced and sensitive method of characterizing flexibility, other indirect characterization methods for flexibility are needed. DMA, DSC, nanoindentation, and König pendulum hardness were all employed to further characterize flexibility.

DMA and DSC

DMA is a technique often used to study the viscoelastic behavior of polymer and can thus be utilized to distinguish between the flexibility of coating systems. The storage modulus denotes the solid-like or elastic behavior of the material and is related to the extent of cross-linking. The higher the storage modulus the higher the strength or rigidity of the polymer network. Results of DMA are shown in Fig 5.2 and Table 5.3. Aside from ApTHF- 170 at 5 wt.%, the addition of all other polyethers as the sole additive results in a decrease in the storage modulus at -50 °C compared to the unmodified epoxy, suggesting decreased chain rigidity and increased flexibility. In all systems investigated, the storage module decreases as temperature increases, indicating a change from a stiffer to a rubberier state. ANOVA results obtained for the storage modulus are given in Table 5.4. An F-value of 2.17 implies the model is significant at the 90% confidence interval. According to the results, the addition of SCA showed statistically and physically significant effects on the storage modulus. However, polyether and the level at which they are added are not statically significant at the 90% confidence interval. The effect charts of the parameters are given in Fig 5.3.

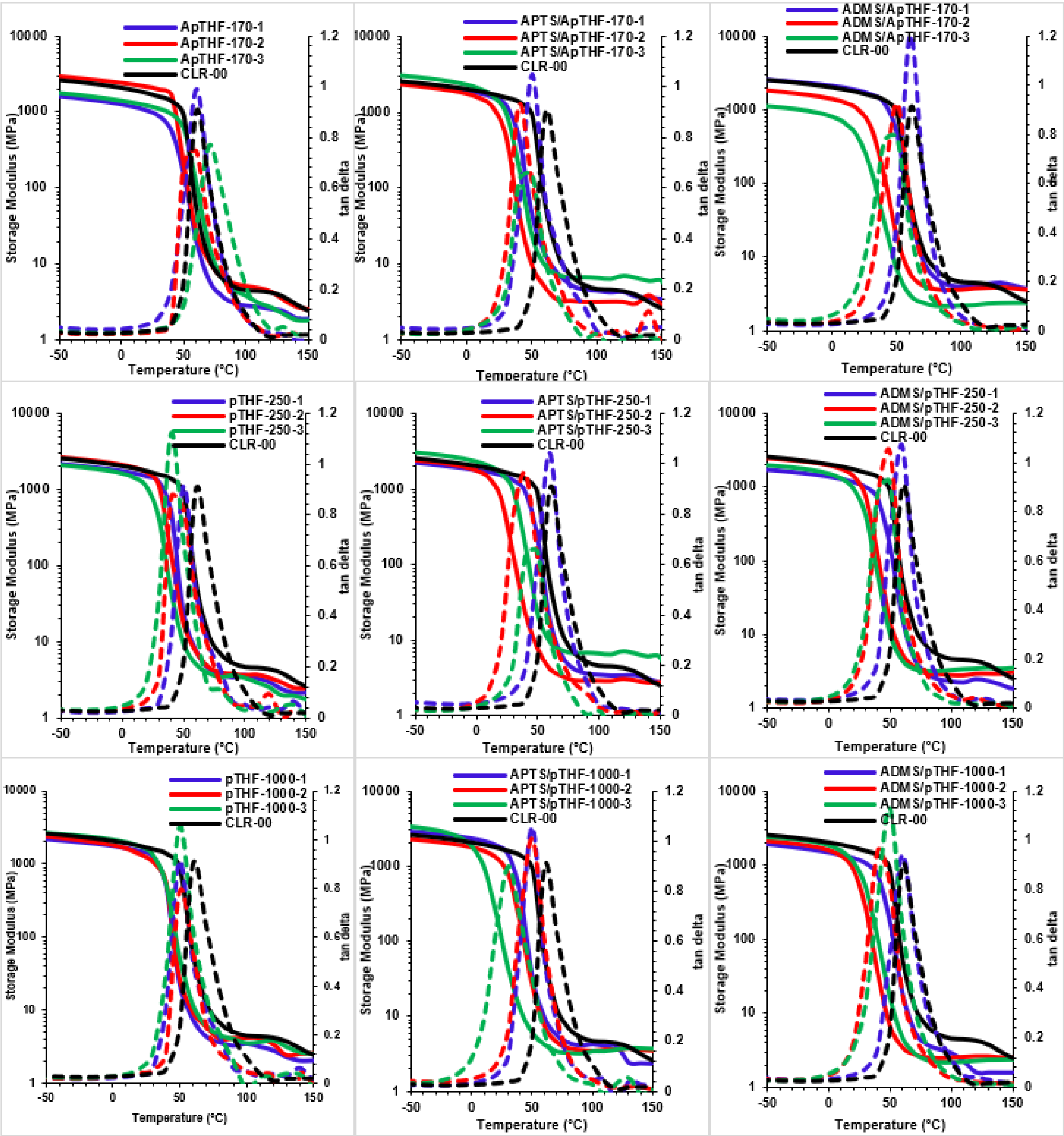

Figure 5.2. DMA results of epoxy modified with polyether (ApTHF-170, pTHF-250, and pTHF-1000) and SCA (APTS and ADMS) at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

Table 5.3. Characteristic of DMA for polyether and SCA modified epoxy coating: T_g, XLD, and storage modulus

Formula	E' at -50° C (Mpa)	Tg (°C)	E' at Tg+50 °C (MPa)	XLD (mol m-3)
ApTHF-170-1	1607	57.99	4.22	0.44
ApTHF-170-2	3007	54.68	4	0.42
ApTHF-170-3	1734	60.28	1.95	0.2
pTHF-250-1	2209			
pTHF-250-2	2614	44	3.53	0.39
pTHF-250-3	2095	42.33	3.83	0.42
pTHF-1000-1	2209	48.11	3.53	0.38
pTHF-1000-2	2432	49.94	4.3	0.46
pTHF-1000-3	2612	51.36	3.79	0.41
APTS/ApTHF-170-1	2439	49.64	4.43	0.48
APTS/ApTHF-170-2	2357	40.88	4.23	0.58
APTS/ApTHF-170-3	3077	43.23	6.57	0.72
APTS/pTHF-250-1	2247	59.15	3.39	0.36
APTS/pTHF-250-2	2383	30.16	2.23	0.25
APTS/pTHF-250-3	3077	30.99	1.79	0.2
APTS/pTHF-1000-1	2899	49.1	4.25	0.46
APTS/pTHF-1000-2	2270	47.92	3.36	0.36
APTS/pTHF-1000-3	3332	33.68	3.19	0.35
ADMS/ApTHF-170-1	2561	60.4	4.13	0.43
ADMS/ApTHF-170-2	1789	49.41	3.61	0.39
ADMS/ApTHF-170-3	1114	45.73	2.2	0.24
ADMS/pTHF-250-1	1703	56.63	2.26	0.24
ADMS/pTHF-250-2	2479	46.61	2.83	0.31
ADMS/pTHF-250-3	1944	43.75	3.28	0.36
ADMS/pTHF-1000-1	1859	61.42	3.71	0.39
ADMS/pTHF-1000-2	2075	43.52	2.46	0.27
ADMS/pTHF-1000-3	2389	39.46	2.23	0.25
CLR-00	2572	62.25	4.32	0.45

Table 5.4. ANOVA results of polyether and SCA on Tg from DMA

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	2.653E+06	6	4.422E+05	2.17	0.0901
A-Polyether	3.191E+05	2	1.596E+05	0.7819	0.4710
B-Additive Level	2.034E+05	2	1.017E+05	0.4984	0.6148
C-SCA	2.130E+06	2	1.065E+06	5.22	0.0150
Residual	4.082E+06	20	2.041E+05		
Cor Total	6.735E+06	26			

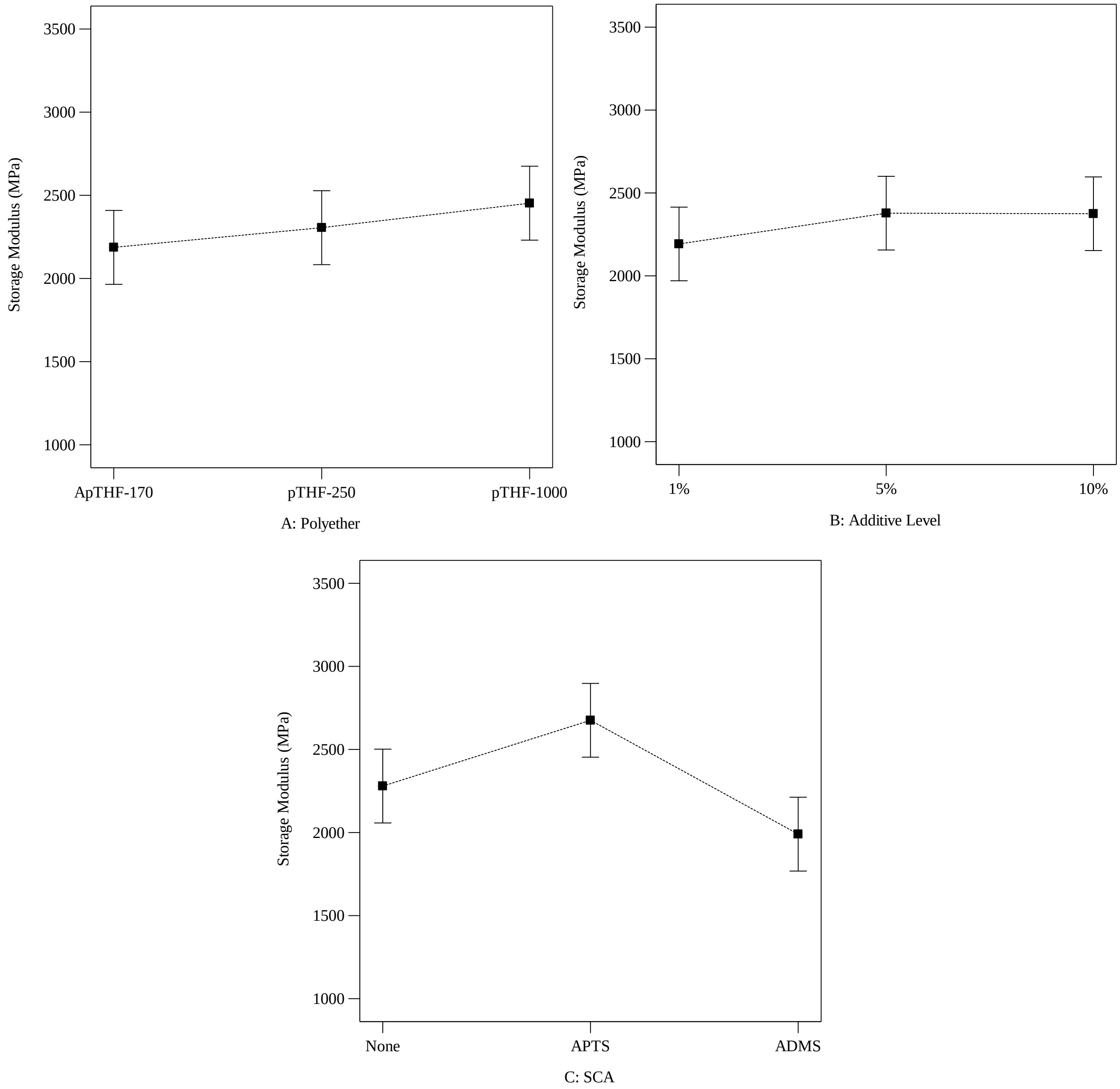

Figure 5.3. Plot of the effect of polyether (ApTHF-170, pTHF-250, and pTHF-1000), level (1,5 and 10 wt.%), and SCA (APTS and ADMS) on storage modulus (-50°C) obtained from DMA

The height and area of the tan δ curves provide information about the ability of the material to dissipate energy. The area of tan δ decreases proportionally with the addition of increasing ApTHF-170 concentration indicating restricted molecular mobility. This result is corroborated by the T_g, ranging from 54.68 to 60.28 °C. ApTHF-170-3 results in the highest T_g of all the polyether investigated. The high molecular weight of ApTHF-170 (1700 g/mol) compared to pTHF-250 (250 g/mol) and pTHF-1000 (1000 g/mol) makes the result a bit surprising however, the observed behavior could be attributed to the presence of the methyl group. The branching effect caused by the presence of the methyl group results in restriction of the segmental mobility thereby leading to an increase in T_g. Even though the segmental motion is limited, the branching of the long poly (tetramethylene ether glycol) chain leads to a large molecular weight between crosslinked, which is reflected in the low XLD of 0.20 mol m^{-3} for ApTHF-170-3, compared to the unmodified epoxy.

The addition of pTHF-250 and pTHF-1000 to the epoxy resin either does not affect the area of the tan δ curve nor result in an increase indicating enhanced molecular mobility. pTHF-1000 modified coating results in an overall 10°C decrease in T_g compared to the unmodified system; changes in the concentration do not have a proportional change in the T_g. An increase in XLD is observed with increasing levels of pTHF-1000 demonstrating that it is a more effective flexibilizer at lower concentrations. Of all the sole polyethers investigated, pTHF-250-3 results in the lowest T_g, gradually decreasing with increasing concentration. This result parallels that of Song *et al.* where they found that lower molecular weight pTHF resulted in the lowest T_g.[165] They attributed the performance of the lower molecular weight pTHF to better dispersion and larger restricting behavior.

The addition of both SCA, APTS, and AMDS, to all three polyethers, results in an overall decrease in T_g, compared to unmodified epoxy and sole polyethers. These results may be attributed to the flexibility of the Si-O bond and an increase in free volume. The low rotation energy barrier of the Si-O bond compared to the C-C bond coupled with the longer chain length results in lower activation energy to impart viscous flow. Thus, a lower T_g and higher degree of flexibility are associated with the presence of Si-O bonds.[166]

Due to the reactivity of amines and oxirane rings, the primary amine of the SCA is expected to react with the epoxy resins forming a prepolymer. This reaction is sequentially followed by the hydrolysis of the alkoxy group due to the presence of atmospheric moisture. Condensation is expected followed by two outcomes (i) the hydroxyl group on the epoxy- SCA prepolymer can hydrogen bond to the hydroxyl group on polyether forming a mixture with two distinct unreacted compounds, or (ii) Zimmer's hydrogenesis can occur resulting in a covalent bond between the epoxy-SCA prepolymer and polyether amine[139]. Gelation of ADMS/pTHF-250-3 and APTS/ApTHF-170-3 within mins after addition of SCA, polyether, and epoxy resin indicates that the second reaction is occurring; these compounds are reacting together to form a large hyperbranched macromolecule resulting in more chain ends and an increase in overall free volume.[128]

ANOVA was performed on the T_g and XLD results, however, the effect of polyether, SCA, and additive level on the XLD was not found to be statistically significant at the 90% or 95% confidence interval. ANOVA results obtained for the T_g from DMA are given in Table 5.5. An F-value of 5.92 implies the model is significant; there is only a 0.13% chance that the F-value could occur due to noise. According to the results, the level of additive and silane coupling agents showed statistically significant effects on the T_g from the DMA ($p < 0.05$).

Table 5.5. ANOVA results of polyether and SCA on Tg from DMA

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1236.91	6	206.15	5.92	0.0013
A-Polyether	152.77	2	76.39	2.19	0.1391
B-Additive Level	690.21	2	345.10	9.90	0.0011
C-SCA	379.97	2	189.98	5.45	0.0135
Residual	662.10	19	34.85		
Cor Total	1899.01	25			

The effect charts of the parameters on T_g from DMA are given in Fig 5.4. As expected, as the additive level increases, the T_g decreases. The ether segments of the chain have significant molecular mobility which readily increases the overall chain flexibility. The lower effect of APTS on T_g compared to no SCA and ADMS could be attributed to the presence of the extra Si-O bond.

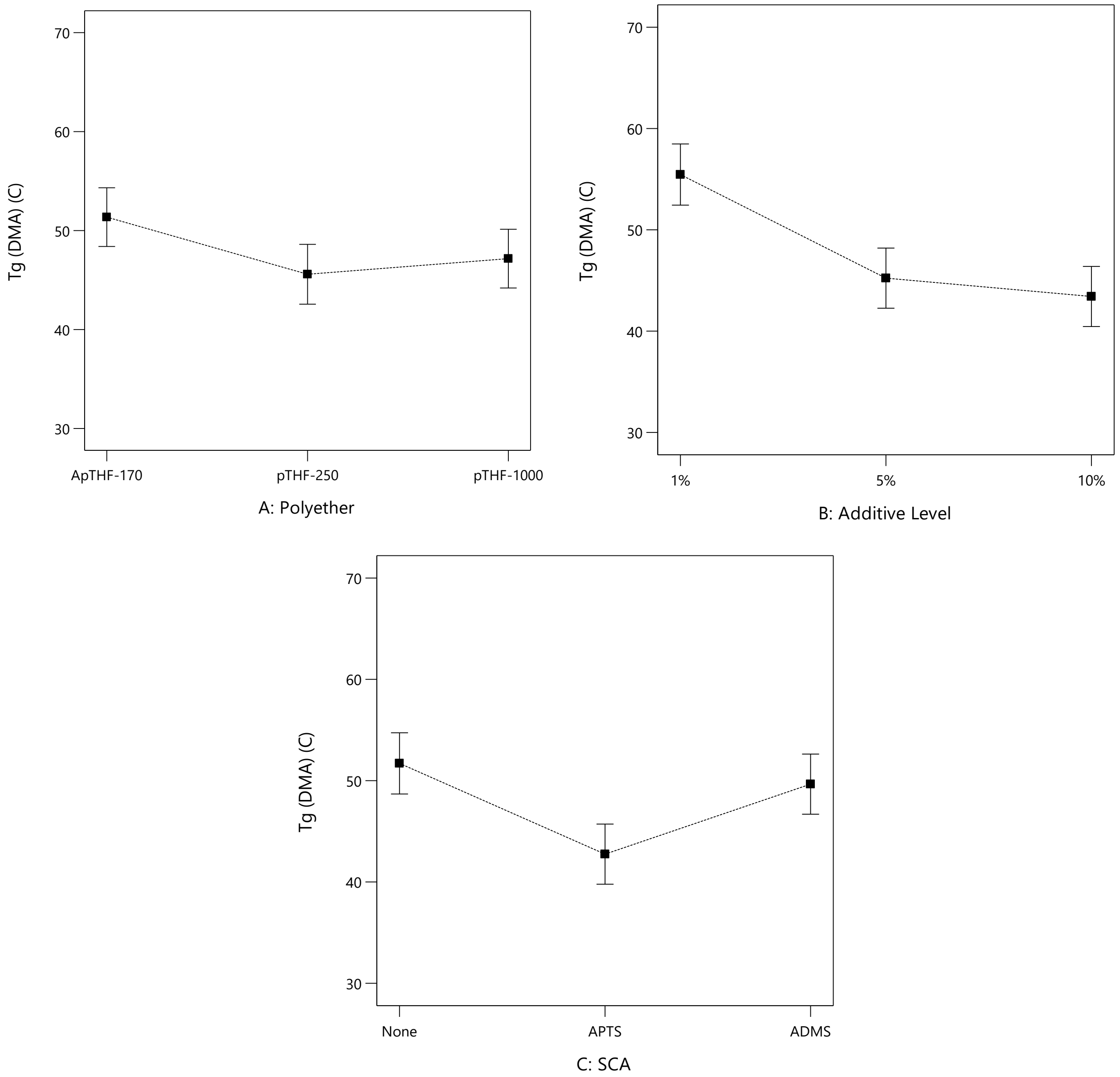

Figure 5.4. Plot of the effect of polyether (ApTHF-170, pTHF-250, and pTHF-1000), level (1,5 and 10 wt.%), and SCA (APTS and ADMS) on glass transition obtained from DMA

As depicted in Fig 5.5, a 20 ° C difference in T_g is observed between the DMA and DSC analysis. ANOVA results obtained for the T_g from DSC analysis are given in Table 5.6. An F-value of 8.26 implies the model is significant; there is only a 0.02% chance that the F-value could occur due to noise. According to the results, all factors examined, including polyether, amount of polyether, and silane coupling agents showed statistically significant effects on the T_g from the DSC ($p < 0.05$).

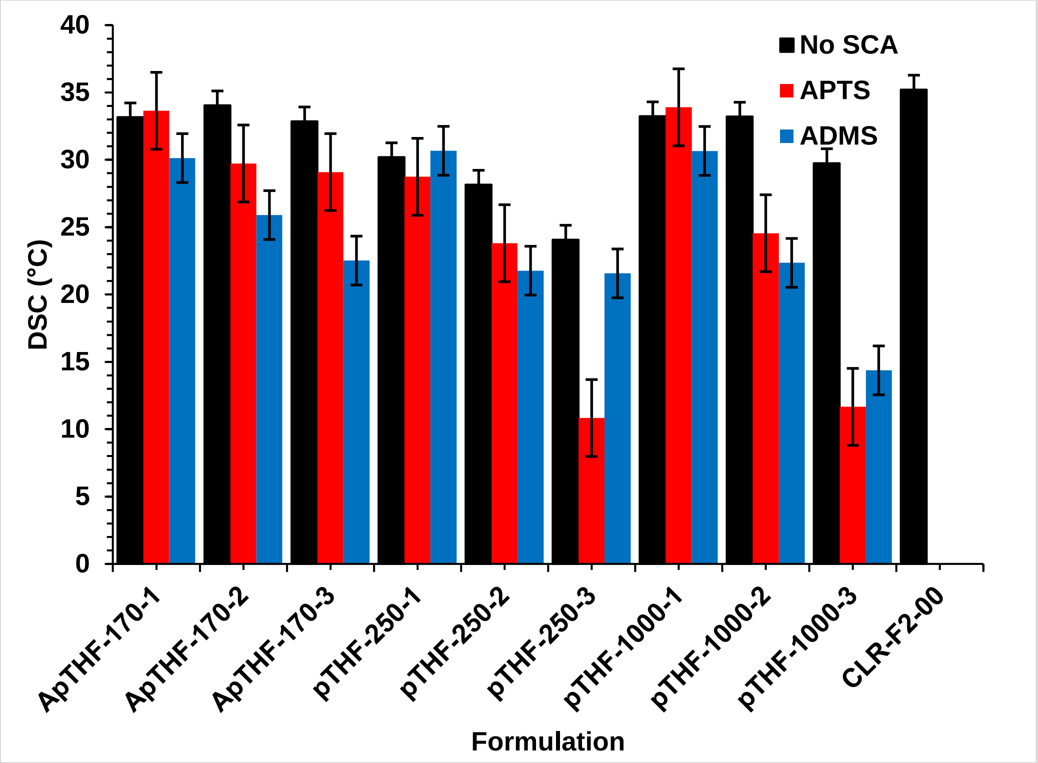

Figure 5.5. Glass Transition of DSC experiment of modified and unmodified epoxy-amine coating with the addition of polyether (ApTHF-170, pTHF-250, and pTHF-1000), coupled with SCA (APTS, and ADMS) at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 5.6. ANOVA results of polyether and SCA on Tg from DSC

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	816.92	6	136.15	8.26	0.0002
A-Polyether	131.78	2	65.89	4.00	0.0356
B-Additive Level	436.75	2	218.38	13.24	0.0003
C-SCA	244.25	2	122.12	7.41	0.0042
Residual	313.28	19	16.49		
Cor Total	1130.19	25			

The effect charts of the parameters are given in Fig 5.6. As observed with the DMA results, as the additive level increases the T_g decreases. APTS and ADMS have similar effects on the T_g. pTHF-250 and pTHF-1000 have a similar effect on T_g.

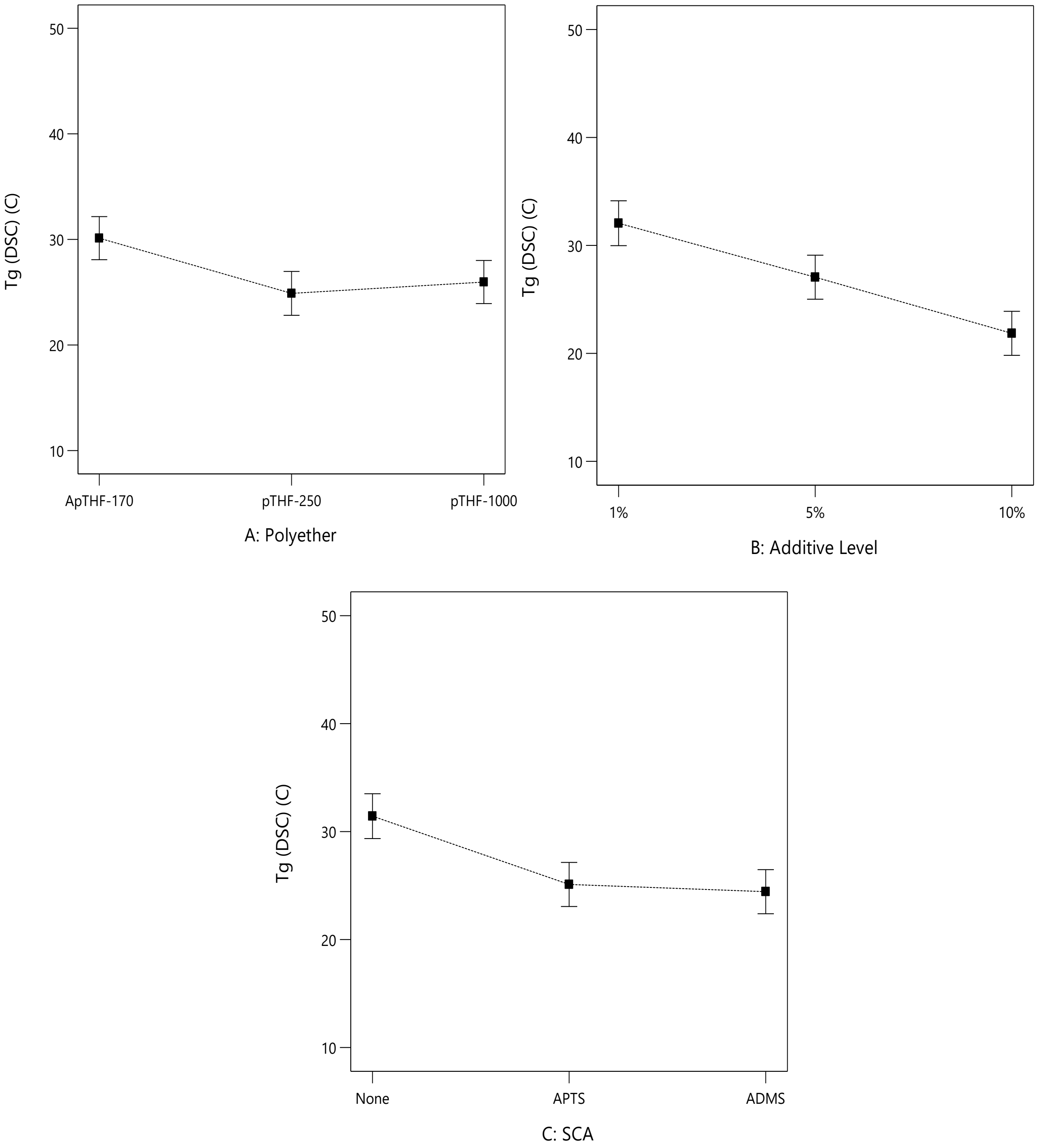

Figure 5.6. Plot of the effect of polyether (ApTHF-170, pTHF-250, and pTHF-1000), level (1,5 and 10 wt.%), and SCA (APTS and ADMS) on glass transition obtained from DSC

Nanoindentation

Nanoindentation was used to determine hardness and elastic modulus; the results are depicted in Fig 5.7 and 5.8. The elastic modulus describes the relative stiffness or rigidity of material; a stiff material will have a high modulus of elasticity, while a flexible material will have a low modulus of elasticity, thus elastic modulus can be used as a measure of flexibility. The experimental coatings showed an elastic modulus range of 200 to 5240 MPa, suggesting a wide range of flexibilities, however, per ANOVA, no statistical significance was determined for elastic modulus and indentation hardness at the 95% and 90% confidence interval. General trends, nonetheless, were observed.

The neat coating without any flexibilizer has an elastic modulus of 2455 MPa. As the concentration of polyether increases, the elastic modulus decreases, showing a change from 2456, 1464, 657 for pTHF-250 at 1 wt.% 5wt%, and 10 wt.%, and 2191, 1616, and 536 for pTHF-1000, respectively. Similarly, to DSC and DMA results, between pTHF-250 and pTHF-1000.

The inclusion of SCA to pTHF disrupts the direct correlation between molecular weight and concentration, with APTS/pTHF-250 at 1 and 10 wt % demonstration comparable elastic modulus to that of CLR-00 at 2220 and 2167, respectively. APTS/pTFH-1000 at 1 and 10 wt. % is more flexible than the neat formulation an elastic modulus of 192 and 200 MPa, respectively. It is worth noting that for pTHF-1000 the inclusion of APTS drastically improves the flexibility as shown by the elastic modulus. Unfortunately, due to the soft elastomeric behavior of the SCA modified coating, indentation measurement could not be obtained for APTS/pTHF-250-3, APTS/pTHF-100-3, ADMS/pTHF-250-2, ADMS/pTHF-250-3, ADMS/pTHF-1000-3. The hardness results parallel that of the elastic modulus.

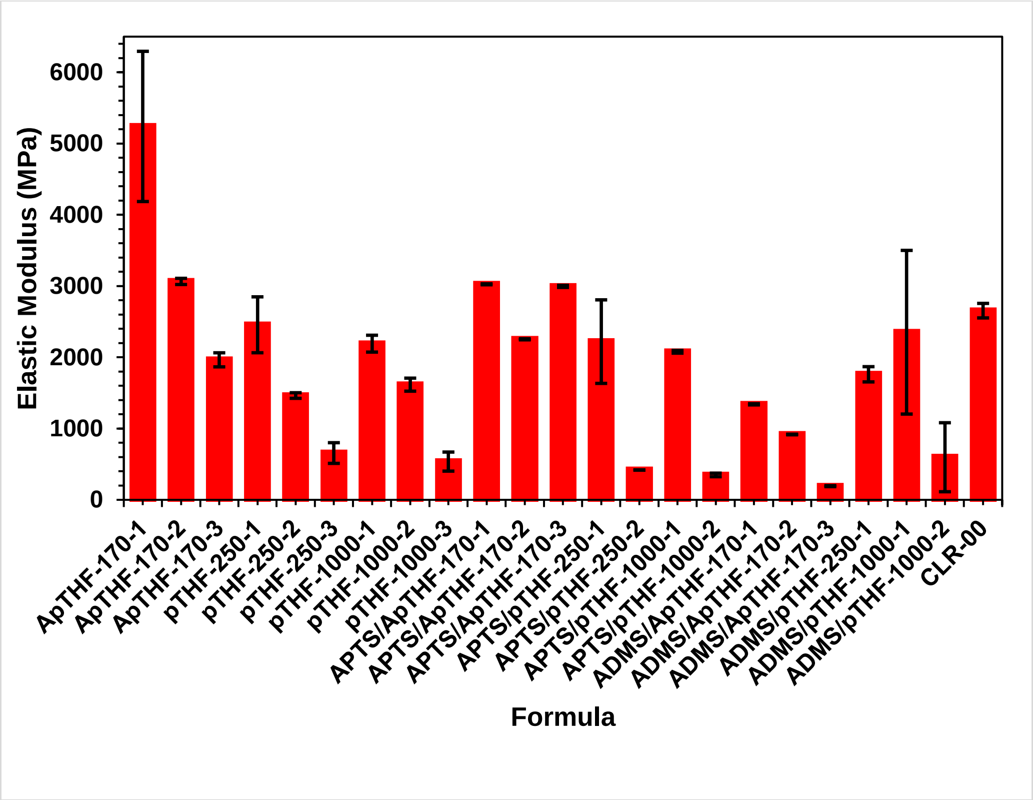

Figure 5.7. Elastic Modulus from nanoindentation experiment of modified and unmodified epoxy-amine coating with the addition of polyether (ApTHF-170, pTHF-250, and pTHF-1000), coupled with SCA (APTS, and ADMS) at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

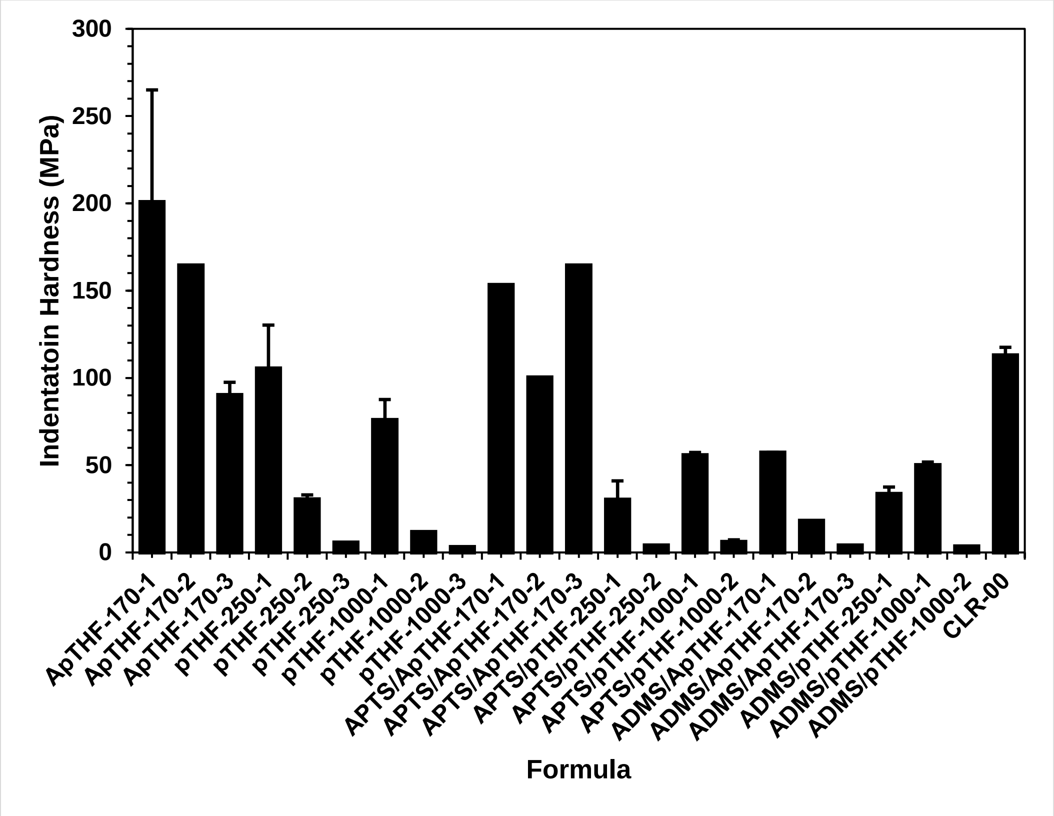

Figure 5.8. Hardness from nanoindentation experiment of modified and unmodified epoxy-amine coating with the addition of polyether (ApTHF-170, pTHF-250, and pTHF-1000), coupled with SCA (APTS, and ADMS) at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

König Pendulum Hardness

Pendulum hardness was performed on the modified formulations and the results are reported in Fig 5.9. From these results, ANOVA was performed and reported in Table 5.7 An F-value of 12.12 implies the model is significant; there is only a 0.01% chance that the F-value could occur due to noise. According to the results, the polyether, and level at which it is added as well as silane coupling agents, have significant effects on the pendulum hardness ($p < 0.05$).

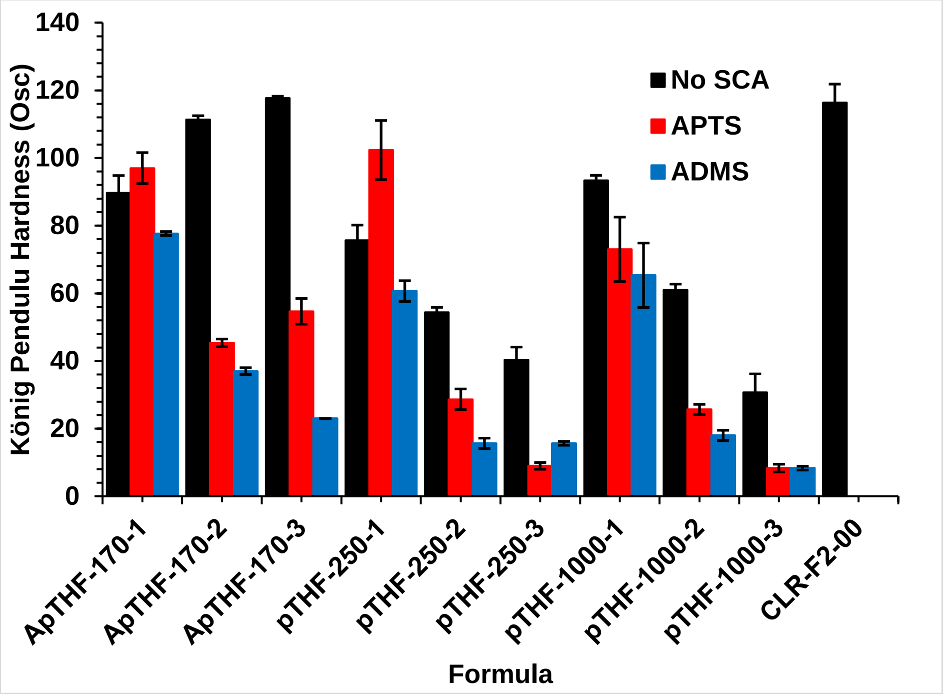

Figure 5.9. Hardness from Konig Pendulum experiment of unmodified and modified epoxy-amine coating with the addition of polyether (ApTHF-170, pTHF-250, and pTHF-1000), coupled with SCA (APTS, and ADMS) at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 5.7. ANOVA results of polyether and silane coupling agent on pendulum hardness

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	23434.02	6	3905.67	12.12	< 0.0001
A-Polyether	5039.61	2	2519.81	7.82	0.0031
B-Additive Level	11271.42	2	5635.71	17.50	< 0.0001
C-SCA	7123.00	2	3561.50	11.06	0.0006
Residual	6442.63	20	322.13		
Cor Total	29876.65	26			

The effect charts of the parameters are given in Fig 5.10. ApTHF-170 results in harder coating compared to pTHF-250 and pTHF-1000. pTHF-250 and pTHF-1000 demonstrate a similar effect on hardness. As the additive level increases, the coating hardness decreases. The incorporation of silane coupling agent results in reduced hardness performance with ADMS having the greatest effect on pendulum hardness.

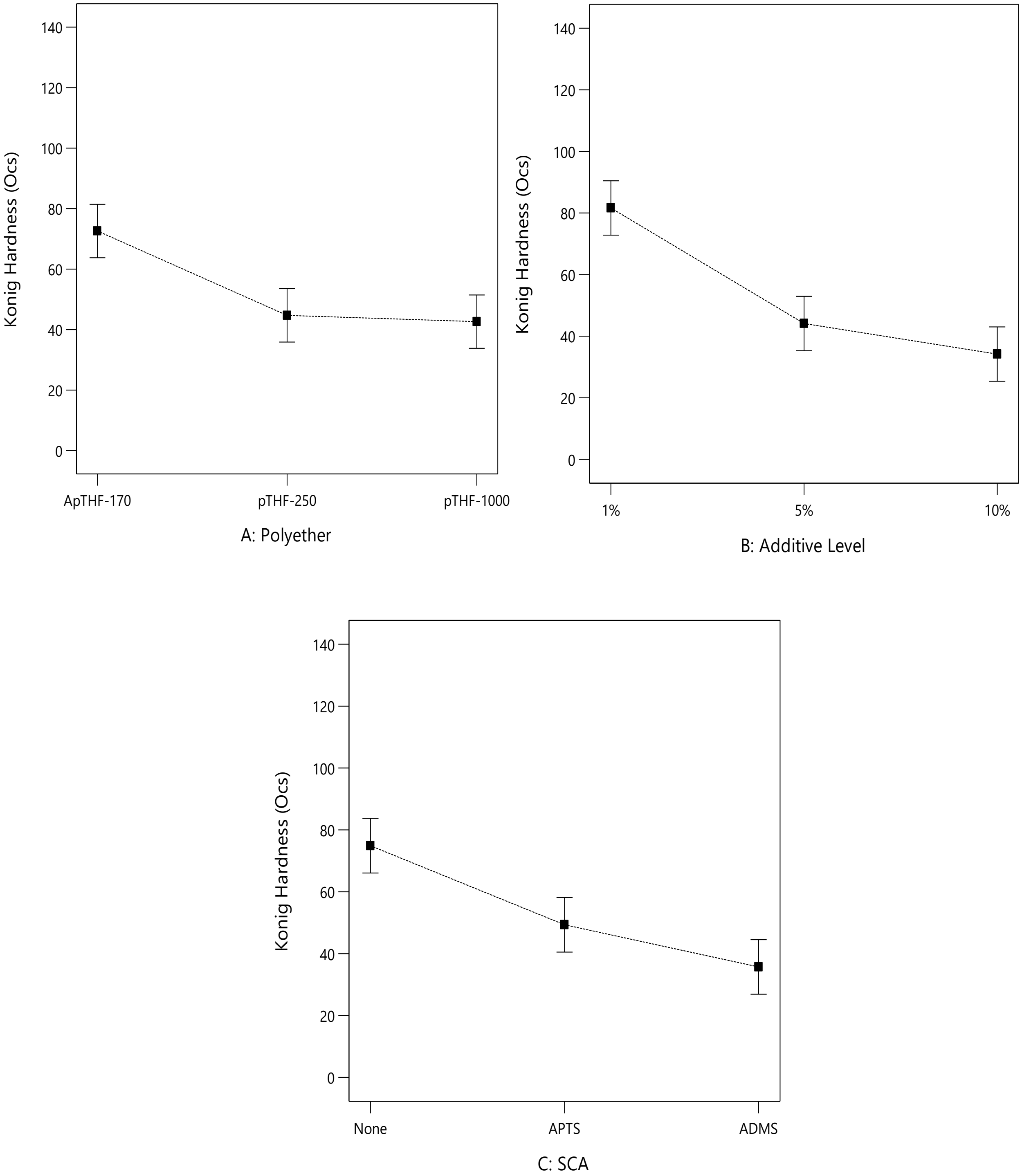

Figure 5.10. Plot of the effect of polyether (ApTHF-170, pTHF-250, and pTHF-1000), level (1,5 and 10 wt.%), and SCA (APTS and ADMS) on pendulum hardness

Adhesion

Adhesion performance on metal substrates (Fe and Al) and composites (CF and FG) were investigated and reported in Fig 5.11. ANOVA results shown in Table 5.8 demonstrates statistical significance ($p>.05$) between the adhesive effect of the substrates. To evaluate the difference between adhesive strength of the various substrates a pairwise Tukey test was performed, and significance was defined as $p <0.05$. Based on the statistical analysis reported in Table 5.9 there is no significant difference between the mean adhesive strength of epoxy resin on Fe and Al, Al and CF, Fe and CF. A noticeable and significant difference was observed between FG and all other substrates. These results are reflected in the adhesives strength of the CLR-00 which are 358, 420, 401, and 2699 MPa for Al, Fe, CF, and FG, respectively. The difference in adhesion strength of the FG to all other substrate is attributed to the difference in substrate thickness. The thin Al, Fe, and CF substrates result in a more peel-off effect due to misalignment of the normal force and deformation of the substrate. The thick FG allows for an accurate representation of the pull-off adhesion test.

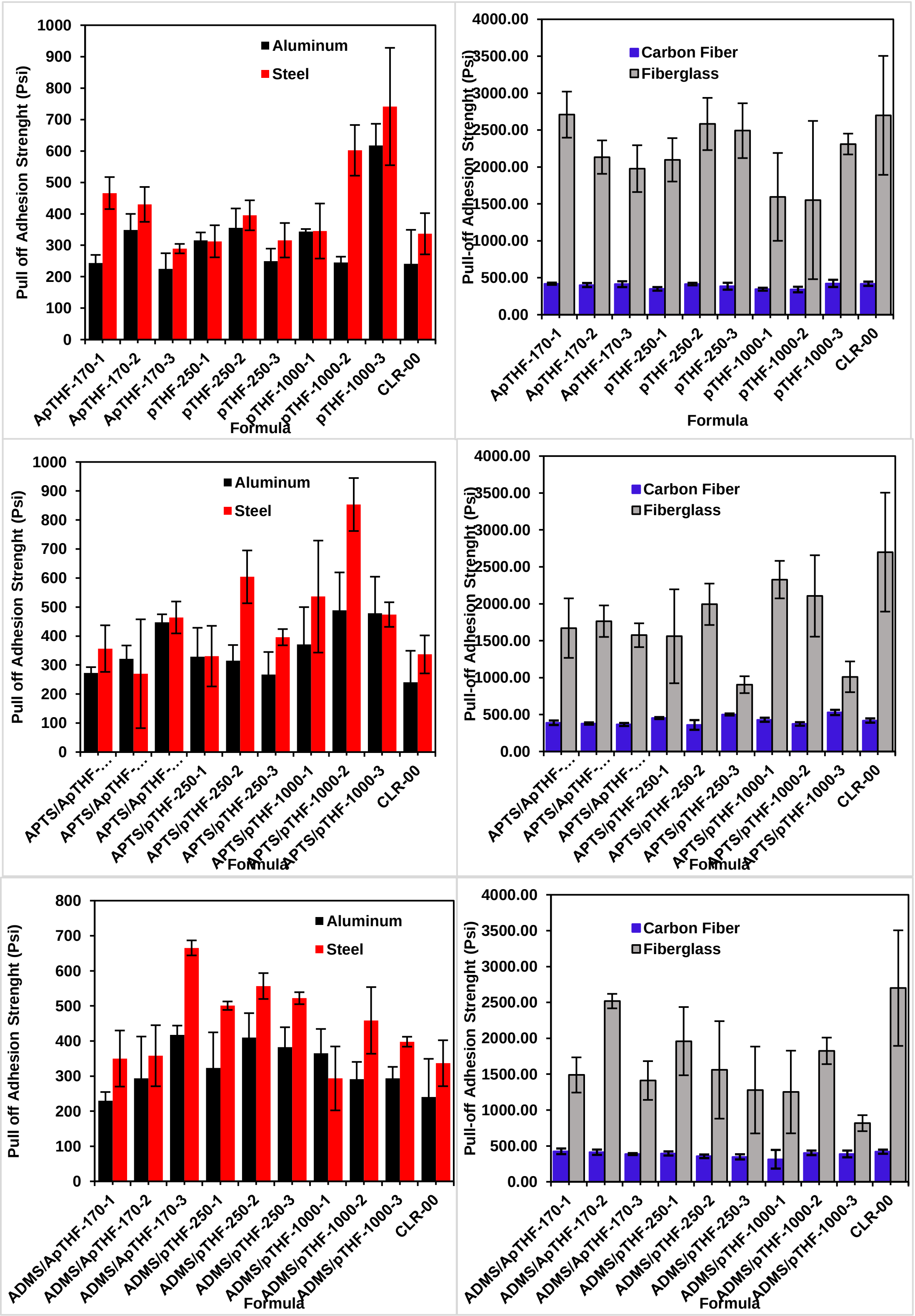

Figure 5.11. Pull-off adhesion strength Top: of sole polyether formulations on metal and composite substrates. Middle: polyether coupled with APTS formulations on metal and composite substrates Bottom: formulation on metal and composite substrate.

Table 5.8. ANOVA result of substrate effect on adhesive strength

Source	Sum of Squares	df	Mean Square	F-value	p-value
Treatment-Substrate	4.32E+07	3	1.41E+07	183.334	1.11E-16
Residual	8.49E+06	108	7.86E+04		
Cor Total	5.17E+07	111			

Table 5.9. Tukey HSD result of substrate effect on adhesive strength

Treatment pairs	Tukey HSD Q statistic	Tukey HSD p value
Al vs Fe	2.1117	0.4440
Al vs CF	1.1066	0.8462
Al vs FG	28.0997	0.0010
Fe vs CF	1.0112	0.8839
Fe vs FG	25.9820	0.0010
CF vs FG	26.9931	0.0010

The effect of the polyether, the level at which they are added, and the use of silane coupling agent on the adhesive strength of Al, Fe, and CF substrates were not statistically significant per the ANOVA test. However, from Fig 5.10, pTHF-1000 at 10 wt.% without the use of a coupling agent shows a substantial increase in adhesive strength to both metal substrates, increasing from 241 and 337 for Al and Fe for the unmodified epoxy to 617 and 741 psi, respectively. This result may be attributed to the modification method. Due to gelation of the epoxy-SCA premixed at 10 wt.% SCA, the SCA, epoxy, and amine crosslinker were mixed simultaneously and applied to the substrate. This procedure may allow for the SCA to migrate to the coating substrate interphase during the curing phase thereby allowing hydrolytic deposition of the SCA onto the metal substrate improving adhesion. The introduction of the silane coupling agent with pTHF-1000 at 10 wt.% results in a reduction in adhesive strength to the metal substrates; AMDS has a more detrimental effect on adhesive strength than APTS when coupled with pTHF-1000. ApTHF-170 and pTHF-250 do not influence adhesion to the metal substrate, however the addition of AMDS to 10 wt.% AptHF-170 result in an increase in the adhesive strength to steel by over 2-fold.

ANOVA results obtained for the pull-off adhesion strength on FB are given in Table 5.10. The F-value of 2.98 implies the model is significant; there is only a 3.02% chance that the F-value could occur due to noise. According to the results, only the addition of silane coupling agents showed statistically and physically significant effects on the pull-off adhesion strength on FG ($p < 0.05$). The effect charts of the parameters are given in Fig 5.12.

Table 5.10. ANOVA results of polyether and silane coupling agent on the adhesive strength of FG substrate

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	3.239E+06	6	5.398E+05	2.98	0.0302
A-Polyether	3.463E+05	2	1.731E+05	0.9566	0.4011
B-Additive Level	1.048E+06	2	5.240E+05	2.90	0.0787
C-SCA	1.845E+06	2	9.223E+05	5.10	0.0163
Residual	3.620E+06	20	1.810E+05		
Cor Total	6.859E+06	26			

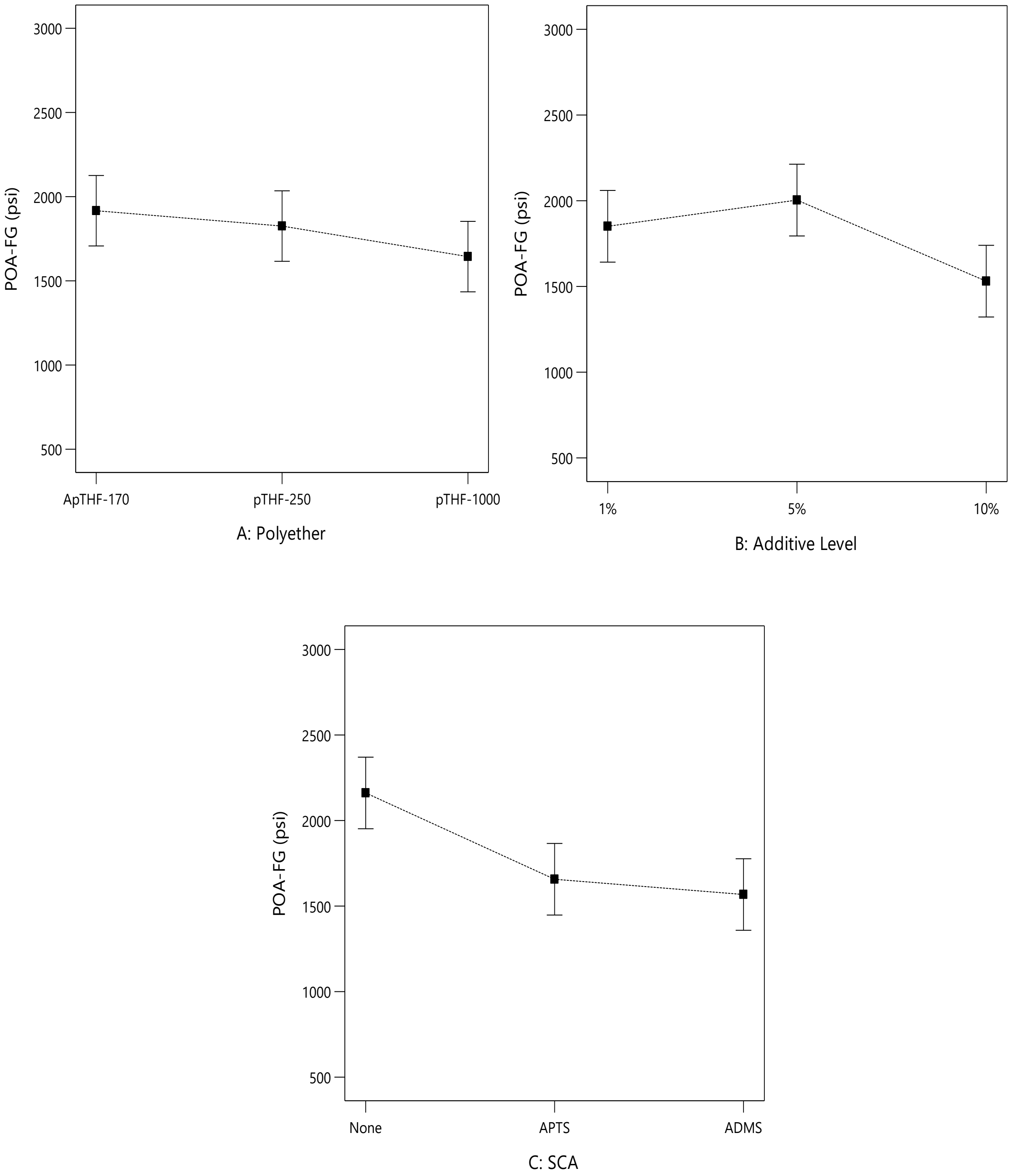

Figure 5.12. Plot of the effect of polyether (ApTHF-170, pTHF-250, and pTHF-1000), level (1,5 and 10 wt.%), and SCA (APTS and ADMS) on pull-off adhesion strength to FB substrate

For the composite substrates, neither the polyether nor the addition of silane coupling agent led to an improvement in adhesive strength. Unfortunately, for fiberglass reinforced polymer, the additives have a detrimental influence on adhesive strength resulting in a decrease in adhesive strength between the coating and substrate compared to the neat formulation. The inclusion of the silane coupling agents appears to have even more of a negative effect on adhesive strength with pTHF-1000 and AMDS at 10 wt.% resulting in the lowest adhesive strength to FG.

Conclusions

In this study, various molecular weight polyethers were coupled with SCA and their effect on the flexibility of DGEBA based epoxy coating system was investigated. The adhesive strength of the modified epoxy was evaluated on aluminum, steel, carbon fiber reinforced plastics, and fiberglass reinforced polymer. ApTHF-170 at 10 wt% results in the lowest XLD, which is to be expected due to the molecular weight of 1700 g/mol compared to 250 and 1000 g/mol, however, T_g is high due to the branching effect of the methyl group. There was no difference between the effect of pTHF-250 and pTHF-1000 on flexibility. APTS results in lower flexibility parameters compared to no SCA and ADMS. The performance of APTS was attributed to the flexibility imparted by the Si-O bond.

For adhesion measurement, polyether, the level at which they are added, and SCA has a statistically significant effect on FG but no other substrate. The addition of SCA compromises the adhesion of modified epoxy on FG. However, APTS/pTHF-1000 at 10 wt% improves adhesion on Al and Fe substrate. The improved adhesion could be attributed to combining the epoxy, SCA, and amine crosslinker simultaneously rather than allowing the SCA and epoxy to pre-react. The SCA is allowed to migrate to the coating substrate interphase during the curing process thereby allowing hydrolytic deposition of the SCA onto the metal substrate improving adhesion.

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CHAPTER 6. MODIFICATION OF EPOXY FOR IMPROVED ADHESION AND FLEXIBILITY FOR MULTI-SUBSTRATE APPLICATION

Introduction

The demand for lightweight, fuel-efficient, and environmentally friendly automobiles, watercraft, and airplanes has prompted increased usage of composites within these infrastructures. Therefore, resulting in mixed-material bodies consisting of aluminum, steel, carbon fiber reinforces plastic and fiberglass reinforced polymer. As a result, several obstacles must be addressed, including barrier performance, adhesion, and flexibility. To protect the metal surfaces from corrosion, coating methods with exceptional barrier performance are required. However, to effectively prevent corrosion and save labor costs when applying these coatings, they must adhere to all substrates in the system. Traditional coatings have weak adherence to composites due to their low surface free energy; consequently, the adhesive strength of these protective coatings must be enhanced. Furthermore, the difference in CLTE of various materials causes dimensional changes, necessitating the use of a coating with a high degree of flexibility to accommodate these structural changes.

Epoxies are commonly used as primers for a variety of applications and are a class of high-performance thermosetting polymers known for exceptional flexibility, adhesion, high modulus, and barrier performance. However, for use as a universal coating system for multiple substrates greater adhesion and a higher degree of flexibility are required.

The flexibility of epoxy resins can be improved by changing the network density, specifically by increasing the molecular weight between chain junctions. This can be accomplished by the introduction of monofunctional or polyfunctional long-chain molecules within the polymer matrixes. These molecules react with the epoxy or amine during curing and function as a flexibilizer. Several researchers have investigated the effect of a variety of flexibilizers on epoxy resin systems.

Urbaczewski-Espuche *et al.* investigated the effect of 1,4 butanediol diglycidyl ether as a potential flexibilizer for epoxy resin. In that study, five formulations were prepared with the 1,4 butanediol diglycidyl ether content varying from 0 to 100% by weight in the prepolymer mixture. The total amine to epoxy ratio was kept equal to 1 to obtain model networks. Flexibility was indirectly measured based on data obtained from DMA, tension, and compression test. Researchers found that the incorporation of 1,4 butanediol diglycidyl ether decreased the average molecular weight between crosslinks while increasing chain flexibility.[167]

Bussi *et al.* utilized hydroxyl-terminated, internally epoxidized polybutadiene rubber to improve the flexibility of DGEBA epoxy. To ensure better bonding between the rubber particles and the epoxy matrix, the epoxidized polybutadiene rubber was pre-reacted with excess epoxide. Increased flexibility of the epoxy was observed with increased concentration of rubber particle.[84,85]

Tong *et al.* perform several studies in which functionalized polysiloxanes were used to improve the flexibility of epoxy. In one study, polysiloxanes were capped with decanedioic acid, hexanedioc acid and polyarlester oligomer. The flexibility of the system increased with molecular weight and particle concentration of polysiloxane increased, and polysiloxane decreased. In another study, polysiloxane rubber particles were grafted with glycidyl methacrylate and methyl methacrylate. Glycidyl methacrylate increased the compatibility between the rubber particles and matrix, thus flexibility improved as glycidyl methacrylate content increased.[168,169]

Kaynak *et al.* published a series of works using HTPB and an SCA to improve the flexural properties of a DGEBA type epoxy resin. It was shown that the use of different mixing orders of the constituents and the addition of SCA enhanced the interaction between HTPB and epoxy matrix. Premixing and pre-reacting the HTPB with SCA and hardener before adding epoxy alters the reaction path, resulting in chain extension and, in some cases, a reduction in crosslinking density and better flexibility.[53–55,68]

In the late 1980s and early 1990s, Wilford *et al.* pioneered the use of liquid polysulfides as flexibilizing/toughening agents and adhesion promoters for epoxy resins. Modification of epoxy with polysulfide resulted in improved adhesion to difficult substrates. Improved adhesion was observed with rust-, oil-, and water-contaminated steel. Polysulfides also reduced the rigidity of the overall polymer matrix and lowered the T_g.[114,115] Abdouss *et al.* prepared a series of polysulfide- epoxy copolymers with alternating blocks of polysulfide and polyepoxide. Increasing epoxy content resulted in increased hardness, tensile strength, and elastic modulus. The change in ductility was attributed to phase separation characterized by DTMA.[170] Thermal and chemical resistance of epoxy-polysulfide blends has been shown to decrease with increasing polysulfide content above 20 wt%.[117] Farajpour *et al.* demonstrated improved flexibility and adhesion to aluminum substrate of epoxy modified with polysulfide. The lower molecular weight polysulfide G4 at Mn~1100 g/mol at 10 wt.% resulted in the best adhesion performance while the higher molecular weight compound G112 (Mn~ 4400g/mol) at 15 wt.% resulted in the highest toughening effect.[171] The mechanism by which polysulfide improves the flexibility or toughening of epoxy depends on the mixing sequences. In the one-step mixing process, the polysulfide additive, epoxy, and crosslinker are mixed in a short time leading to the formation of a block copolymer consisting of soft polysulfide and hard epoxy segments. The phase morphology leads to more of a toughening effect as observed with liquid rubber. In contrast, in a two-step mixing process, the polysulfide and epoxy are premixed followed by the addition of the curing agent leading to the forming an intermediate oxirane-terminated flexible polyether. This prepolymer is later cross-linked with the hardener forming a continuous phase morphology resulting in moderate strength but high elongation and flexibility.[114–116] Other factors such as polysulfide type, molecular weight, curative type, curative amount, and curative schedule all influence the mechanism of polysulfide/epoxy systems thus it is imperative to investigate the effect of each system. Furthermore, manufacturers of commercially available polysulfide advertise it as a high-performance adhesive that can be used on a variety of substrates. However, aluminum, steel, concrete, and wood have been the primary substrates for research and commercial use. Their impact on composites has gone unnoticed. As a result, the flexiblizing and adhesive effects of Thioplast EPS 25 and Thioplast EPS 80 on DGEBA -Epikure 3164 for metallic and composite substrates were investigated in this study.

This study seeks to not only expand upon the library of potential flexibilizer for bisphenol epoxy resin systems but also investigate their effect on adhesion to various substrates. Commercial additives, such as poly (phenyl glycidyl ether)-co-formaldehyde, Thioplast EPS, 1,3-propane-diol bis (4-aminobenzoate), and Jeffamine D-2000 were incorporated into a model EP coating system at 1, 5, and 10 wt.% to improve adhesion and flexibility performance relative the model formulation.

Experiments

Materials

EPON 828, also chemically known as bisphenol-A-(epichlorohydrin), was supplied by Hexion Specialty Chemicals. The curing agent, Epikure 3164 was supplied by BASF

Corporation. Sigma Aldrich (now Millipore) was used to obtain ~ 345 and ~570 average Mn Poly(phenyl glycidyl ether)-co-formaldehyde (PPGEF-345 and PPGEF-570), as well as 1,3-propanediol bis(4-aminobenzoate) (PBAB), and xylene. Thioplast EPS 25 and Thioplast EPS 80 (polysulfide polymer with epoxy end groups) provided by Akzo-Nobel. Steel (QD-35) and Aluminum (A-36) panels were obtained from Q-Panel. MacMaster-Carr provide the carbon fiber reinforced plastics sheets (Ultra-Strength Lightweight 1/16" thick) and fiberglass reinforced polymer (3/16'' thick).

Experimental Design

The study was designed using five types of additives at three levels (1%, 5%and 10% based on Epon 828 weight) on four different substrates (aluminum, steel, carbon fiber reinforced plastics, fiberglass reinforced polymer). The representative chemical structures of the additives used are shown in Fig 6.1. The coatings were designed as a three-factor factorial study where types of additives, weight percent of additives, and substrate type were considered factors. Factor one (type of additives) had five levels, Factor two (wt. % of additive) had three levels, Factor three (substrate type) had four levels, resulting in 15 different formulations and 60 treatment combinations. The formulations are listed in Table 6.1. The statistical analysis of response variables was calculated using Design expert 13 (Stat-Ease Inc., USA).

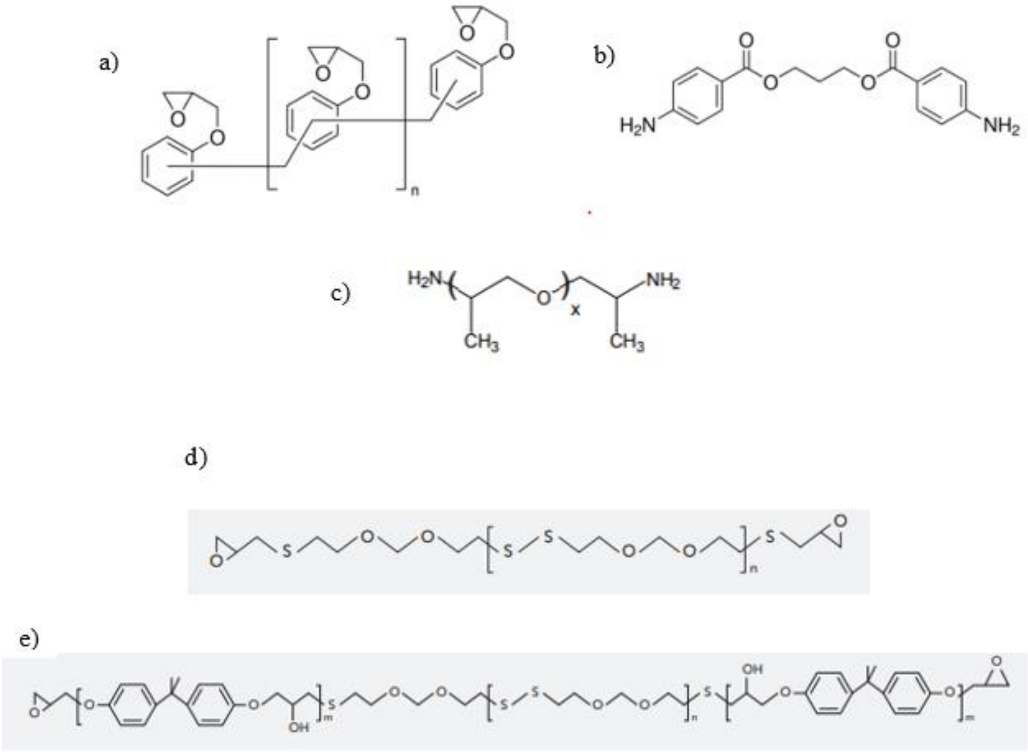


Figure 6.1. Chemical structure of additives used for the experiment. a) poly (phenyl glycidyl ether)-co-formaldehyde, b) 1,3-propanediol bis(4-aminobenzoate) c.) polyetheramine- Jeffamine D-2000, d) Thioplast EPS-25 polysulfide polymer with epoxy end groups e) Thioplast EPS-80 polysulfide polymer with epoxy end groups

Table 6.1. Properties of additives used in the study

Additives	Function	Description	AHEW (g/eq)	Epoxy Equivalent	Mn (mol/wt)
JeffD2K	Flexibilizer	polyetheramine	514	16.5	
PPGEF-345	Adhesion Promoter	Poly(phenyl glycidyl ether)-co-formaldehyde Mn=345		156.82	345
PPGEF-570	Adhesion Promoter	Poly(phenyl glycidyl ether)-co-formaldehyde Mn=570		158.33	570
PBAB	Flexibilizer	1,3-Propanediol bis(4-Aminobenzoate)	157		
TEPS-25	Flexibilizer	Thioplast EPS 25; polysulfide polymer with epoxy end groups		600-800	
TEPS-80	Flexibilizer	Thioplast EPS 80; polysulfide polymer with epoxy end groups		280-350	

Coating Formulation

The formulations were prepared by the following procedure. A Flaktek speed mixer was used to form an epoxy base consisting of Epon 828 (74 wt.%) and xylene (26 wt.%) The non-amine additives (1, 5, and 10% based on Epon 828) were added to the epoxy base and mixed for 30 mins. After which, Epikure 3164 was added at a 1:1 equivalent (hydroxyl: amine) ratio. The formulation was hand-mixed for a few minutes and allowed to sweat at room temperature for 20 minutes. For the amine-terminated additive, 1,3-Propanediol bis(4-Aminobenzoate), it was added to the Epikure 3164. A control, CLR-00, consisting of epoxy and amine crosslinker without the incorporation of additives is also made. Table 6.2 shows all the experimental coating formulations.

Table 6.2. Composition of additive modified epoxy coatings

Formulation	Additive (g)	Xylene (g)	Epon 828 (g)	Epikure 3164 (g)
JeffD2K-1	0.40	9.88	29.73	40.11
JeffD2K-2	1.91	8.37	29.73	38.96
JeffD2K-3	3.66	6.62	29.72	37.46
PPGEF-345-1	0.41	9.88	29.73	40.61
PPGEF-345-2	1.93	8.35	29.71	42.45
PPGEF-345-3	3.65	6.63	29.72	44.67
PPGEF-570-1	0.42	9.98	29.61	40.58
PPGEF-570-2	1.93	8.47	29.60	42.42
PPGEF-570-3	3.69	6.71	29.61	44.57
PBAB-1	0.40	9.86	29.75	39.64
PBAB-2	1.91	8.34	29.75	37.76
PBAB-3	3.69	6.57	29.75	35.58
TEPS-25-1	0.43	9.82	29.75	40.24
TEPS-25-2	1.92	8.33	29.74	40.67
TEPS-25-3	3.78	6.48	29.75	41.20
TEPS-80-1	0.40	9.85	29.76	40.37
TEPS-80-2	2.00	8.26	29.76	41.30
TEPS-80-3	3.65	6.60	29.75	42.43
CLR-00		9.82	29.76	40.16

Coating Application and Curing

The formulations were applied at an 8 mils wet drawdown on steel, aluminum, fiberglass reinforced polymer, and carbon fiber reinforced plastics substrates. Drawdowns were also made on PTFE films to produce free-standing films of the formulations. All substrates were cleaned with acetone before application of the coating. The coatings were left at room temperature for 20 minutes for the solvents to flash off and for the formation of uniform coating. The coatings were then cured at 80°C for another 20 minutes and allowed to fully crosslink at room temperature for 24 hours before testing. Using an Elcometer thickness gauge, an average dry film thickness of 60 µm ± 5 µm on the Al and Fe was obtained for all formulations investigated.

Pull Off-Adhesion Testing

A portable Pull-off adhesion tester (PosiTests, DeFelsko Corporation, New York) was utilized to determine the adhesive strength between the coatings and various substrates per ASTM D4541. Dollies of 20 mm diameter were glued to the coated specimens using a two-component epoxy (3M ™ Scotch-Weld ™ Epoxy Adhesive 460) formulated to a 1:1 volume mix ratio. A 220-grit sandpaper sheet was utilized to abrade the coating surface before the application of the glue to ensure proper adhesion of the glue. The glue was allowed to fully cure for 24 hours at ambient temperature. Excess adhesive around the dolly was removed using a 20 mm cutting tool. Vertical tension force was applied on the dollies until failure occurred. Triplicates were performed for each sample the arithmetic mean was reported.

Reverse Impact Test

The reverse impact resistance was determined according to ASTM Standard D 2794. The samples were subjected to the impact of a 4-lb weight ball falling from different heights. The maximum drop height of the instrument is 43 inches. The height at which cracking, crazing, or loss of adhesion was observed was recorded as the impact resistance for each formulation. Samples that did not fail were noted as having impact strength of >169 in.-lb.

Conical Mandrel

The conical mandrel test was also used according to ASTM D 522 for the determination of the flexibility of the coatings on steel and aluminum substrates. The results of the flexibility test were reported as the length of a crack (cm) formed on the coating after the testing panel was bent over a steel frame of varying radius.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed by TA Instruments Q-800 Dynamic Mechanical Analyzer under nitrogen atmosphere and tension mode. Storage modulus and tan δ were calculated for rectangular specimens of the size 10 mm × .5 mm × .10 mm at frequency ω = 1 Hz. The temperature was ramped from -80 to 150 °C with a heating rate of 5 °C/min. The peak Tan δ was utilized to determine glass transition temperature and storage modulus at 120 °C was utilized to determine crosslink density.

Differential Scanning Calorimetry

DSC experiments were performed on cured samples using TA Instruments TI Q2000 Modulated DSC. 10-15 mg samples were placed in aluminum pans, heated from -80 °C to 200 °, cooled to -80°, and heated again to 200°C at a scan rate of 5°C/mins. Glass transition temperature (T_g) was studied from the DSC thermograms.

Nanoindentation

A Hysitron Inc. TriboScope® Nanomechanical Test Instrument with 2D transducer and Berkovich diamond indenter was used to measure hardness and young’s modulus. The maximum load applied for all samples was 1000 μN with a holding time of five s, followed by a five s unloading to zero N. The results of nine indentations were averaged to obtain acceptable values of hardness (H) and elastic modulus (E) Hardness and elastic modulus were calculated from the slope of the unloading curve, per the Oliver and Pharr method.

König Pendulum Hardness

The hardness of coated films on the aluminum substrate was measured by monitoring the damping time of the oscillations of a pendulum swinging at a specific amplitude, from 6° to 3°. The tests were performed according to ASTM standard D 4366 using a Byk pendulum hardness tester. Six replicates for each formulation were performed and the arithmetic mean was reported.

Results and Discussion

Flexibility

Conical Mandrel and Reverse Impact

Conical mandrel bend and reverse impact tests were used to assess the flexibility and impact resistance of the metal-coated substrates. For the conical mandrel, the results of all formulations put on metal substrates evaluated were 0 cm of cracking, the greatest possible flexibility outcomes. For all formulations examined, the reverse impact test yielded the highest attainable impact strength. Steel coated panels assessed at 169 in-lbs. for all formulas, while substrate failure occurred at 100 in-lbs. Other indirect characterization approaches for flexibility are required because the conical mandrel and impact resistance were unable to give a more subtle and sensitive means of assessing flexibility. To further characterize flexibility, DMA, DSC, nanoindentation, and König pendulum hardness were all used.

DMA and DSC

The thermal-mechanical properties, as well as the cross-linking densities, of the modified and unmodified epoxies, were investigated by DMA. Storage modulus relates to the ability of materials to store energy and is determined from the in-phase response of the material to an applied oscillating strain. Loss modulus determined to form the out-of-phase response is attributed to dissipative and viscous loss in the material. The ratio of storage to loss modulus is the tan δ or mechanical damping. The peak of the tan δ marks the T_g of the polymer network. The DMA curves are the modified and unmodified epoxies are shown in Fig 6.2 and DMA characterization data is reported in Table 6.3. ANOVA was performed on storage modulus in the glassy region (-50°C), T_g, and XLD. The effect of the additives on storage modulus were not statistically significant at the 95% or 90% confidence interval. The ANOVA results of T_g and XLD are given in Table 6.4. According to the results, the additives investigated have a significant effect on the T_g ($p<0.05$), but not the XLD. However, the level at which the additives are added has significant effects on both the T_g and XLD ($p < 0.05$). The interaction chart of the parameters for T_g and XLD is given in Fig 6.3 and, Fig 6.4, respectively.

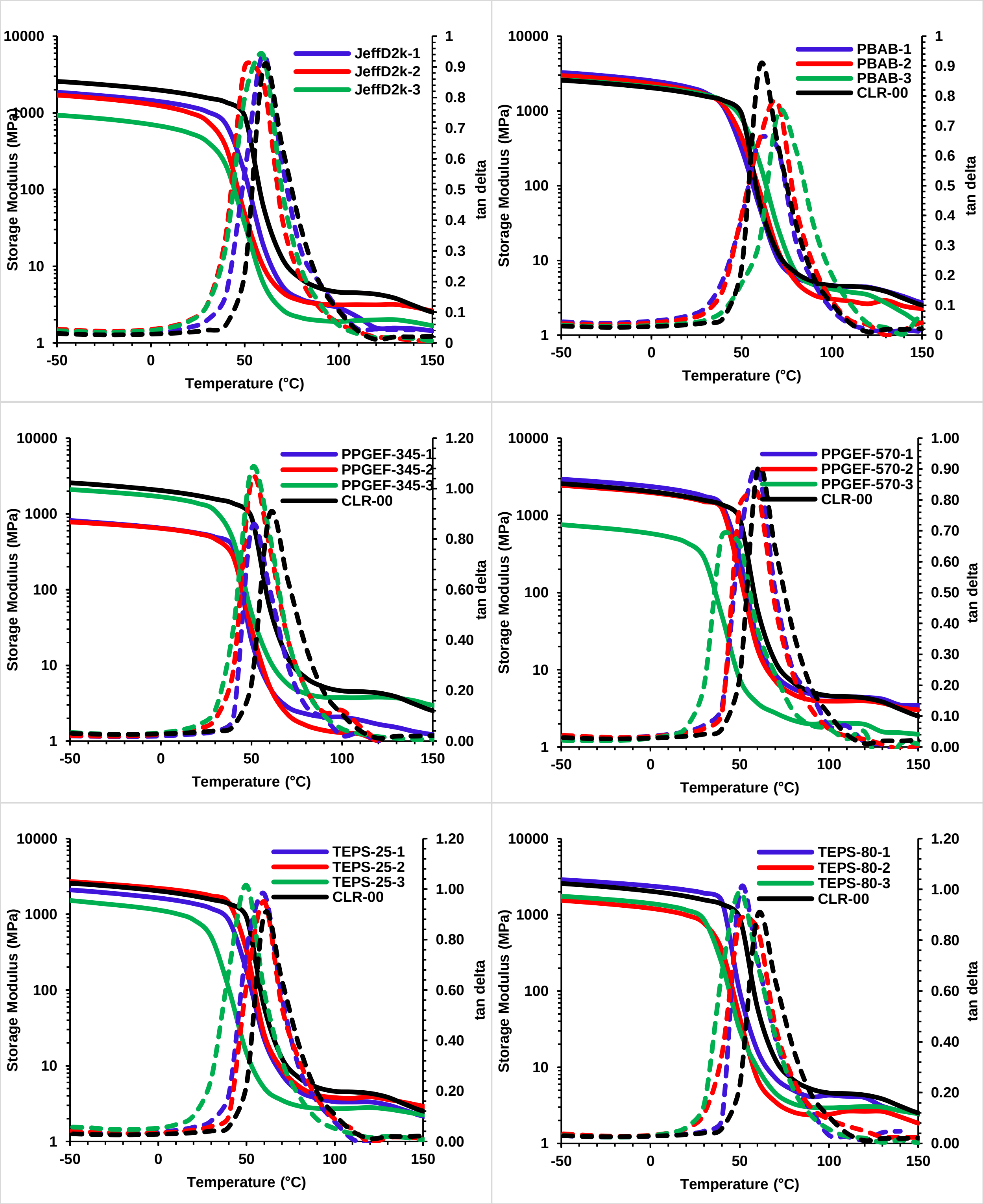


Figure 6.2. DMA results of epoxy modified with additive JeffD2K, PBAB, PPGEF-345, PPGEF-570, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 6.3. Characteristic of DMA for adhesion promoter and flexibilizer modified epoxy coatings: T_g, XLD, and storage modulus

Formula	E' at -50° C (MPa)	T_g (°C)	E' at T_g+50 °C (MPa)	XLD (mol m^{-3})
JeffD2K-1	1859	44.44	2.36	0.24
JeffD2K-2	1702	39.03	3.14	0.32
JeffD2K-3	931.3	38.81	1.93	0.2
PPGEF-345-1	819.2	49.96	4.34	0.44
PPGEF-345-2	780.9	55.2	3.98	0.41
PPGEF-345-3	2094	46.04	3.75	0.38
PPGEF-570-1	2938	56.85	4.66	0.5
PPGEF-570-2	2442	52.25	3.95	0.4
PPGEF-570-3	757.2	41.88	1.89	0.19
PBAB-1	3264	55.92	4.42	0.45
PBAB-2	2970	57.91	2.72	0.28
PBAB-3	2607	56.13	1.83	0.19
TEPS-25-1	2100	52.37	3.19	0.33
TEPS-25-2	2708	49.05	2.82	0.37
TEPS-25-3	1520	41.64	2.35	0.24
TEPS-80-1	2888	51.97	4.07	0.42
TEPS-80-2	1544	49.95	3.75	0.38
TEPS-80-3	1750	47.04	2.91	0.3
CLR-00	2572	62.25	4.32	0.45

Table 6.4. ANOVA results of flexibilizer and adhesion promoter on T_g of DMA

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	544.67	7	77.81	7.31	0.0028
A-Additive	395.91	5	79.18	7.44	0.0037
B-Additive Level	148.77	2	74.38	6.99	0.0126
Residual	106.38	10	10.64		
Cor Total	651.06	17			

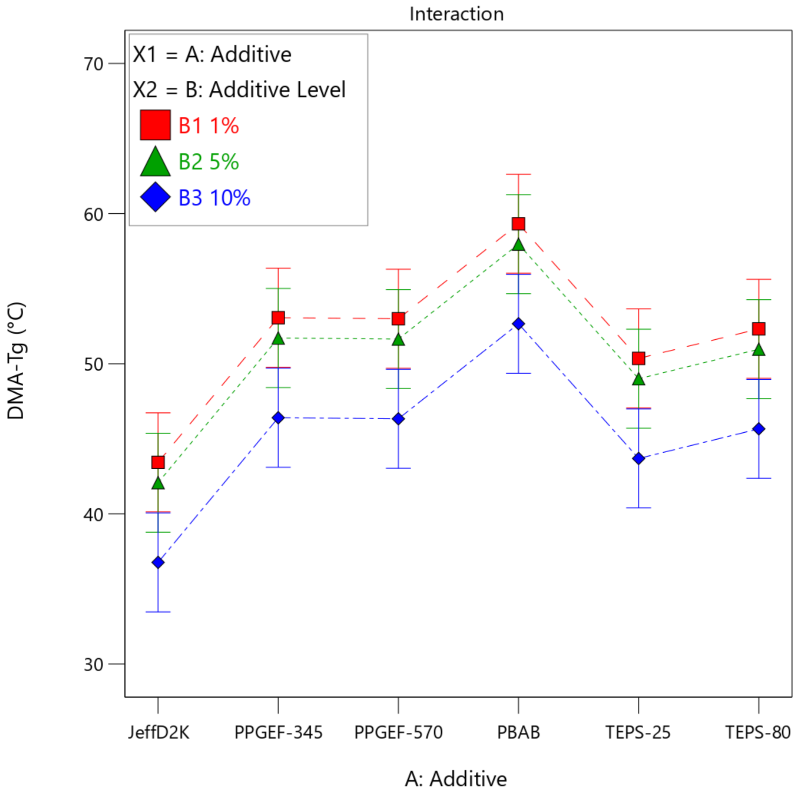


Figure 6.3. Interaction plot of T_g from DMA of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 6.5. ANOVA results of additives on XLD from DMA

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	0.1174	7	0.0168	4.10	0.0221
A-Additive	0.0474	5	0.0095	2.32	0.1203
B-Additive Level	0.0699	2	0.0350	8.56	0.0068
Residual	0.0408	10	0.0041		
Cor Total	0.1582	17			

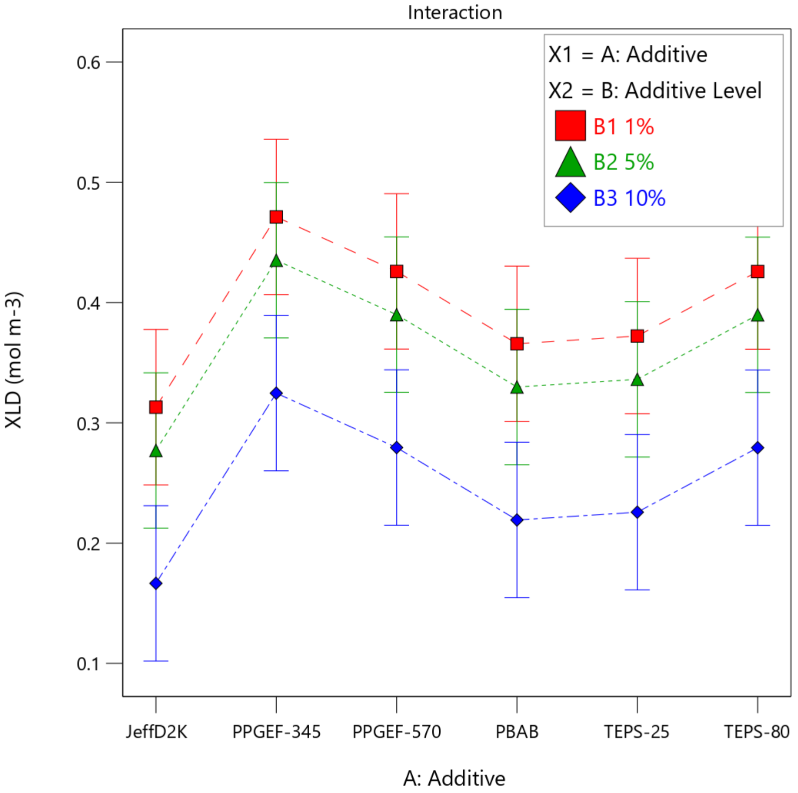


Figure 6.4. Interaction plot of XLD from DMA of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

As the amount of each additive increases from 1 to 10 wt%, the T_g and XLD decrease accordingly. JeffD2K results in the lowest T_g and crosslink density. The decrease in T_g and XLD compared to the unmodified epoxy correlates well with the storage modulus further suggesting increased flexibility. The addition of JeffD2K at 1, 5, and 10 wt% results in a proportional decrease of the storage modulus at -50 °C indicating increasing chain mobility and overall flexibility at a lower temperature. This result is attributed to introduction of the flexible polyether group of Jeffamine into the epoxy resin backbone.[172]

PBAB has the largest effect on the T_g resulting in the maximum T_g observed. The addition of PBAB to epoxy results in increased storage modulus at -50 °C compared to the unmodified epoxy. However, as the concentration of PBAB increases the storage modulus decreases proportionally. The opposite trend is observed for T_g, as the PBAB level in the system increases, the T_g increases, suggesting reduced chain mobility. These results are attributed to the bulky aromatic groups' presence in PBAB. Since T_g is the temperature at which long-range segmental motion begins, any structural element that precludes free movement of polymer chain segments will increase the T_g. The atoms along the polymer chain must be able to freely rotate around the bonds joining them for this segmental motion to occur. As a result, the bulky double aromatic groups within the backbone will prevent rotation and raise the T_g. The decrease in XLD with PBAB concentration is due to an increase in molecular weight between crosslinks.

The molecular weight of poly (phenyl glycidyl ether)-co-formaldehyde did not appear to affect the T_g. However, the addition of both PPGEF-345 and PPGEF-570 results in a reduction in T_g and XLD compared to the unmodified epoxy. These results are contrary to what is expected. Novolac phenolic resins such as PPGEF are known for being brittle due to their high functionality and degree of crosslinking. The decrease in T_g with the addition of PPGEF may be attributed to the branching effect. The high functionality of the oxirane ring with PPGEF could result in the presence of secondary hydroxyl leading to increased branching of the modified matrix compared to the unmodified system. Branching has two major effects: it reduces local motions by reducing linear segmental length while concurrently increasing the number of chain endpoints, which improves segmental mobility. The increase in chain endpoints increases free volume which can lead to lower T_g. The corresponding decrease in XLD is a further indication that the excess oxirane group of the PPGEF is not participating in crosslinking.

As the concentration of polysulfide increased, the XLD and T_g decreased proportionally denoting increased chain mobility and overall network flexibility. The superior flexibility performance of TEPS-25 to TEPS-80 is attributed to the linear aliphatic structure found in TEPS-25 compared to the bulking and rigid aromatic units found in TEPS-80.

DSC analysis was also used to measure the T_g of the coatings and is reported in Fig 6.5. ANOVA result is reported in Table 6.6 and the interaction plot is reported in Fig 6.6.

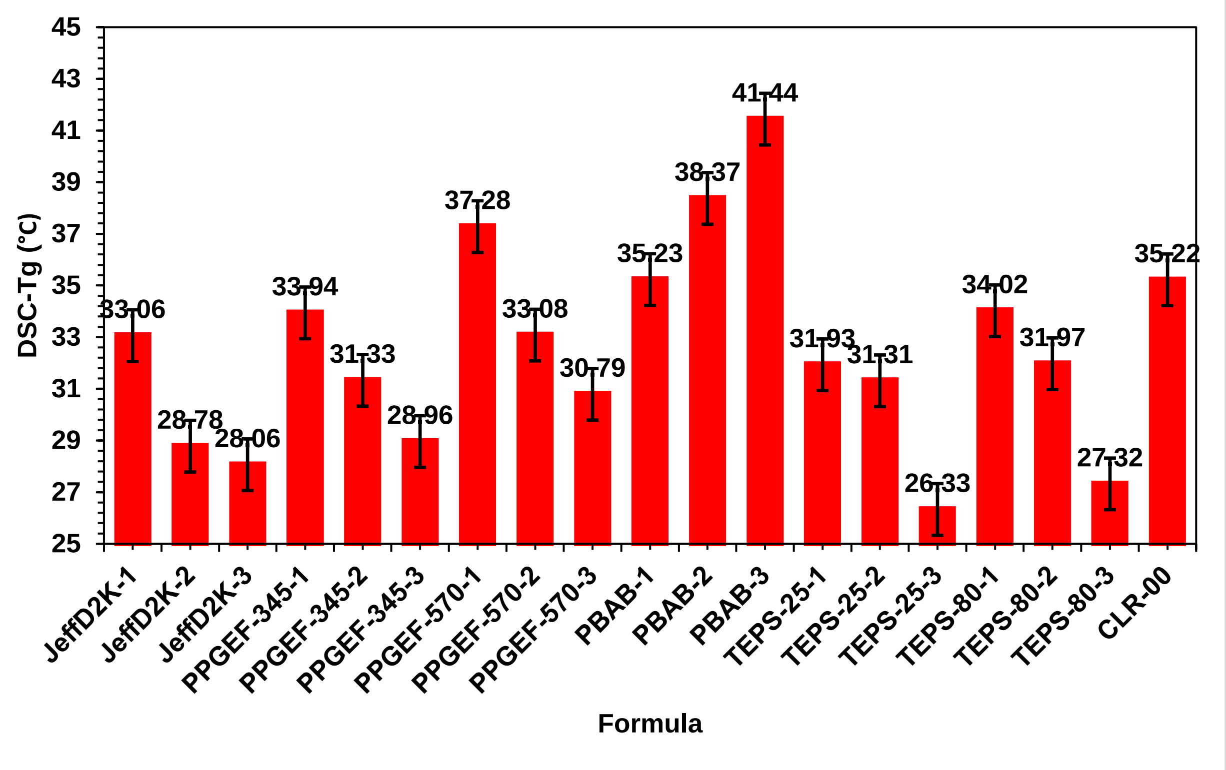


Figure 6.5. Glass Transition of DSC experiment of modified and unmodified epoxy-amine coating with addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 6.6. ANOVA result of additives on Tg from DSC

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	198.90	7	28.41	4.18	0.0208
A-Additive	156.44	5	31.29	4.61	0.0193
B-Additive Level	42.46	2	21.23	3.13	0.0882
Residual	67.93	10	6.79		
Cor Total	266.84	17			

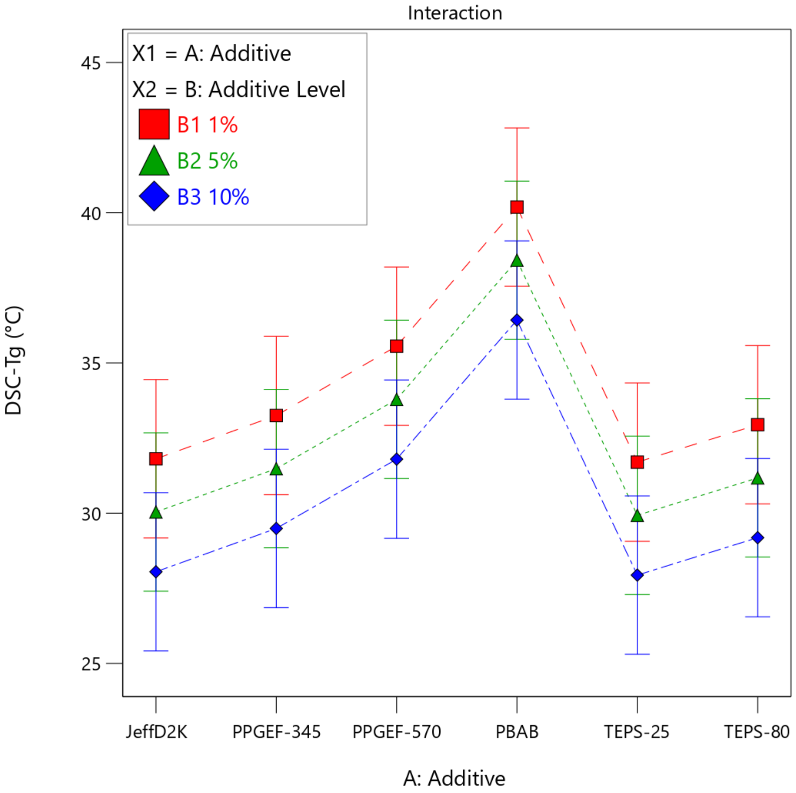


Figure 6.6. Interaction plot of T_g from DSC of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

An F-value of 4.18 suggests the ANOVA model is significant; there is only a 2.08% chance that the F-value could occur due to noise. The additives had statistically and physically significant effects on the T_g ($p < 0.05$). Similarly, to the T_g from the DMA, JeffD2K results in the lowest T_g demonstrating the highest degree of flexibility. PBAB results in the highest T_g, and lower flexibility.

Nanoindentation

The effect of the type and level of the additives on the modulus of elasticity and hardness of the prepared epoxies were evaluated using nanoindentation and the result are displayed in Fig 6.7 and 6.8. The experimental coatings showed a wide range of elastic modulus (1277 to 3417MPa) and hardness (22 to 182 MPa) suggesting a broad range of flexibilities. CLR-00, the neat epoxy, has a modulus of elasticity of 2455 MPa and a hardness of 112 MPa. ANOVA was performed on the elastic modulus and indentation hardness results and are reported in Table 6.7 and 5.8, respectively. The additive studied, as well as the level at which they are introduced, has significant effects on the modulus of elasticity ($p < 0.05$). For hardness, only the level at which the additives are added has a significant effect ($p<0.05$). The interaction charts of the parameters for elastic modulus and indentation hardness are given in Fig 6.9 and 6.10, respectively.

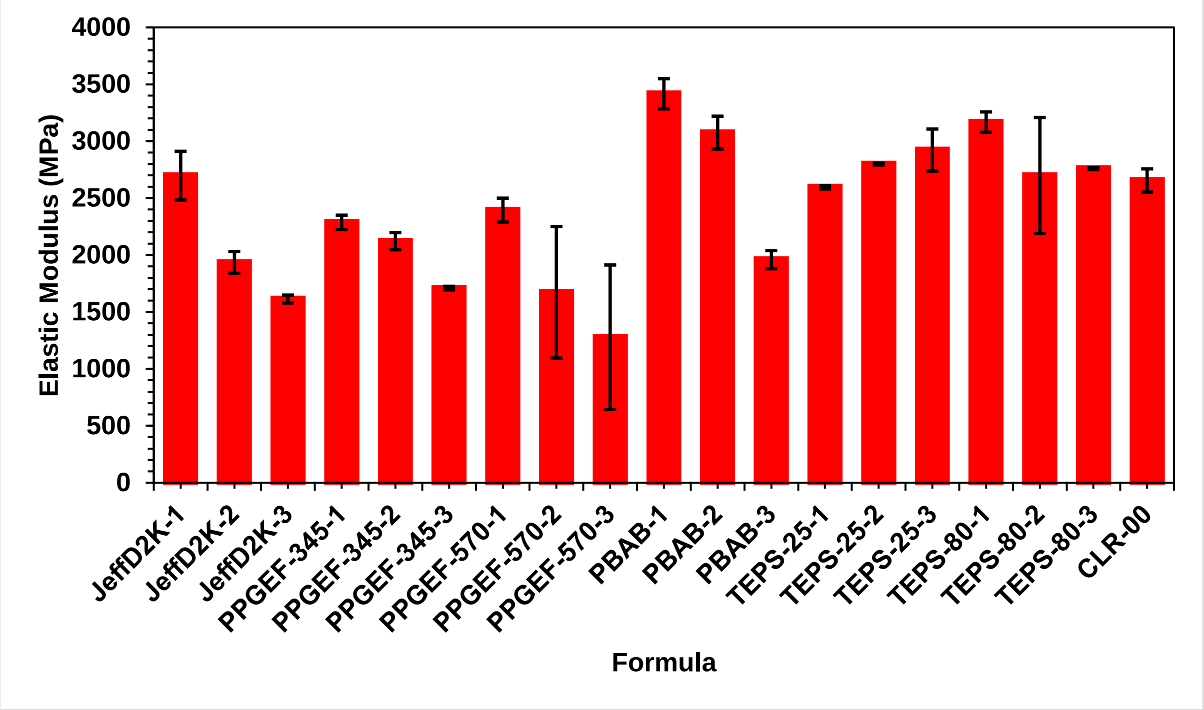


Figure 6.7. Elastic Modulus from nanoindentation experiment of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and, TEPS-80 at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

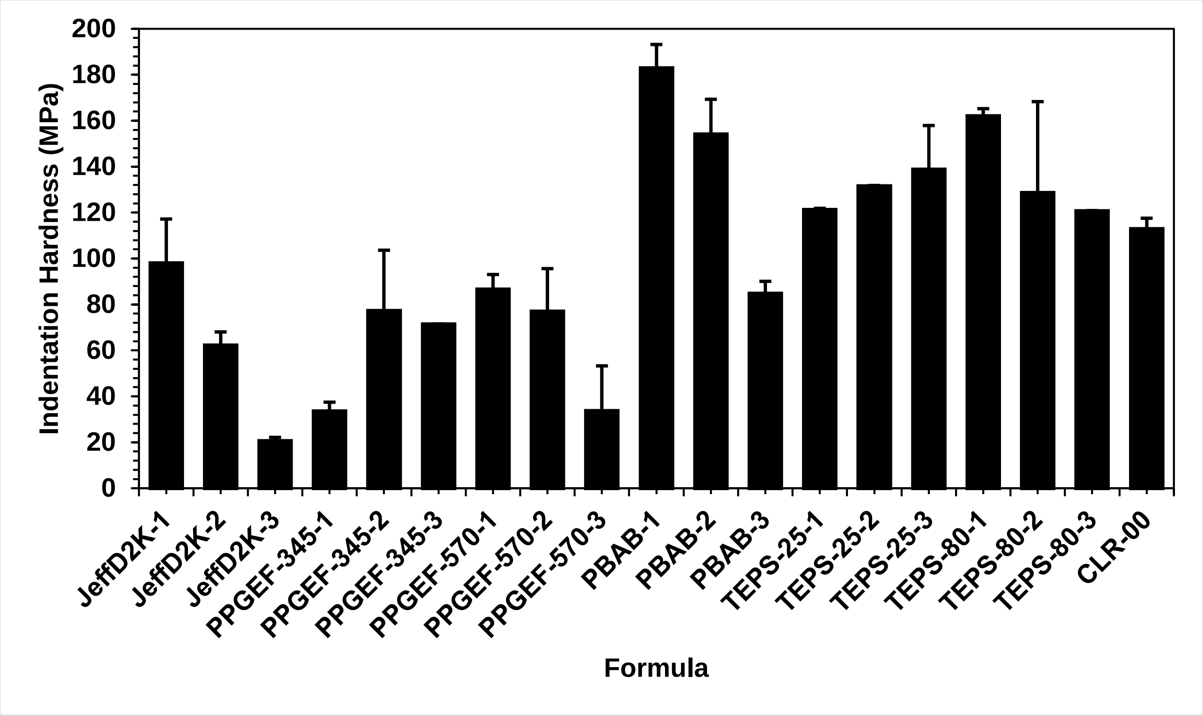


Figure 6.8. Hardness from nanoindentation experiment of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

Table 6.7. ANOVA Result of the effect of flexibilizer and adhesion promoter on elastic modulus obtained from nanoindentation

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	5.011E+06	7	7.159E+05	5.82	0.0067
A-Additive	3.456E+06	5	6.912E+05	5.62	0.0101
B-Additive Level	1.555E+06	2	7.776E+05	6.32	0.0168
Residual	1.231E+06	10	1.231E+05		
Cor Total	6.242E+06	17			

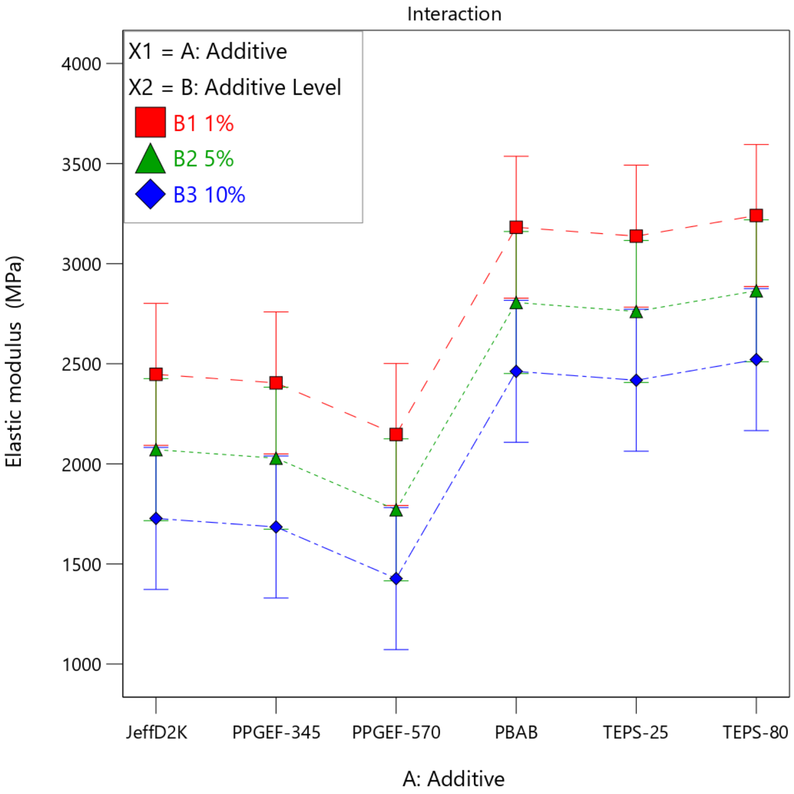


Figure 6.9. Interaction plot elastic modulus of nanoindentation of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 6.8. ANOVA Result of the effect of flexibilizer and adhesion promoter on hardness obtained from nanoindentation

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	28873.90	7	4124.84	5.31	0.0093
A-Additive	24734.81	5	4946.96	6.36	0.0066
B-Additive Level	4139.09	2	2069.55	2.66	0.1184
Residual	7774.94	10	777.49		
Cor Total	36648.84	17			

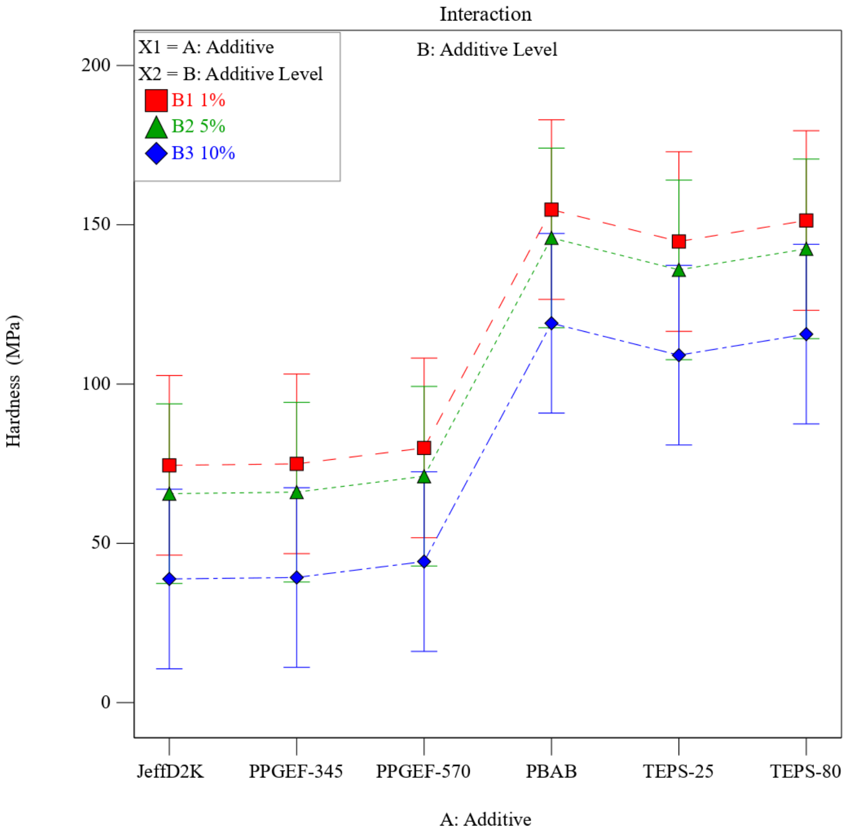


Figure 6.10. Interaction plot hardness from nanoindentation of modified and unmodified epoxy-amine coating with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25, and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%), and 3 (10 wt.%)

As the amount of each additive increases from 1 to 10 wt%, the elastic modulus decreases accordingly. JeffD2K, PPGEF-345 and PPGEF- 570 results in the lowest elastic modulus and indentation hardness. These results are attributed to the increase in flexibility demonstrated by DMA. PBAB, TEPS-25, and TEPS-80 results in high modulus of elasticity and indentation hardness. The high elastic modulus and hardness attributed to the addition of PBAB can be attributed to the bulky aromatic group and reduce chain flexibility. The increase in elastic modulus by the addition of polysulfide is due to increased chain rigidity. The contradictory effect associated with the decrease T_g and XLD and simultaneous increase elastic modulus has been observed in the literature. A disulfide bonds is about 2.05 Å in length, which is approximately

0.5 Å longer than a C−C bond.[173] The barrier of rotation around a disulfide bond is lower than C-C, thus less energy is required to induce change mobility.[174] The decreased in T_g and XLD of polysulfide additives can be explained by the length and lower rotational energy barrier of disulfide bond compared to carbon-carbon bond. Another potential explanation for the high modulus of elasticity and indentation hardness could be attributed to the test method. Nanoindentation is performed by slow penetration of a diamond tip into the coating. A viscoelastic material composed of C-C, C-O, or C-N bonds is expected undergo reversible elastic deformation until the yield point after which irreversible plastic deformation occurs until the failure point. Disulfide bonds are weak (having a 210-270 k/mols bond dissociation energy) and reversible in nature thereby allowing cleaved bonds to reform.[175,176] Thus, during mechanical characterization analysis such as nanoindentation, as the load increases and deformation starts to occur, the weak disulfide bond start to break but also simultaneously reform resulting in less dimensional change with increase load. The lack of shape change is interpreted as structural rigidity and high modulus of elasticity.

Pendulum Hardness

Another approach for determining flexibility was to use the hardness of a pendulum. Fig 6.11 shows the hardness findings of the modified and unmodified epoxy. ANOVA revealed a statistically significant difference of ($p<0.01$) for additive and the level at which they are added. Table 6.9 and Fig 6.12 depicts the parameter interaction chart.

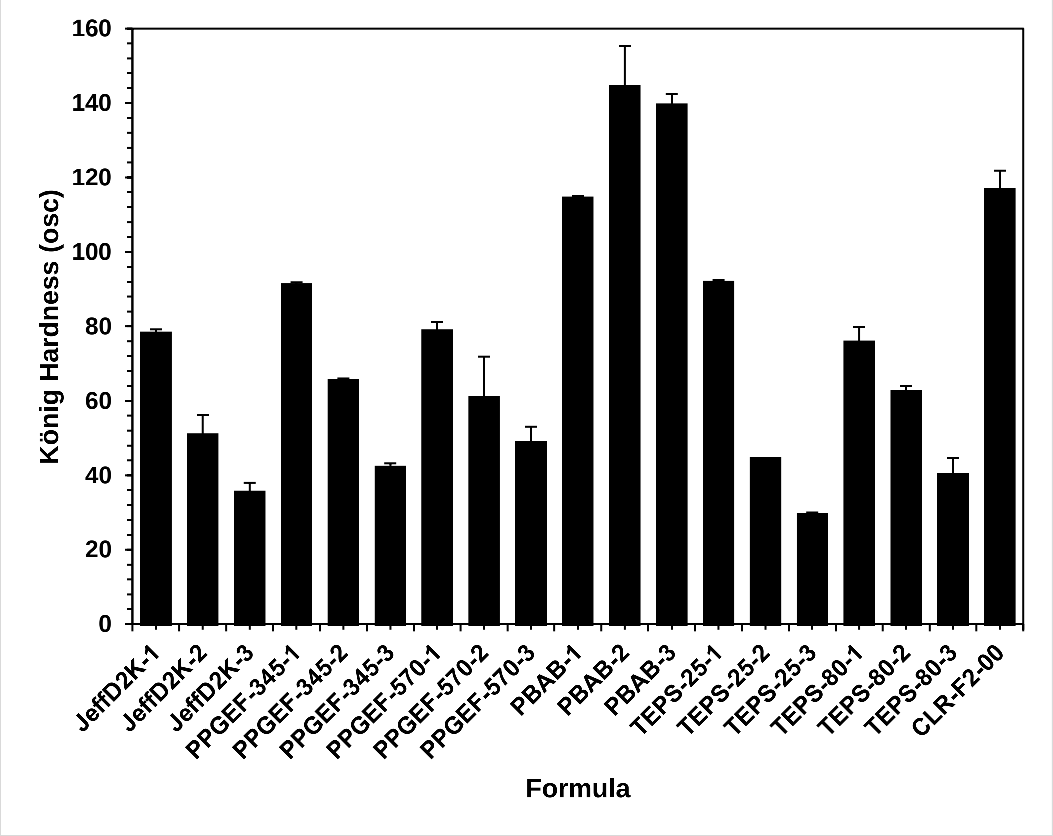


Figure 6.11. Hardness from König pendulum experiment for modified and unmodified epoxy-amine coatings with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

Table 6.9. ANOVA results of flexibilizer and adhesion promoter on pendulum hardness

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	16804.04	7	2400.58	8.84	0.0013
A-Additive	13644.03	5	2728.81	10.05	0.0012
B-Additive Level	3160.01	2	1580.01	5.82	0.0211
Residual	2714.80	10	271.48		
Cor Total	19518.85	17			

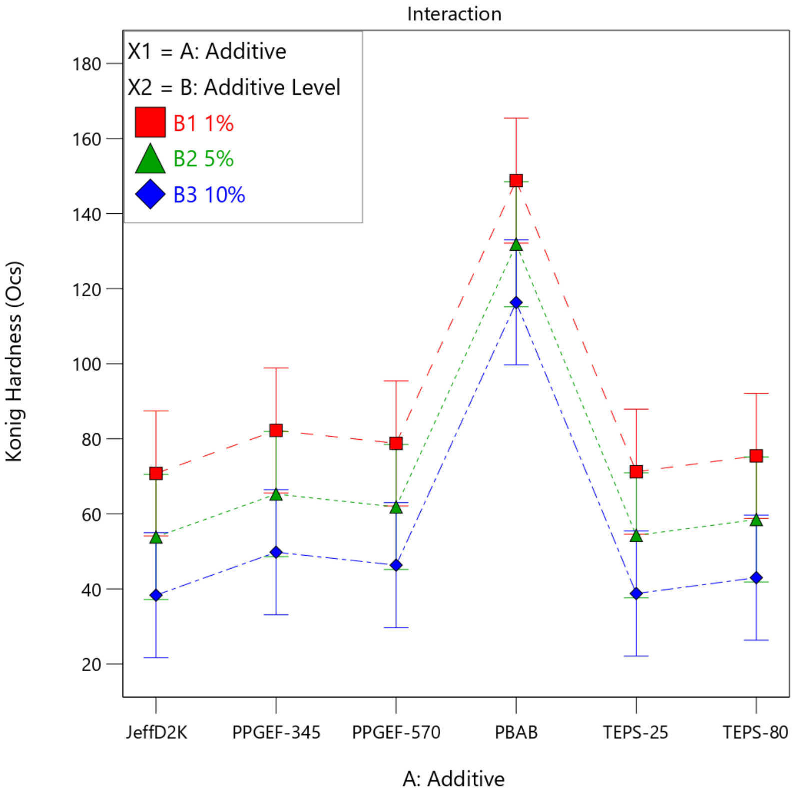
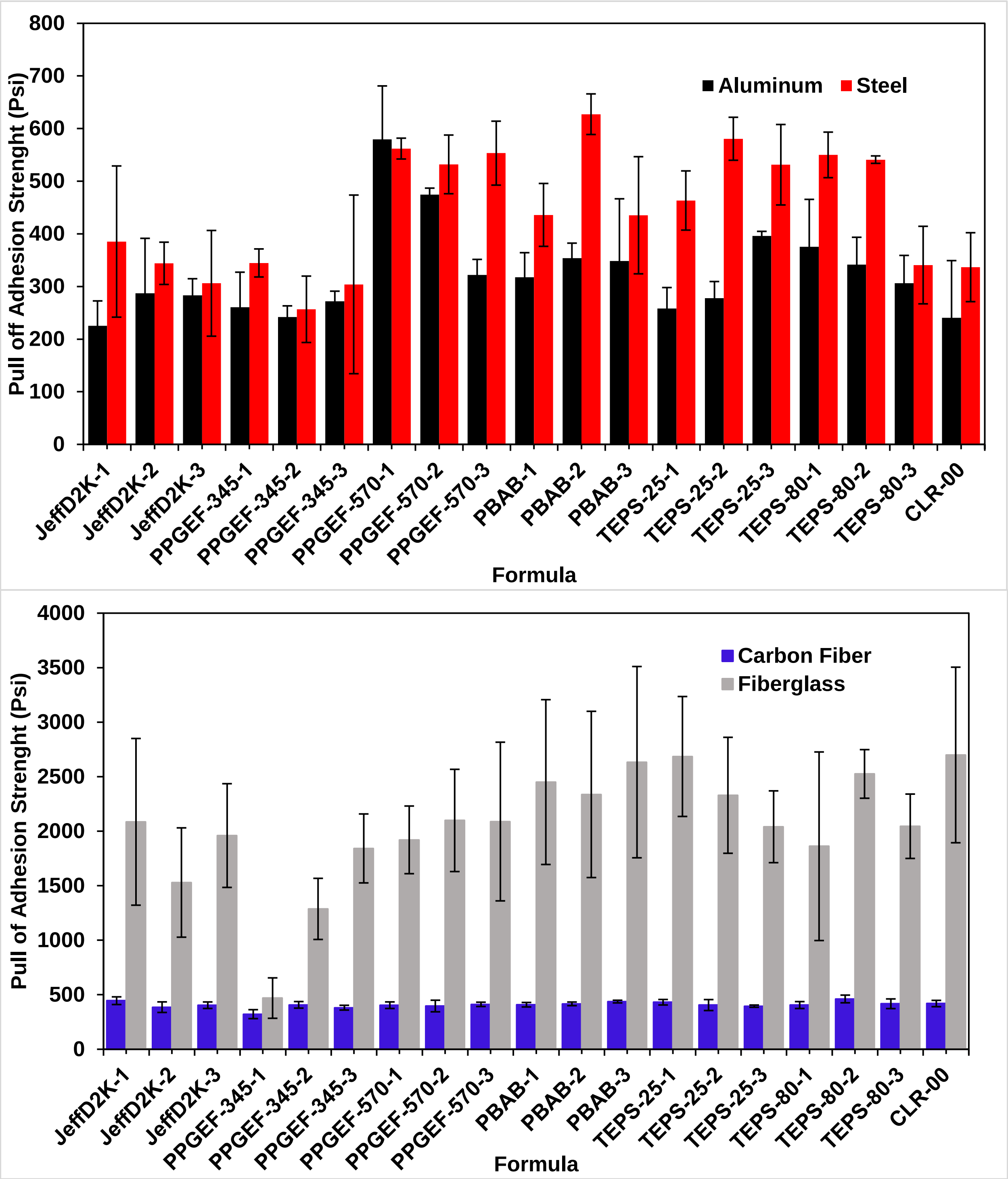


Figure 6.12. Interaction plot of pendulum hardness for modified and unmodified epoxy-amine coatings with the addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%)

As the amount of each additive increases from 1 to 10 wt%, the indentation hardness decreases accordingly. PBAB has the largest influence on pendulum hardness, resulting in the highest hardness at 1 wt.%. All other additives have similar effect of pendulum hardness.

Adhesion

Adhesion performance on metal substrates (Fe and Al) and composites (CF and FG) were investigated and reported in Fig 6.13, respectively. To evaluate the difference between adhesive strength of the various substrates a pairwise Tukey test was performed and significant was defined as $p < 0.05$. Based on the statistical analysis reported in Table 6.10, there is no difference between the mean adhesive strength of the coatings on Al and Fe, AL and CF, Fe and CF. However, there is a significant difference between FG and Fe, FG and Al, and FG and CF. These results are reflected in the adhesives strength of the CLR-00 which are 358, 420, 401, and 2699 MPa for Al, Fe, CF, and FG, respectively. Two potential forces could be responsible for the high adhesive strength between FG and the epoxy coating: mechanical and chemical bonding. The abrasion of the substrate with sandpaper prior to the application of the coating produced a rough surface consisting of peaks and valleys. This roughening caused an increase of total surface area, thus as the resin is applied the total contact between it and the adherend is improved. Since interfacial and intermolecular attraction are the basis for adhesion, the increased in area of contact will increase the total energy of surface interaction by a proportional amount, thereby increasing the bond strength. All the substrate investigated were abraded with the same grit sandpaper, thus mechanical interlocking and abrasion alone does not fully explain the superior adhesive strength observed by FG. Another potential cause of the FG adhesive performance could be attributed to the surface energy. For a cured adhesive to bond to a substrate, the attractive bond between the adhesive and substrate must be higher than the cohesive bond of the adhesive. In the case of epoxy, the hydroxyl bond along the polymer chain forms strong polar attraction to the surface. Substrates with high polarity have high surface energy and attractive forces and thus stronger adhesion. Hydrogen bonding is an electrostatic force of attraction between a covalently bond hydrogen atom and a more electronegative atom. While a hydrogen bond is considering a weak force (1-40 kcal/mol) depending on the donor and acceptor atoms as well as environment increased, surface area can result in substantial increase in adhesion. The surface free energy of each substrate was similar enough that it could not explained the difference in adhesion performance of FG.



Figures 6.13. Pull-off Adhesion strength of formulation, top: on metal substrates, bottom: on composites.

Table 6.10. ANOVA results for adhesive strength of substrates

Source	Sum of Squares	df	Mean Square	F-value	p-value
Treatment-Substrate	3.79E+07	3	1.26E+07	153.6730	1.11E-16
Residual	5.91E+06	72	8.21E+04		
Cor Total	4.38E+07	75			

Table 6.11. Tukey HSD for adhesive strength of substrate

Treatment pairs	Tukey HSD Q statistic	Tukey HSD p value
Al vs Fe	1.8158	0.5675
Al vs CF	1.2765	0.7793
Al vs FG	25.7769	0.0010
Fe vs CF	0.5393	0.9000
Fe vs FG	23.9611	0.0010
CF vs FG	24.5004	0.0010

ANOVA results obtained for the pull-off adhesion strength of the modified coatings on Fe substrate are given in Table 6.12**.** The model has an F-value of 4.62 representing significance. The additives showed statistically and physically significant effects on adhesive strength on Fe ($p < 0.05$). The interaction plot is given in Fig 6.14

Table 6.12. ANOVA results of additives on pull-off adhesion strength on Fe substrate

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1.694E+05	7	24206.48	4.62	0.0150
A-Additive	1.549E+05	5	30979.35	5.91	0.0085
B-Additive Level	14548.60	2	7274.30	1.39	0.2937
Residual	52400.51	10	5240.05		
Cor Total	2.218E+05	17			

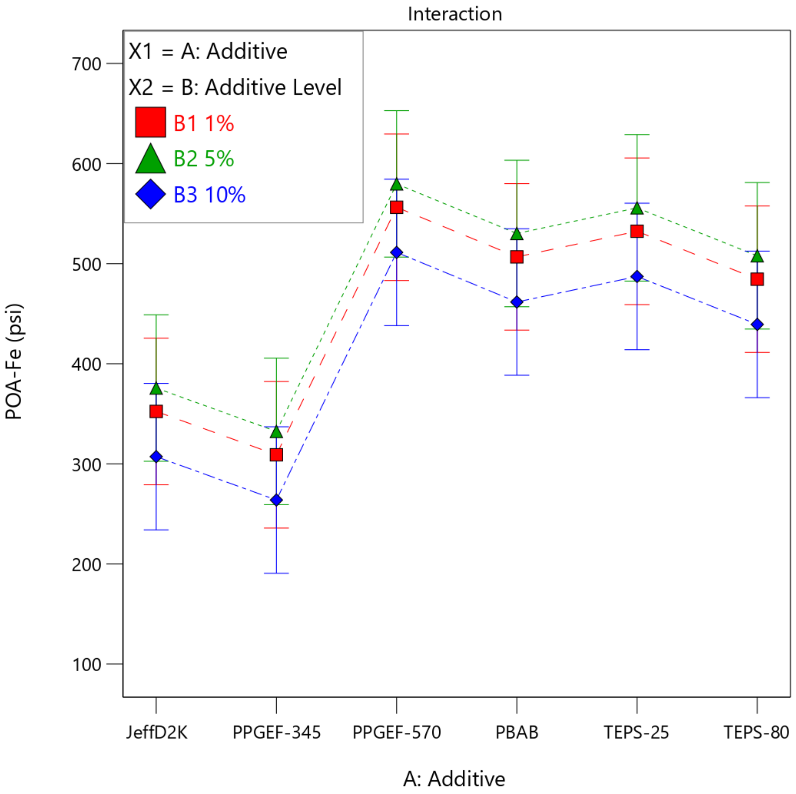


Figure 6.14. Interaction plot pull-off adhesion of modified epoxy-amine coating with addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%) on Fe substrate

For the steel substrate, additives PPGEF-570, PBAB, and TEPS-25 and TEPS-80 results in improved adhesive strength at all levels. PPGEF-570-1 (555 MPa) displayed the highest increase in the adhesion compared to the neat epoxy, CLR-00 (337 MPa). As the concentration of PPGEF-570 increases from 1%, 5%, and 10%, the adhesive strength on steel decreases from 562, to 533, to 554, respectively. The improved adhesion performance of PPGEF is attributed to increase presence of hydroxyl group within the altered network.[142,143] It has been suggested that only 1% of the available atomic sites on the adherend are required to produce significant increases in interfacial adhesion strength.[143] The effect of PBAB on adhesive strength does not appear to be concentration dependent. The performance of PBAB is attributed to greater interfacial bonding energy. Increased in Van der Waals force and coulomb electrostatic force with PBAB and metal oxide has been demonstrated.[177] Tsai *et al.* attributed the improved adhesion of disulfide additives to extremely low topology freezing transition temperature and activation energy values. These factors allow for easier rearrangement of disulfide bonds and increases likelihood of bond cleavage leading to faster release of internal stress occurs, and adhesion is improved.[178] Modifying the epoxide with the polysulfide additives increased the adhesion strength of the coating. Increasing in adhesion strength could be attributed to the improved “wetting” and “polarity” due to the presence of the sulfide bond. The higher flexibility imparted by the sulfur bond allows for increased molecular chain mobility and better diffusion into the substrate pores.

Per ANOVA, the effect of additive and level at which they are introduced on Al substrate had no significance on adhesion at the 95% and 90% CI. However, similarly to steel, PPGEF-570-1 (579 MPa) demonstrated in the highest increase in the adhesion compared to the neat epoxy, CLR-00 (241 MPa). As the concentration of PPGEF-570 increases the adhesive strength on aluminum decreases.

As for the composite, the incorporation of additives does not appear to impact the adhesive strength of epoxy to carbon fiber reinforced plastics. ANOVA for adhesive strength of the modified coatings on FG is given in Table 6.13. The additives showed statistically and physically significant effects on adhesive strength on FG ($p < 0.05$). The interaction plot is reported in Fig 6.15.

Table 6.13. ANOVA results of additives on pull-off adhesion strength on FG substrate

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	5.003E+06	7	7.148E+05	7.83	0.0022
A-Additive	4.909E+06	5	9.817E+05	10.75	0.0009
B-Additive Level	94599.70	2	47299.85	0.5180	0.6109
Residual	9.132E+05	10	91316.53		
Cor Total	5.916E+06	17			

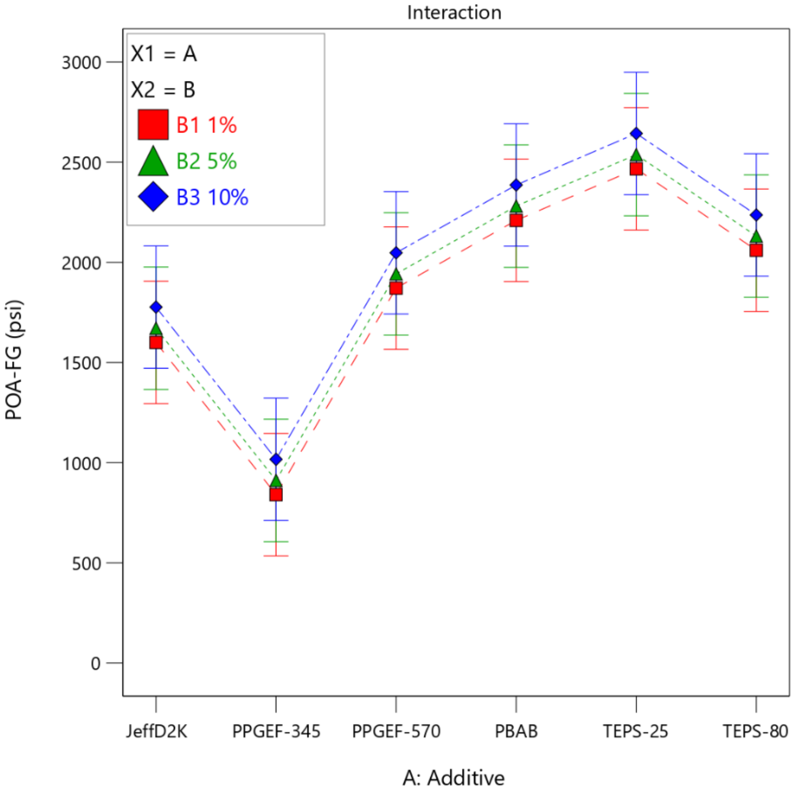


Figure 6.15. Interaction plot pull-off adhesion of modified and unmodified epoxy-amine coating with addition of JeffD2K, PPGEF-345, PPGEF-570, PBAB, TEPS-25 and TEPS-80 at levels 1 (1 wt%), 2 (5 wt%) and 3 (10 wt.%) on Fe substrate

PPGEF-345 has the most detrimental effect on adhesion on FG. The thioplast and PBAB has the least detrimental effect on FG adhesion.

Conclusions

This study investigated the flexibilizing and adhesion-promoting effect of various additive epoxy-amine coating systems. The DMA nanoindentation results indicated that the JeffD2K imparted the highest degree of flexibility. The flexible polyether chain of the JeffD2k is attributed to these findings. According to the DSC data, TEPS-25 and TEPS-80 had the lowest T_g implying increased flexibility. This lower T_g is attributed to the disulfide bond. The improved adhesion performance of PPGEF on the metallic surfaces is attributed to the increased presence of the hydroxyl group within the altered network. Of all additives investigated in this study, PBAB demonstrates superior performance on FG and Fe. The increased interfacial bonding energy imparted by van der Waals force and Coulomb electrostatic force could be attributed to PBAB performance.

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CHAPTER 7. DEVELOPMENT OF HIGH-PERFORMANCE MODIFIED EPOXY PRIMER FOR MULTI-SUBSTRATE APPLICATION: A STATISTICAL APPROACH

Introduction

Coatings based on epoxy resin offer a unique combination of performance characteristics such as exceptional adhesion and corrosion resistance, excellent chemical resistance, low shrinkage, high strength, good heat resistance, and toughness. Due to their exceptional properties, they have been used extensively as primers for automotive, watercraft, and aircraft since their commercialization. Epoxy prepolymers are converted to a usable thermoset coating by reacting their oxirane right with a suitable hardener to achieve desired properties.[15,179,180]

Over the last few years, OEMs have increased the use of lightweight composite and metals within these industries to reduce VOC leading to the need for primer suitable for multi-substrate application.[145,146] To meet these needs, the traditional epoxy primer must be formulated to improve flexibility, adhesion, and barrier performance. Additives, such as adhesion promoter and flexibilizer can be incorporated within traditional primer to meet desired attributes.

In the previous chapters various commercially available additives were screened in a model epoxy clear coat and ANOVA was utilized to analyze the flexiblizing effect (low T_g, hardness, storage modulus, and elastic modulus) and adhesive strength on multiple substrates. The top six performing additives are PPGEF-570, pTHF-1000, APTS, ApTHF-170, PBAB, and TEPS-80. PPGEF-570 displayed improved adhesion-promoting capabilities on the steel and aluminum substrates. The polyether resulted in the maximum improvement in flexibility for all additives investigated, with pTHF-1000 and ApTHF-170 being the apex. APTS was shown to improve the adhesion performance of pTHF-1000 on metallic substrates as well as result in a higher flexiblizing effect. PBAB demonstrated improved adhesion on steel and resulted in one of the least detrimental adhesive effects on fiberglass reinforced polymer. Noticeable improvements in adhesive strength on the metallic substrates were observed by the incorporation of TEPS-80.

In this study, the statistical design of experiments was used to examine the effects of variables such flexibilizing agents and adhesion promoters at multiple levels. Here is a model for determining optimal formulation for developing a multi-substrate primer using analysis of variance (ANOVA). This method can give valuable results with minimal experimentation

Experiments

Materials

Diglycidyl ether of bisphenol A resin, Epon 828, (Hexion Specialty Chemicals) was used as the primary resin. Polyamine, Epikure 3164, was used as the curing agent (BASF Corporation). N-butylated urea resin, CYMEL® U-216-10LF, (Allnex) was used as a secondary crosslinking agent. A reactive diluent, Epodil 748 (Evonik), was used to reduce the viscosity of the epoxy resin. TiO2 R-706 (Ti-Pure),10 S Wollastocoat (Imery), and Barium Sulfate (Spectrum) were incorporated into the paints as filler pigments. Anti-corrosion pigment SHIELDEX® AC5 (Grace) and modified zinc orthophosphates Heucophos ZPO (Heubach) were used to impart corrosion protection. Solvents include 2-heptanone, methyl acetate, and acetone (Sigma Aldrich, now Millipore). Additives ~1000 average Mn polytetrahydrofuran (pTHF-1000), ~570 average Mn poly(phenyl glycidyl ether)-co-formaldehyde (PPGEF-570), 1,3-propanediol bis(4-aminobenzoate) (PBAB)(Sigma Aldrich, now Millie Pore), Thioplast EPS 80 (TEPS-80) (Akzo-Nobel), and Jeffamine THF 170 (ApTHF-170) (Huntsman) were used as flexibilizing agent and adhesion promoter. Substrates used are steel (QD-35), aluminum (A-36) (Q-Panel), carbon fiber reinforced plastics sheets (Ultra-Strength Lightweight 1/16” thick), and fiberglass reinforced polymer (3/16’’ thick) (MacMaster-Carr).

Experimental Design

A fractional factorial experimental design (2^{6-1}) was employed in the development of a multi-substrate primer. In this design, the 2 represents the number of levels (1 and 10 wt% of additives based on F1-00), 6 refers to different additives reported in Fig 7.1 (PPGEF-570, APTS pTHF-1000, PBAB, ApTHF-170, and TEPS-80), and 1 is the number of generators, which determine how the interactions of the treatment are confounded. The design leads to 32 total formulations. The statistical analysis of response variables was calculated using Design expert 13 (Stat-Ease Inc., USA).

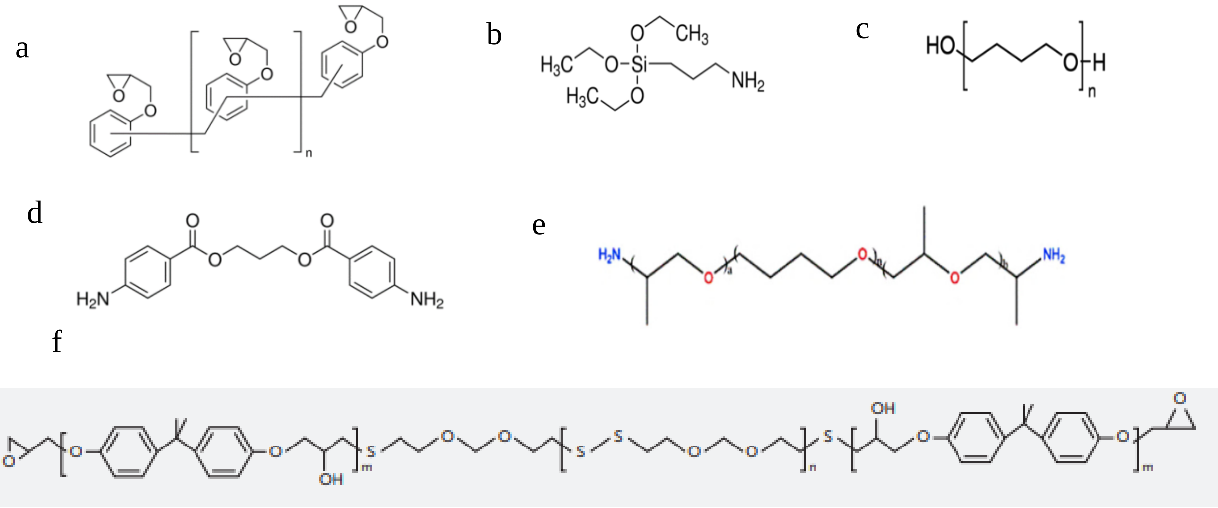

Figure 7.1. Chemical structure of additives used for the experiment. a) poly(phenyl glycidyl ether)-co-formaldehyde, b) 3-Aminopropyl-triethoxysilane, c) polytetrahydrofuran, d) 1,3-propanediol bis(4-aminobenzoate), e) polyetheramine, f) Thioplast EPS 80

Formulation of Basis Epoxy Primer

To investigate the effect of the flexibilizing agents and adhesion promoter, a primary formula (F1-00) is needed to serve as the basis for the experimental design. Formulation of F1-00 is as follows: pigments, titanium dioxide, 10 ES Wollastocoat, barium sulfate, Shieldex AC5, and zinc phosphate, were slowly added to a metal beaker containing slowly mixing Epon 828.

The speed mixer was slowly increased to ensure that all the pigments remained undisputed as they wetted by the epoxy resin. After which, the sample was dispersed at 50 rpm for 30 mins-1 hr. The temperature was periodically measured to ensure it did exceed 50°C. The fineness of the grind vehicle was checked by the Hegman gauge to get the fineness value of 7+ µm (ASTM D 1210). Once the pigment was fully dispersed, the speed of the mixer was decreased and Cymel 216 10 LF and Epodil 748 were slowly added. The speed was then increased to 30 rpm for another 5 minutes. Solvents, methyl acetate, 2-heptanone, and acetone were added to the solution and mixed an additional 10-15 minutes at 15 rpm. The paint was cooled at room temperature and filtered using a 190 µm strainer.

Formulation for Experimental Designed Primer

The 32 formulations from the experimental design are reported in Table 7.1. A general formulation procedure is described as follows, epoxy-functional additives such as PPGEF-570 and TEPS-80, were added to F1-00 and the solution was mixed for 30 mins to produce component A. Amine or hydroxyl functional additives such as PBAB (dissolved in 30 wt% acetone), ApTHF-170 (dissolved in 30 wt% acetone), pTHF-1000, and APTS were at to Epikure 3164 and mixed for 30 minutes creating component B. The two components were added, hand-mixed for a few minutes, and an induction time of 20 mins was observed. The amount of Epikure 3164 was selected to result in epoxy amine ratio of 1:1.

Table 7.1. Formulations according to the factorial experiment design method

Formula	PPGEF-570	APTS	PTHF-1000	PBAB	ApTHF-170	TEPS-80	F1-00	Epikure 3164
F1-01	0.31	0.3	0.3	0.31	0.3	0.31	40.02	12.99
F1-02	3.01	0.3	0.3	0.3	0.3	3.02	39.99	18.73
F1-03	0.3	3	0.31	0.31	0.3	3.01	40.01	12.11
F1-04	3.01	3.04	0.33	0.3	0.31	0.33	40.08	13.7
F1-05	0.31	0.3	2.99	0.3	0.3	2.98	40.06	15.08
F1-06	3	0.3	3	0.3	0.3	0.3	40.01	16.65
F1-07	0.3	3	3	0.3	0.3	0.29	40	10.09
F1-08	3	3.03	3	0.3	0.3	2.98	40.01	15.78
F1-09	0.3	0.3	0.3	3	0.31	2.98	40	10.92
F1-10	3	0.31	0.3	18.08	0.3	0.37	40.01	12.51
F1-11	0.29	3	0.3	3	0.31	0.32	39.99	5.88
F1-12	3.02	3.02	0.28	2.98	0.3	3.03	40.02	11.63
F1-13	0.31	0.29	3	3	0.31	2.99	40.2	8.85
F1-14	3.02	0.29	3	3	0.3	3.01	40	14.56
F1-15	0.3	3	2.99	3	0.31	3.03	40	7.95
F1-16	2.99	3.02	2.98	2.98	0.31	0.32	40.01	9.58
F1-17	0.3	0.31	0.3	0.3	3.01	3	40.01	13.35
F1-18	3	0.29	0.31	0.3	3.01	0.29	39.99	14.94
F1-19	0.28	3.03	0.31	0.31	3.01	0.34	40.05	8.31
F1-20	3	3	0.3	0.3	3	3	40	14.06
F1-21	0.29	0.31	3	1.8	3	0.31	40.05	11.26
F1-22	2.99	0.32	3.02	0.3	3.02	3.02	40.01	17.08
F1-23	0.31	3.01	3	0.3	3	3	40.01	10.4
F1-24	3.01	3	3.01	0.3	3	0.35	39.99	12
F1-25	0.3	0.31	0.34	2.99	3	0.34	40.04	7.18
F1-26	3.01	0.3	0.3	2.99	3.01	3.02	40	12.91
F1-27	0.3	3.01	0.3	3	3.01	2.99	40.01	6.27
F1-28	3	3.02	0.3	3	3	0.27	40.07	7.83
F1-29	0.3	0.3	3.01	3	3.01	3.05	39.99	9.19
F1-30	3.02	0.32	3.06	3.01	2.99	0.32	40.05	10.82
F1-31	0.3	3.02	2.99	3.01	3.01	0.3	40.02	4.16
F1-32	3	3.03	3.03	3	2.99	3.03	40.08	9.95

Coating Application and Curing

All formulations were applied on steel, aluminum, fiberglass reinforced polymer, and carbon fiber reinforced plastics substrates. The substrates were degreased for the removal of grease and oil contamination before the application of the coatings. Coatings were applied at 8 mils wet film drawdown. The coatings were left to sit at room temperature for 7 days before baking to ensure the formation of a uniform film. The coatings were baked at 80°C for 20 mins. All formulations were air-dried for at least 7 days before testing. An average dry film thickness of 60 µm ± 5 µm was obtained using an Elcometer thickness gauge on the metallic substrates (Al and Fe). Drawdowns were also made on PTFE films to produce free-standing films of the formulations for DSC and DMA.

Pull Off-Adhesion Testing

The test was performed using a PosiTests (DeFelsko Corporation, New York) electronic adhesive meter compliant with ASTM D 4541. The instrument uses the pull-off method, measuring the force required to release a dolly glued to a small surface area of the organic coating. The force required to detach the dolly off this surface is a measure of adhesive strength. The 20 mm diameter dollies were firmly glued to the surface of the panel coated using a two-component epoxy adhesive (3M ™ Scotch-Weld ™ Epoxy Adhesive 460). The adhesive was cured at room temperature for 24 hours. After curing, slots were drilled around the dolly through the film unto the substrate to avoid the effects of peripheral coatings. The normal-tension force was applied on the dollies until failure occurred. Triplicates were performed for each sample the average arithmetic mean value was reported.

Reverse Impact Resistance

Reverse impact strength of the coatings was determined following ASTM D 2794 using a Gardner impact tester. In this test, a 4 lbs steel ball is dropped unto the uncoated side of aluminum and steel coated substrate from a different height. The minimum height at which crazing, cracking, or loss of adhesion was noted, and the impact resistance was calculated and reported in inch-pounds (in.-lb). Samples that did not fail at the maximum height of 43 inches were noted as having impact strength of >169 in.-lb.

Conical Mandrel

A flexibility test of the coatings steel and aluminum substate was performed on a conical mandrel bend tester as per the standard ASTM D522. After bending the coated substrate over the mandrels, the tested panels were visually examined for any cracks in the coating, loss of adhesion, or any other forms of failure.

Nanoindentation

Hardness and young’s modulus of aluminum-coated substrates were characterized by the Oliver and Pharr method. Those calculations are derived from the unloading part of the force and depth curve. A Berkovich indenter tip was used for the indentation. Nine indentations are made in each sample and the average hardness and young’s modulus are presented. A Hysitron Inc. TriboScope® Nanomechanical Test Instrument was used.

König Pendulum Hardness

The hardness was measured in per ASTM D 4366 using a Byk pendulum hardness tester. The oscillation of the pendulum is damped over time depending on the viscoelastic properties of the coating. The hardness of the coatings is given by the number of oscillations made by the pendulum within the specified limits of amplitude; from 6° to 3°. Aluminum-coated substrates were used for hardness measurements. An average of six replicate for each formulation is used.

Electrochemical Impedance Spectroscopy (EIS)

EIS measurements for the epoxy-coated metal systems were performed in 3.5% NaCl solution by using a three-electrode system. The epoxy-coated metal acts as the working electrode, a saturated calomel electrode (SCE) as the reference, and a platinum mesh as the counter. A test area is ∼1 cm2 was used. A Gamry Potentiostat REF600-06704 was used. A sinusoidal AC perturbation of 10 mV amplitude coupled with the open circuit potential was applied to the metal/coating system. At the beginning period of immersion, the EIS test was performed in the high-frequency range and after a significant immersion in the range of 100 kHz–10 mHz. All the measurements were conducted at room temperature (∼25 °C) with the solution exposed in a Faraday cage.

Results and Discussion

Flexibility

To determine the effect of the additives on flexibility, each coating was applied to metal substrates and conical mandrel bend, reverse falling impact, pendulum hardness, and nanoindentation were used to characterize their performance. Table 7.2 shows the average values of each test. The conical mandrel tests result in 0 cm of cracking, the highest possible flexibility results, thus the value is not reported in Table 7.2. ANOVA and the Coefficient Estimate results from the reverse impact test are shown in Table 7.3 and 7.4, respectively.

Table 7.2. Average mechanical properties values of coatings

Sample	Reverse Impact (in-lbs.)	Indentation Hardness (Mpa)	Elastic Modulus (Mpa)	Pendulum Hardness (ocs)
F1-01	15.68	66	2534	115
F1-02	168.56	42	1851	11
F1-03	7.84	4	142	40
F1-04	15.68	79	2714	97
F1-05	47.04	2	41	18
F1-06	168.56	78	2403	65
F1-07	78.4	34	795	52
F1-08	156.8	84	2104	30
F1-09	11.76	97	3734	109
F1-10		110	2682	150
F1-11	3.92	397	8684	132
F1-12	3.92	265	5205	133
F1-13	113.98	30	1781	60
F1-14	98	33	1179	33
F1-15	169	42	1559	66
F1-16	105.84	74	2358	101
F1-17	168.56			39
F1-18	168.56	67	1785	75
F1-19	78.4	119	3228	92
F1-20	168.56	123	3156	65
F1-21	168.56			24
F1-22	168.56	2	62	21
F1-23	168	8	428	27
F1-24	169	22	760	46
F1-25	169	30	1505	83
F1-26	117.6	57	2179	105
F1-27	169	75	2220	78
F1-28	164.64	129	3421	133
F1-29	169	3	118	37
F1-30	169	16	643	57
F1-31	169	41	1320	26
F1-32	169	41	1369	80

Table 7.3. ANOVA results from reserve impact

Source	Sum of Sq	df	Mean Sq	F-value	p-value
Model	75184.70	6	12530.78	6.18	0.0005
A-PPGEF-570	2173.06	1	2173.06	1.07	0.3111
B-APTS	1048.80	1	1048.80	0.5168	0.4791
C-pTHF-1000	16527.53	1	16527.53	8.14	0.0088
D-PBAB	83.26	1	83.26	0.0410	0.8412
E-ApTHF-170	52969.71	1	52969.71	26.10	< 0.0001
F-TEPS-80	601.63	1	601.63	0.2965	0.5911
Residual	48701.78	24	2029.24		
Cor Total	1.239E+05	30			

Table 7.4. Coefficient Estimate results from reserve impact

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	118.15	1	8.12	101.39	134.92
A-PPGEF-570	8.52	1	8.23	-8.47	25.51
B-APTS	-5.84	1	8.12	-22.60	10.92
C-pTHF-1000	23.49	1	8.23	6.50	40.48
D-PBAB	-1.65	1	8.12	-18.41	15.12
E-ApTHF-170	41.50	1	8.12	24.74	58.26
F-TEPS-80	4.42	1	8.12	-12.34	21.19

An F-value of 6.18 implies the model is significant; there is only a 0.05 % chance that the F-value could occur due to noise. According to the results, pTHF-1000 and ApTHF-170 are the only additives that have a significant effect on the impact flexibility of the coatings. Per the coefficient estimate, ApTHF-170 has the largest effect of impact flexibility; an average increase of 41.50 in-lbs. is observed from a 1wt% to 10 wt% increase in ApTHF-170. pTHF-1000 results in an average increase of 23.49 in-lbs. per 10 wt% increase. These results are attributed to the high molecular weight flexible polyether chains.

ANOVA and the Coefficient Estimate results from the elastic modulus from nanoindentation are shown in Table 7.5 and 7.6, respectively. An F-value of 4.06 implies the model is significant; there is only a 0.064 % chance that the F-value could occur due to noise. According to the results, APTS, pTHF-1000, ApTHF-170, and PBAB have a significant effect on the elastic modulus of the coatings. As the concentration of the polyether within the formulation increases, the elastic modulus decreases indicating a reduction in the stiffness and rigidity of the coating. A 10 wt% increase in pTHF-1000 and ApTHF-170 results in an 813.28 and 548.00 MPa decrease in the modulus of elasticity, respectively. The reduction in chain mobility due to methyl branching could explain the effect of the ApTHF-170 compared to pTHF-1000.[128,181] PBAB and APTS have detrimental effects on flexibility; a 10 wt.% increase in both additives leads to a 559.83 and 528.99 MPa increase in modulus of elasticity, respectively. The performance of PBAB has ascribed increased chain stiffness due to the presence of bulky aromatic groups.[182,183] The flexibility imparted by the Si-O-Si group of APTS improves the overall flexibility of the coating once pigment and other additives are introduced.

Table 7.5. ANOVA results from nanoindentation-elastic modulus

Source	Sum of Sq.	df	Mean Sq.	F-value	p-value
Model	4.543E+07	6	7.572E+06	4.06	0.0064
A-PPGEF-570	2.278E+06	1	2.278E+06	1.22	0.2804
B-APTS	8.207E+06	1	8.207E+06	4.40	0.0471
C-pTHF-1000	1.939E+07	1	1.939E+07	10.40	0.0037
D-PBAB	9.192E+06	1	9.192E+06	4.93	0.0365
E-ApTHF-170	8.808E+06	1	8.808E+06	4.72	0.0403
F-TEPS-80	3.084E+06	1	3.084E+06	1.65	0.2112
Residual	4.288E+07	3	1.864E+06		
Cor Total	8.831E+07	29			

Table 7.6. Coefficient Estimate results from nanoindentation-elastic modulus

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	1937.40	1	252.13	1415.83	2458.96
A-PPGEF-570	281.25	1	254.44	-245.11	807.61
B-APTS	528.99	1	252.13	7.43	1050.56
C-pTHF-1000	-813.28	1	252.16	-1334.92	-291.64
D-PBAB	559.83	1	252.13	38.27	1081.40
E-ApTHF-170	-548.00	1	252.13	-1069.56	-26.43
F-TEPS-80	-321.37	1	249.86	-838.25	195.50

ANOVA and the Coefficient Estimate results from the indentation hardness are shown in Table 7.7 and 7.8, respectively. An F-value of 3.28 implies the model is significant; there is only a 1.77 % chance that the F-value could occur due to noise. According to the results, APTS and pTHF-1000 are the only additives that have a significant effect on the indentation hardness at the 95% confidence interval. At the 90% confidence interval, PBAB and ApTHF-170 have a significant effect on indentation hardness. Similarly, to the modulus of elasticity result, an increase in the concentration of the polyether within the formulation increases results in a decrease in hardness. A 10 wt.% increase of pTHF-1000 and ApTHF-170 results in a 33.63 and 23.62 decrease in hardness. An increase in APTS and PBAB increases in hardness.

Table 7.7. ANOVA results from nanoindentation-hardness

Source	Sum of Sq	df	Mean Sq	F-value	p-value
Model	88805.29	6	14800.88	3.28	0.0177
A-PPGEF-570	5996.88	1	5996.88	1.33	0.2609
B-APTS	26051.70	1	26051.70	5.77	0.0248
C-pTHF-1000	33154.70	1	33154.70	7.34	0.0125
D-PBAB	16572.73	1	16572.73	3.67	0.0679
E-ApTHF-170	16363.97	1	16363.97	3.63	0.0695
F-TEPS-80	4064.22	1	4064.22	0.90	0.3526
Residual	1.038E+05	23	4514.03		
Cor Total	1.926E+05	29			

Table 7.8. Coefficient Estimate results from nanoindentation-hardness

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	66.32	1	12.41	40.66	91.98
A-PPGEF-570	14.43	1	12.52	-11.47	40.33
B-APTS	29.80	1	12.41	4.14	55.47
C-pTHF-1000	-33.63	1	12.41	-59.29	-7.96
D-PBAB	23.77	1	12.41	-1.89	49.43
E-ApTHF-170	-23.62	1	12.41	-49.28	2.04
F-TEPS-80	-11.67	1	12.29	-37.10	13.77

ANOVA and the Coefficient Estimate results from the pendulum hardness are shown in Table 7.9 and 7.10, respectively. An F-value of 6.26 implies the model is significant; there is only a 0.04 % chance that the F-value could occur due to noise. According to the results, pTHF-1000, PBAB, and TEPS-80 are the only additives that have a significant effect on the indentation hardness at the 95% confidence interval. A 10wt% increase in additives pTHF-1000 and TEPS-80 results in a 16.68 and 13.00 osc decrease in hardness. PBAB has a detrimental effect on flexibility. A 10 wt.% increase in PBAB results in a 17.69 osc increase in pendulum hardness.

Table 7.9. ANOVA results from König pendulum hardness

Source	Sum of Sq.	df	Mean Sq.	F-value	p-value
Model	28254.80	6	4709.13	6.26	0.0004
A-PPGEF-570	2254.67	1	2254.67	2.99	0.0959
B-APTS	1200.50	1	1200.50	1.59	0.2183
C-pTHF-1000	8766.67	1	8766.67	11.64	0.0022
D-PBAB	10011.13	1	10011.13	13.30	0.0012
E-ApTHF-170	1568.00	1	1568.00	2.08	0.1614
F-TEPS-80	5408.00	1	5408.00	7.18	0.0128
Residual	18821.20	25	752.85		
Cor Total	47076.00	31			

Table 7.10. Coefficient Estimate results from König pendulum hardness

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	68.75	1	4.85	58.76	78.74
A-PPGEF-570	8.46	1	4.89	-1.61	18.53
B-APTS	6.12	1	4.85	-3.86	16.11
C-pTHF-1000	-16.68	1	4.89	-26.75	-6.61
D-PBAB	17.69	1	4.85	7.70	27.68
E-ApTHF-170	-7.00	1	4.85	-16.99	2.99
F-TEPS-80	-13.00	1	4.85	-22.99	-3.01

Per all method utilized to measure flexibility, ApTHF-170 and pTHF-1000 impart the greatest degree of flexibility in a fully pigmented epoxy primer. The flexibility performances are attributed to the long-chain length and bond rotation of the ether group found in the backbone of these additive.[124,127] PBAB and APTS appear to have detrimental effects on flexibility. Formulation with the highest amount of ApTHF-170, pTHF-1000, and the lowest amount of PBAB and APTS were down-selected for flexibility. The reduced effect of APTS could be related to a interaction between the hydrolyzable group and metal oxide pigments such as titanium dioxide, which improves the coating's cohesive strength while reducing flexibility. The flexibility of PBAB is due to the bulking aromatic group.

Adhesion

To determine the effect of the additives on substrate adhesion, each coating was applied unto an Al, Fe, FG, and CF substrate the pull-off adhesion was used to access adhesion performance. Due to the thickness variation in the substrate, Al, Fe, and CF demonstrate more of a peel adhesion effect due to substrate deformation. FG results represent a pull of effect of adhesion. Table 7.11 show the average results in the formulation on each substrate.

Table 7.11. Average adhesive strength of coatings on Al, Fe, CF, and FG

Sample	POA-Al (psi)	POA-Fe (psi)	POA-CF (psi)	POA-FG (psi)
F1-01	175	251	363	1081
F1-02	116	167	263	655
F1-03	205	231	399	1256
F1-04	217	323	357	1004
F1-05	215	209	401	1111
F1-06	154	249	386	1477
F1-07	103	112	221	437
F1-08	250	275	330	1427
F1-09	186	213	400	1093
F1-10	195	229	363	947
F1-11	91	123	162	395
F1-12	108	186	207	465
F1-13	99	135	197	529
F1-14	238	261	355	1299
F1-15	84	98	149	602
F1-16	124	103	321	845
F1-17	313	321	363	1646
F1-18	123	154	279	1138
F1-19	211	229	368	1549
F1-20	329	373	392	1753
F1-21	244	307	417	1050
F1-22	179	223	301	1073
F1-23	269	283	341	1411
F1-24	135	186	287	958
F1-25	204	253	370	1225
F1-26	183	188	333	967
F1-27	205	234	353	1181
F1-28	248	282	421	1289
F1-29	137	179	245	843
F1-30	101	157	292	824
F1-31	90	153	237	963
F1-32	115	159	317	754

Per ANOVA, statistical analysis of the effect of the additives on the metal substrates and CF could not be established at 95% or 90% confidence interval. However, as shown in Fig 7.2, notable formulations such as F1-02, F-18, F-19, and F1-20 resulted in improved adhesion performance on the metal substrates.

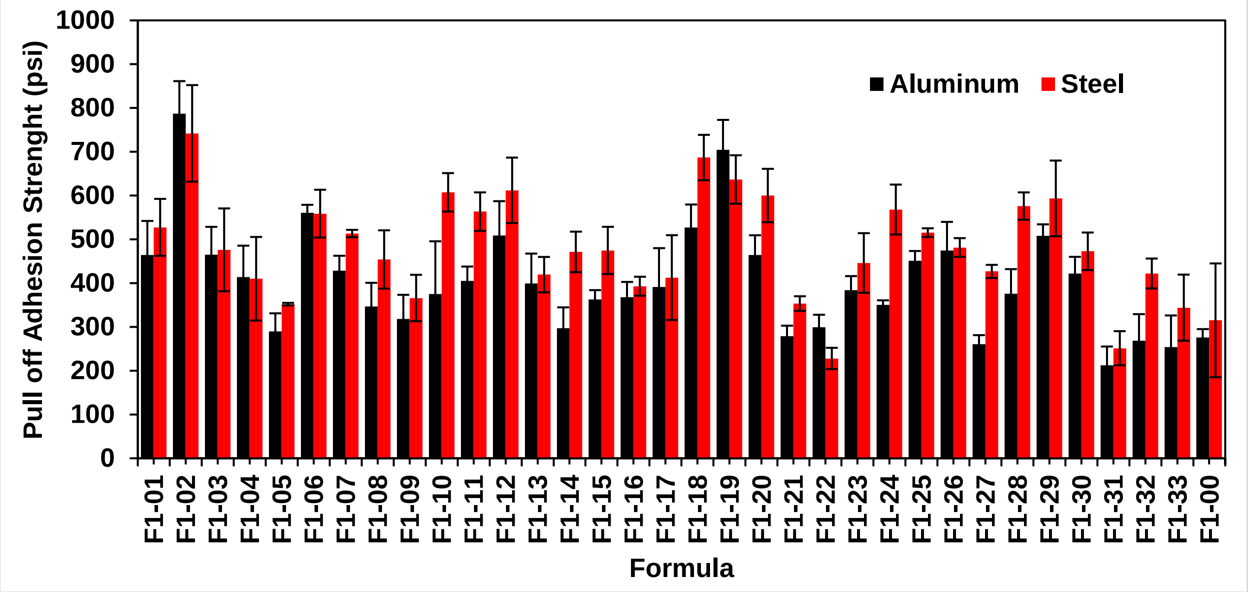

Figure 7.2. Pull-off Adhesion strength of formulation on metal substrates

ANOVA and the Coefficient Estimate results for the effect of the additives on adhesion performance on FB are shown in Table 7.12 and 7.13, respectively. An F-value of 2.47 implies the model is significant ($p<0.1$); there is only a 5.18 % chance that the F-value could occur due to noise. According to the results, ApTHF-170 and PBAB are the only additives that have a significant effect on the adhesive strength to FG. PBAB becomes more detrimental adhesion to FG once pigment, fillers, extender, and other additives are incorporated into the coating. A 1 to 10 wt.% increase in ApTHF-170 results in a 125.04 psi increase in adhesive strength on FG.

Table 7.12. ANOVA results from adhesive strength-FG

Source	Sum of Sq.	df	Mean Sq.	F-value	p-value
Model	1.415E+06	6	2.359E+05	2.47	0.0518
A-PPGEF-570	14568.01	1	14568.01	0.1523	0.6996
B-APTS	14028.08	1	14028.08	0.1467	0.7050
C-pTHF-1000	66776.87	1	66776.87	0.6981	0.4113
D-PBAB	7.222E+05	1	7.222E+05	7.55	0.0110
E-ApTHF-170	5.003E+05	1	5.003E+05	5.23	0.0309
F-TEPS-80	1.042E+05	1	1.042E+05	1.09	0.3066
Residual	2.391E+06	25	95650.92		
Cor Total	3.807E+06	31			

Table 7.13. Coefficient Estimate results from adhesive strength-FG

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High
Intercept	1038.90	1	54.67	926.30	1151.50
A-PPGEF-570	21.51	1	55.10	-91.99	135.00
B-APTS	-20.94	1	54.67	-133.54	91.66
C-pTHF-1000	-46.04	1	55.10	-159.53	67.45
D-PBAB	-150.23	1	54.67	-262.83	-37.63
E-ApTHF-170	125.04	1	54.67	12.44	237.64
F-TEPS-80	57.06	1	54.67	-55.54	169.66

Barrier

Based on the adhesion and flexibility performance, 6 formulations were selected, and their barrier performances were evaluated. The key role of the primer is to act a as barrier layer to prevent or delay the penetration of the corrosive medium unto the metal/substrate interface. EIS is one of the most effective methods to study the mechanism of metal corrosion and coating barrier performance. It is commonly understood that the absolute impedance modulus of EIS at 0.1 Hz is an important parameter to evaluate the anticorrosion and barrier performance of the coating. When |Z|0.1Hz is greater than 106 Ω cm2, the barrier performance of the coating is considered adequate. Figs 7.3 and 7.4 have Bode diagrams of the Fe coated panels.

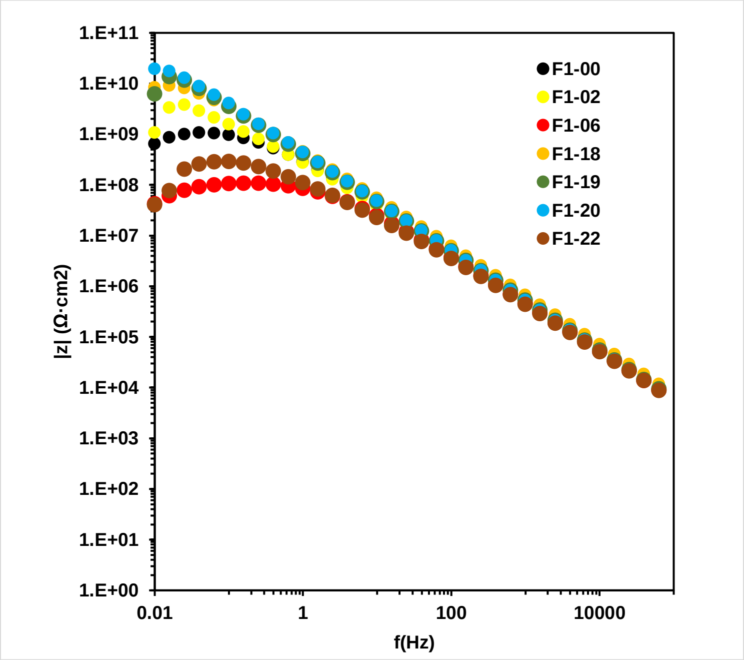

Figure 7.3. EIS data modified, and unmodified epoxy coated Fe substrate

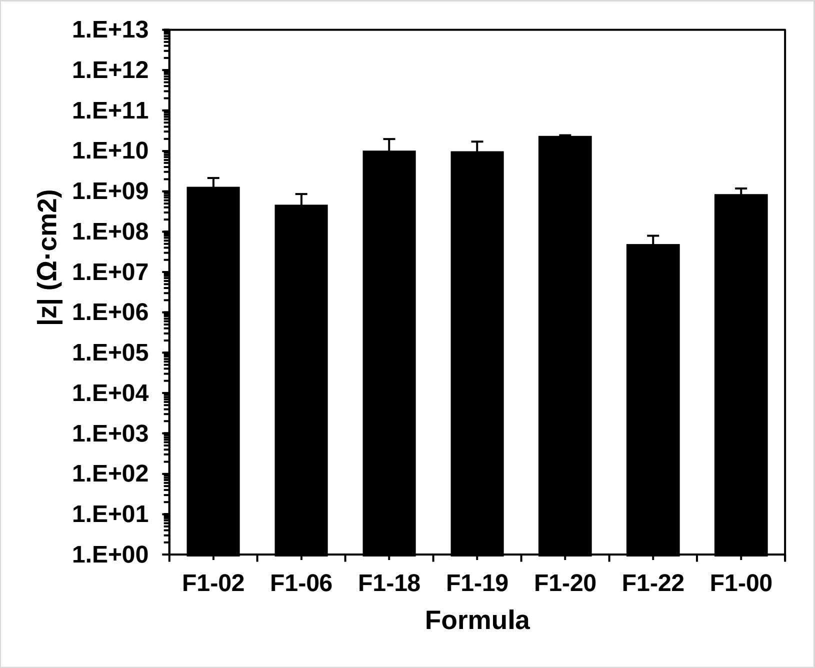

Figure 7.4. |Z|0.1Hz of modified, and unmodified epoxy coated Fe substrate

All formulations investigated have a $|Z|_{0.1\text{Hz}}$ greater than 10^6 Ω cm^2 indicating adequate barrier performance. The barrier performance is in order F1-18 > F1-02=F1-19=F1-20>F1-06=F1-00>F1-22. The barrier performance of the modified coating is ascribed to the adhesive strength on Fe. F1-22 has the lowest impedance in the low-frequency range representing poor barrier performance. These results are attributed to the poor adhesion of F1-22 onto the Fe substrate.

Conclusions

Using the statistical design of experiments, the effects of flexibilizing agents and adhesion promoters were investigated in the fully pigmented epoxy primer. According to ANOVA results, high molecular weight polyether (ApTHF-170 and pTHF-1000) conferred the best degree of flexibility by all matrices. PBAB and APTS both have a negative impact on flexibility. A potential explanation for the reduced effect of APTS could be due attributed to the potential interaction of the hydrolyzable group and metal oxide pigments such as titanium dioxide, improving the cohesive strength of the coating while diminishing flexibility. The bulking aromatic group in PBAB is responsible for its flexibility.

The effect of the six additives on the adhesive strength of Fe, Al, and CF was not statistically significant at the 95% or 90% confidence intervals, per ANOVA. Notable formulations (F1-02, F1-18, F1-19, and F1-20) did, however, result in significantly better adhesion on metal substrates. The additives PBAB and ApTHF-170 had the greatest impact on the primer's adhesion strength to FG. PBAB had the largest negative effect on adhesion among the statistically significant additions, while ApTHF-170 had the least negative effect. Overall, the primer's adhesive strength was decreased to FG by adding additives.

Based on EIS on Fe, the top six performing modified primers and the unmodified control all had a $|Z_{|0.1Hz}$ greater than 10^6 Ω cm^2, demonstrating adequate barrier performance according to industry standards. F1-22 on the other hand was an $|Z|_{0.1Hz}$ Ω^2 order of magnitude lower than that of the control. The highest $|Z|_{0.1Hz}$ was achieved by F1-18 and F1-20. The adhesive strength of the coatings to Fe was found to be the most crucial factor in their barrier performance; F1-22 had the weakest adhesive strength to Fe.

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CHAPTER 8. ACCELERATED WEATHERING OF EPOXY PRIMER FOR MULTI-SUBSTRATE APPLICATION

Introduction

Coatings based on Bisphenol -A (BPA) epoxide resins are one of the common primers for vehicles due to their exceptional performance. However, to continue their usage as primers to multi-substrate vehicles, traditional epoxide must be modified to improve flexibility, adhesion, and barrier performance.[20] Based on previous work, epoxy-amine primers have been modified with a silane coupling agent, polysulfide, and polyethers to demonstrate improved flexibility and adhesion to aluminum, steel, carbon fiber reinforced plastics, and fiberglass reinforced polymer. However, the greatest measure of adequate flexibility of a coated substrate is performance under service conditions. Most flexibility and adhesion tests are performed on fresh-coated panels, typically a minimum of 7 days posted cured, in an atmospheric indoors environment. The results obtained are thus not applicable to service conditions involving degrading atmosphere.

Moisture, temperature changes, and exposure to sunlight (ultraviolet wavelengths) encountered in outdoor exposure are factors that are known to reduce the flexibility, toughness, adhesion, and barrier of organic coatings. Hence, it is advantageous to perform tests for flexibility, adhesion, and barrier after periods of weathering to determine the coating performance under actual weather conditions. However due to time limitations, long-term outdoor exposure experimentation may not be feasible, thus accelerated weathering of the coating is needed for analysis of coating performances.[184]

In this work, the effect of accelerating weathering, salt spray, on flexibility, adhesion, and barrier performance of modified and unmodified epoxy primer is investigated.

Experiments

Materials

Diglycidyl ether of bisphenol A resin, Epon 828, (Hexion Specialty Chemicals) was used as the primary resin. Polyamine, Epikure 3164, was used as the curing agent (BASF Corporation). N-butylated urea resin, CYMEL® U-216-10LF, (Allnex) was used as a secondary crosslinking agent. A reactive diluent, Epodil 748 (Evonik), was used to reduce the viscosity of the epoxy resin. TiO_2 R-706 (Ti-Pure),10 S Wollastocoat (Imerys), and Barium Sulfate (Spectrum) were incorporated into the paints as filler pigments. Pigments SHIELDEX® AC5 (Grace) and modified zinc orthophosphates Heucophos ZPO (Heubach) were used to impart corrosion protection. Solvents include 2-heptanone, methyl acetate, and acetone (Sigma Aldrich, now Millie Pore). Additives ~1000 average Mn Polytetrahydrofuran (pTHF-1000), ~570 average Mn Poly(phenyl glycidyl ether)-co-formaldehyde (PPGEF-570), 1,3-Propanediol bis(4-Aminobenzoate)(PBAB)(Sigma Aldrich, now Millie Pore), Thioplast EPS 80 (TEPS-80) (Akzo-Nobel), and Jeffamine THF 170 (ApTHF-170) (Huntsman) were used as flexibilizing agent and adhesion promoter. Substrates of interest are steel (QD-35), aluminum (A-36) (Q-Panel), carbon fiber reinforced plastics sheets (Ultra-Strength Lightweight 1/16" thick), and fiberglass reinforced polymer (Structural FRP Fiberglass 3/16'' thick) (MacMaster-Carr).

Formulation of Primer

The modified formulation is based on a primary formula (F1-00). Formulation of F1-00 is as follows: pigments, titanium dioxide, 10 ES Wollastocoat, barium sulfate, Shieldex AC5, and zinc phosphate, were slowly added to a metal beaker containing slowly mixing Epon 828. The speed mixer was slowly increased to ensure that all the pigments remained undisputed as they wetted by the epoxy resin. After which, the sample was grind at 50 rpm for 30 minutes-1 hr. The temperature was periodically measured to ensure it did exceed 50°C. The fineness of the grind vehicle was checked by the Hegman gauge to get the fineness value of 7+ µm (ASTM D 1210). Once the pigment was fully grinded, the speed of the mixer was decreased and Cymel 216 10 LF and Epodil 748 were slowly added. The speed was then increased to 30 rpm for another 5 minutes. Solvents, methyl acetate, 2-heptnon, and acetone were added to the solution and mixed an additional 10-15 minutes at 15 rpm. The paint was cooled at room temperature and filtered using a 190 µm strainer.

For the modified formulations a general formulation procedure is described as follows, epoxy -functional additives such as, PPGEF-570, and TEPS-80, were added to F1-00 and the solution was mixed for 30 mins to produce component A. Amine or hydroxyl functional additives such as PBAB (dissolved in 30 wt% acetone), ApTHF-170 (dissolved in 30 wt% acetone), pTHF-1000, and APTS were at to Epikure 3164 and mixed for 30 mins creating component B. The two components were added hand-mixed for a few mins and an induction time of 20 mins was observed. The amount of Epikure 3164 was selected to result in an epoxy amine ratio of 1:1. Table 8.1 shows the composition of the modified primer.

Table 8.1. Formulation of modified epoxy

Formula	PPGEF-570	APTS	PTHF-1000	PBAB	ApTHF-170	TEPS-80	F1-00	Epikure 3164
F1-18	3	0.29	0.31	0.3	3.01	0.29	39.99	14.94
F1-20	3	3	0.3	0.3	3	3	40	14.06

Coating Application and Curing

All formulations were applied on steel, aluminum, fiberglass reinforced polymer, and carbon fiber reinforced plastics substrates. The substrates were degreased for the removal of grease and oil contamination before the application of the coatings. An airless spray gun was used to apply the coatings to substrates. The coatings were left to sit at room temperature for 7 days before to baking to ensure the formation of a uniform film. The coatings were baked at 80°C for 20 mins. All formulations were air-dried for at least 7 days before testing. Using an Elcometer thickness gauge, an average dry film thickness of 120 µm ± 15 µm on the Al and Fe was obtained for all formulations investigated.

Salt Spray

Neutral salt spray testing was conducted according to ASTM B117 in Q-FOG™ CCT 600 neutral salt fog cyclic corrosion tester. Salt spray testing was conducted for all test samples until failure or 1000 h if no failure occurred. An “X” incision was scribed through the coated metal panels by using (Elcometer™ scriber) making sure that the coating was scribed to the substrate for visual assessment of corrosion. The test panels were reported for flexibility, adhesion, and barrier performance at 200 h, 400 h, 600 h, 800 h, and 1000 h. After the allowed period, the sample was rinsed with DI water and allow to dry at room temperature for 7 days before testing were performed.

Pull-off Adhesion Testing

The pull-off adhesion test uses hydraulic pressure to provide the force required to pull a specified test diameter of a coating away from its substrate. The adhesion tests were conducted with ASTM D454. In the current study, an automatic PosiTests pull-off adhesion tester (DeFelsko Corporation, New York) is used. Dollies of 20 mm diameter were glued to the coated specimens using a two-component epoxy (3M ™ Scotch-Weld ™ Epoxy Adhesive 460) formulated to a 1:1 volume mix ratio. A 220-grit sandpaper was utilized to abrade the coating surface before the application of the glue to ensure proper adhesion of the glue. The glue could fully cure for 24 hours at ambient temperature. Before testing, the adhesive around the edges of the dolly was cut through with a 20 mm cutting tool, and any excess adhesive was removed. The greatest tensile pull-off strength needed for failure to occur was reported in MPa. The breaking points, demonstrated by fractured surfaces, occurred along the weakest plane within the system consisting of the dolly, adhesive, coating layers, and substrate. For each sample, at least three replicates of the specimens were performed, and the average value was reported

Reverse Impact Resistance

Reverse impact strength of the coatings was determined following ASTM D 2794 using a Gardner impact tester. In this test, samples were subjected to the impact of a 4-lb weight ball falling from different heights The height at which failure occurs is used to calculate the impact strength. The maximum drop height is 43 inches. Samples that did not fail were noted as having impact strength of >169 in.-lb.

Conical Mandrel

A conical mandrel tester was used to determine the flexibility of coated metallic substrates. The coatings were secured in the mandrel and bent over the frame of the instrument. The films were then examined for delamination, cracks, or crazing.

König Pendulum Hardness

The König Pendulum is performed per ASTM D 4366. For this test, two steel balls attached to the pendulum are placed on the coating. Depending on the viscoelastic properties of the coating, the oscillation of the pendulum diminishes over time. The decay time of the pendulum from an initial amplitude of 6 ° to a final amplitude of 3 ° is a measure of the hardness. Byk's pendulum hardness tester was used as the hardness tester. All pendulum hardness tests were performed on an aluminum-coated substrate. The hardness measure for each formulation is repeated six times.

Nanoindentation

Nanoindentation on epoxy coatings was performed using a Hysitron Inc. TriboScope® Nanomechanical Test Instrument. A Berkovich diamond tip was used for the indentations. Hardness and elastic modulus were determined from the unloading part of the force–depth curve. Nine indentations are made in each sample and the average hardness and young’s modulus are reported.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) measurements were conducted in tensile mode on a TA Instruments Q800 Dynamic Mechanical Analyzer. An oscillation amplitude of 10 μm was applied to the sample (10 mm x 0.5 mm x 0.10 mm), at a frequency of 1 Hz The temperature was increased at a rate of 5 °C/min from -80 °C to 150 °C under nitrogen gas. The dynamic storage, loss moduli, and tan δ (E”/E’) were recorded as a function of temperature. The peak Tan Delta was utilized to determine glass transition temperature and storage modulus at 120 °C was utilized to determine crosslink density.

EIS

A three-electrode system in a 3.5 percent NaCl solution was used to conduct EIS measurements on epoxy-coated metal structures. The counter is a platinum mesh, and the working electrode is an epoxy-coated metal. The reference electrode is a saturated calomel electrode (SCE), and the working electrode is an epoxy-coated metal. A test area of 1 cm2 was used. In this experiment, the Gamry Potentiostat REF600-06704 was used. A 10-mV amplitude sinusoidal AC perturbation with the open-circuit voltage was applied to the metal/coating system. The EIS test was conducted in the high-frequency range at the beginning of the immersion time and then in the range of 100 kHz–10 mHz after a long immersion period. All the tests were done with the solution in a Faraday cage at ambient temperature (25 °C).

Results and Discussion

Flexibility

The effect of the accelerated salt spray test on the flexibility of modified and unmodified epoxy primer was investigated per conical mandrel bend, reverse falling impact, pendulum hardness, and nanoindentation. Fe coated panels were characterized at 0 h, 200 h, 600 h, 800 h, and 1000 h. The flexibility test for the coated panel conducted on the conical mandrel showed no appearance of cracks or delamination with longer exposure time to the corrosive environment. The high flexibility of the coating is attributed to the inherent chemical structure of epoxy resin as well as high adhesion to the substrate. The coated panels were also subjected to a reverse falling impact test and the results are reported in Fig 8.1. Failure occurs for the control, F1-00, at 3.72 in-lbs., the minimal measure for the instrument. F1-18 maintains an impact resistance of 169 in-lbs. for the duration of the exposure tests showing excellent toughness, flexibility, and long-term adhesion. 200 h after exposure, the impact resistance of F1-20 decreases from 169 in-lbs. to 98 in-lbs. indicating a slight decrease in flexibility and adhesion. The impact resistance of F1-20 remains constant after from 200 h to 1000 h.

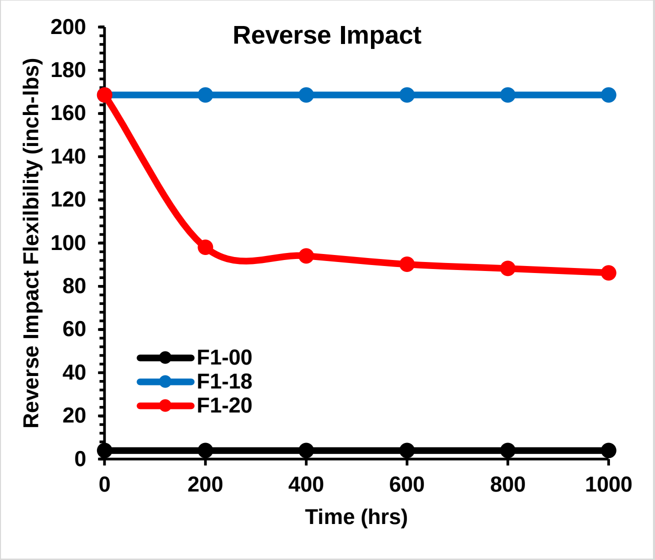


Figure 8.1. Impact flexibility of modified and unmodified epoxy coating Fe substrate vs B117 Salt Spray exposure time

König pendulum hardness was monitored over exposure time and is plotted in Fig 8.2. Hardness remains unchanged over the 1000 h of salt spray exposure, suggesting consistent flexibility.

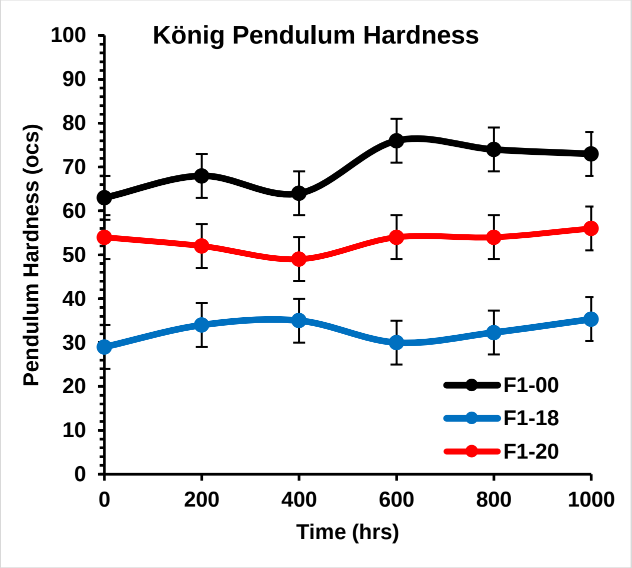


Figure 8.2. König pendulum hardness of modified and unmodified epoxy coating Al substrate vs B117 Salt Spray exposure time

Fig 8.3 gives the results of the elastic modulus obtained from nanoindentation. Before salt spray exposure, F1-00 and F1-20 have a similar modulus of elasticity implying similar flexibility. The elastic modulus of F1-00 remains consistent for the duration of the exposure period, however, F1-20 decreases after 200 h and remains constant for the rest of the test. This outcome is surprising; elastic modulus measures the resistance of a material to elastically deformed under a load. A stiff material has a high modulus of elasticity and changes its shape only slightly under elastic loads. A flexible material has a lower modulus of elasticity and changes its shape. The observed decrease in elastic modulus of F1-20 is suggestive of increased flexibility, which is contradictory to conical mandrel and impact resistance test. F1-18 undergoes a slight decrease after 200 h but remain unchanged for the duration of the accelerated weathering test.

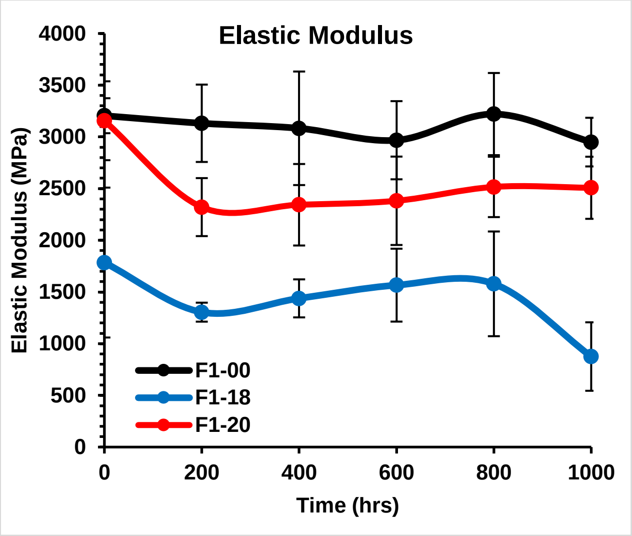


Figure 8.3. Elastic Modulus of modified and unmodified epoxy coating Fe substrate vs B117 Salt Spray exposure time

Hardness performance from the nanoindentation test is given in Fig 8.4. Like the pendulum hardness data, indentation hardness remains unchanged over the 1000 h of salt spray exposure, signifying consistent flexibility. F1-18 is the most flexible of the coatings.

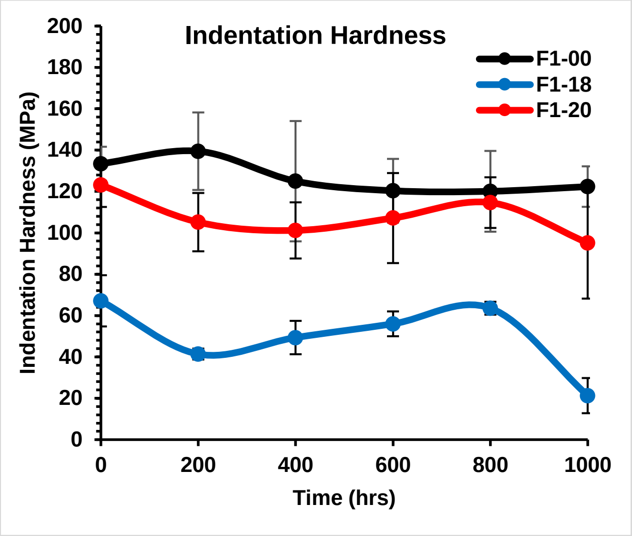


Figure 8.4. Indentation hardness of modified and unmodified epoxy coating Fe substrate vs B117 Salt Spray exposure time

DMA technique was conducted to further investigate the influence of salt spray exposure on the flexibility of the primers. As shown in Fig 8.5 the T_g of F1-00 remains unchanged over the 1000 h of B117 exposure, denoting consistent flexibility. The T_g of F1-18 slightly increases after 200 but remains consistent for the duration of the test. F1-20 undergoes the most drastic change, increasing from 50.88° C to 76.64° C. According to the literature, when an epoxy-amine network is exposed to water, two major interactions occur. Depending on the difference in the bond complex and activation energy of the polymer either a Type I (plasticizing) or Type II (anti plasticizing) binding occurs. For the plasticizing effect, water molecule bonds with the resin network disrupting Van der Waals forces and hydrogen bonds. Thereby, resulting in greater mobility of the chain segment and thus decreasing T_g. This water molecule possesses lower activation energy and is easier to remove from the resin. In the anti-plasticizing or crosslinking effect, the polar interactions between the water and the polymer backbone led to hydrogen bonding and the creation of secondary crosslink networks that would further restrict the molecular motion leading to a decrease in chain mobility. This water molecule possesses higher activation energy and is harder to remove. Type II bonding depends strongly on the exposure time and temperature.[185] The XLD is reported in Fig 8.6 are more indicative of Type II bonding.

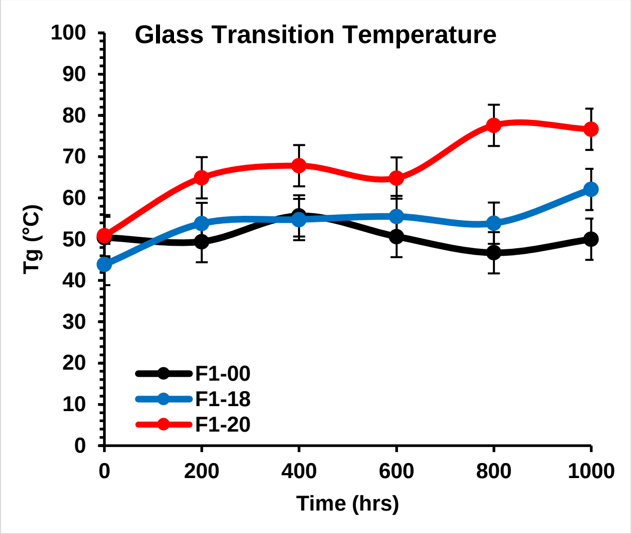


Figure 8.5. T_g (DMA) of modified and unmodified epoxy coatings vs B117 Salt Spray exposure time

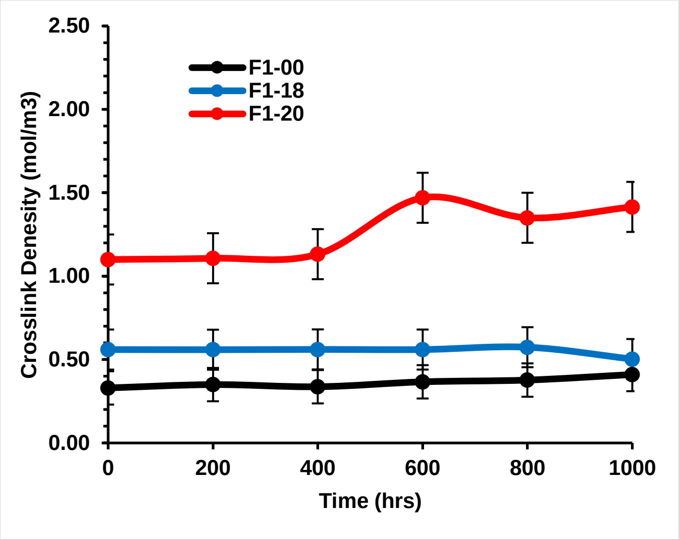


Figure 8.6 XLD (DMA) of modified and unmodified epoxy coatings vs B117 Salt Spray exposure time

Adhesion and Barrier Performance

Effects of salt spray aging were on the adhesive of the modified and unmodified epoxy on Al, Fe, CF, and FG were investigated. Pull-off adhesion test was performed at 200 h increments on all substrates of interest. Shown in Fig 8.7 and 8.8, the adhesive strength of all coatings investigated remain unchanged on CF for the duration of the 1000 h salt spray exposure. As previously stated, pull-off adhesion measurement results in delamination failure of the CF, suggesting that the cohesive strength between the carbon fiber and resin used within the matrix of the composite is weaker than that of adhesive strength of the epoxy coating. Thus, the pull-off adhesion measurement is not an effective method of monitoring the effectiveness of the modified substrate over the 1000 h salt spray exposure. Furthermore, delamination of CF has been observed at 30° C.[186]

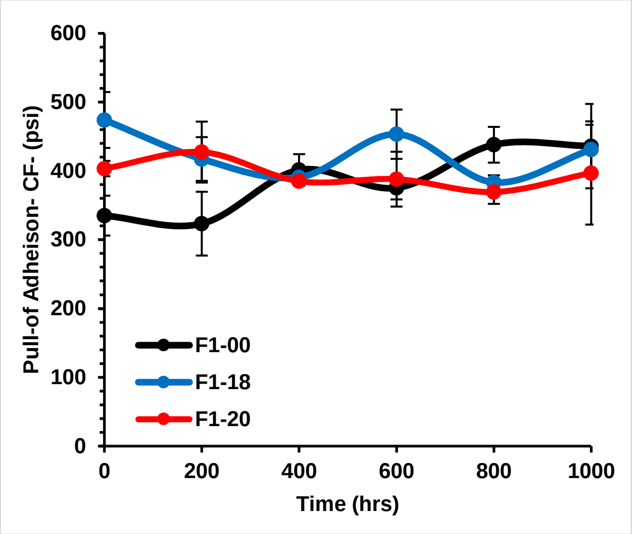
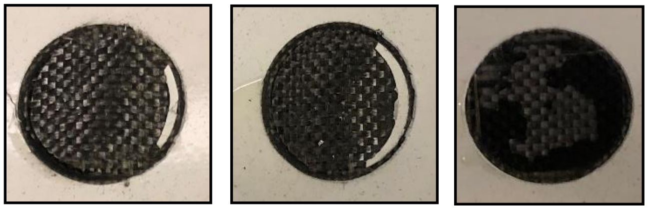


Figure 8.7. Adhesive strength of modified and unmodified epoxy coatings to CF substrate vs B117 Salt Spray exposure time



F1-00 F1-18 F1-20

Figure 8.8. Substrate failure of coated CF after 1000 h of B117 salt spray exposure

Fig 8.9 shows the adhesive strength of the epoxy coatings on FG with increasing aging time. A drastic decrease in adhesive strength is observed for all coating after the initial 200 h exposure followed by a plateau. At 1000 h, the modified and unmodified coatings have the same adhesive strength on FG. The loss in adhesive strength of the coatings is associated with degradation of the composite laminate.[187] The permeation of water molecules, Na+, and Cl- ions within coatings is expected to penetration into the composite, stimulating a fast epoxy-matrix softening damaging the matrix, fiber, and fiber-matrix interface.[188,189] Water uptake of composite laminates is known to quickly increase followed by a plateau.[190] The early stage of water absorption by the composite is predominant in the physical and chemical degradation of the composite.[191] Swelling, plasticizing of the resin matrix, and hydrolysis leads to degradation of the polymeric chains of the matrix. This damage coupled with osmosis, internal stress leads to damage of the matrix/fiber interfacing and debonding phenomena.[187,192]

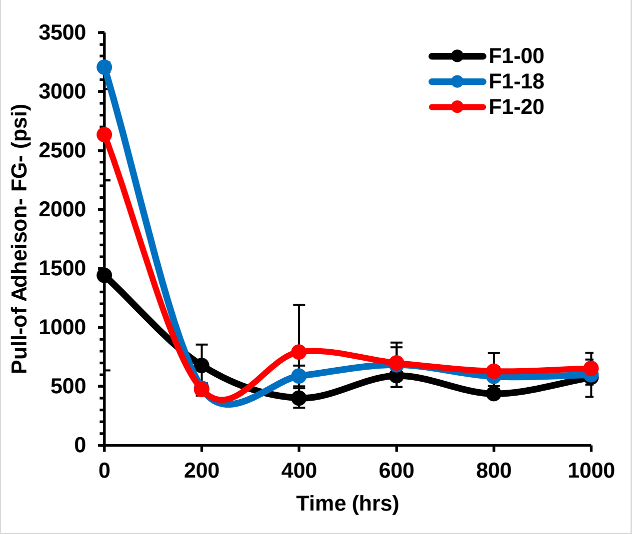


Figure 8.9. Adhesive strength of modified and unmodified epoxy coatings to CF substrate vs B117 Salt Spray exposure time

The correlation between adhesive strength and barrier performance to metal substrates is well established, thus it is imperative to discuss the two in conjunction with each other when evaluating the performance of the modified and unmodified epoxy. The visual appearance of modified and unmodified epoxy on Fe substrate after 1000 h of salt spray test is given in Fig 8.10. These findings clearly show the blistering and accumulation of corrosion products around the scribe of F1-00 and F1-18 after 200 h. Blistering for F1-00 becomes larger with increased exposure time, however corrosion products stay constant after 200 h. After the initial formation of the blisters at 200 h for F1-18, the blister remains constant. However, red rust increases with exposure time. In F1-20 blister does not form for the duration of the 1000 h exposure. These findings could be attributed to SCA and polysulfide. SC, APTS, is present at a 10, 1, and 0 wt% in F1-20, F1-18, and F1-00, respectively. SCA are well-known adhesion promoters, and their mechanism is as follows. The alkoxyl group is hydrolyzed in the presence of water to form a hydroxyl alcohol group. In the presence of a substrate with an oxide layer, condensation between the hydroxyl group of the coupling agent and substrate occurs resulting in the formation of the covalent bond. The organic functional group, in this case, the amine functional group reacts with the epoxy backbone to produce another covalent bond tethering the organic and inorganic material, thereby improving adhesion. The addition of polysulfide to epoxy is known to improve adhesive strength in metal substrates. The large production of red rust observed in F1-18 and F1-20 could be attributed to the interaction between the modifying agents and the zinc orthophosphate corrosion inhibitor. Zinc orthophosphate forms a microscopic film on metal surfaces that works as a barrier against corrosive media. In a neutral environment (pH 6.5 - 8.3) zinc orthophosphate precipitates into zinc and phosphate ions. It is proposed that the zinc ions form a film on the cathodic site, whereas the orthophosphates ions form films on the anodic site. As a result, unwanted corrosion products like iron, lead, and copper are avoided, and steel substrates are protected. The addition of ApTHF-170 to the modified primers could increase the pH of permitting water molecules. Amines are basic due to the presence of lone pair electrons on the nitrogen. This increase in pH, potentially aided by pTHF-1000, could negatively impact the precipitation of zinc and phosphate ions, thereby preventing the formation of the microscopic film resulting in the excess red rust corrosion observed in F1-18 and F-20, compared to F1-00.

The adhesion performance noted in Fig 8.10, does not translate to the pull-off adhesion results in Fig 8.11. While the modified primer demonstrated higher adhesive strength compared to the unmodified primer for Fe substrate, after approximately 1000 h of accelerated salt spray test, all formulations have a similar pull-off adhesion result. This may imply that pull-off adhesion is not the most effective method of assessing the durability of coatings after exposure to corrosive environments. Potential delamination and blistering may not be observed. The disparity between blistering and pull-off adhesion may be due to the plasticizing effects. As mentioned previously, the physical diffusion of water molecules in the adhesive disrupted van der Waal forces and hydrogen bonding of the polymer. As water and oxygen diffuse through the material, dissolved species are produced, generating osmotic pressure that deforms and debonds the coatings leading to blisters. As noted by Effendy et al., blisters are generated in areas with low critical adhesion stress and/or high local solute concentration. Blisters are propagated by growth and/or deformation. Growth occurs when adhesion stress surpasses the metal/coating pair's critical adhesion stress, while deformation occurs when osmotic pressure exceeds the elastic stress of the coating. Unchecked growth leads to delamination while unchecked deformation leads to ruptures. Based on the large irregular blister of F1-00 a combination of low critical adhesion stress and high local solute concentration is responsible for the blisters. The uniform circular blisters of the F1-20 are representative of blister growth due to osmotic pressure. Osmotic pressure can come from two sources, entrapped solutes, or corrosion products. Blistering due to osmotic pressure arising from entrapped solutes and osmotic pressure arising from corrosion products Osmotic pressure generated by corrosion products stretches the coating into a sphere segment. This phenome is also supported by increased corrosion product observed in F1-20 but not F1-18.[193] Furthermore, the lack of blister observed in F1-20 compared to F1-18 is attributed to the higher amount of polysulfides and APTS.

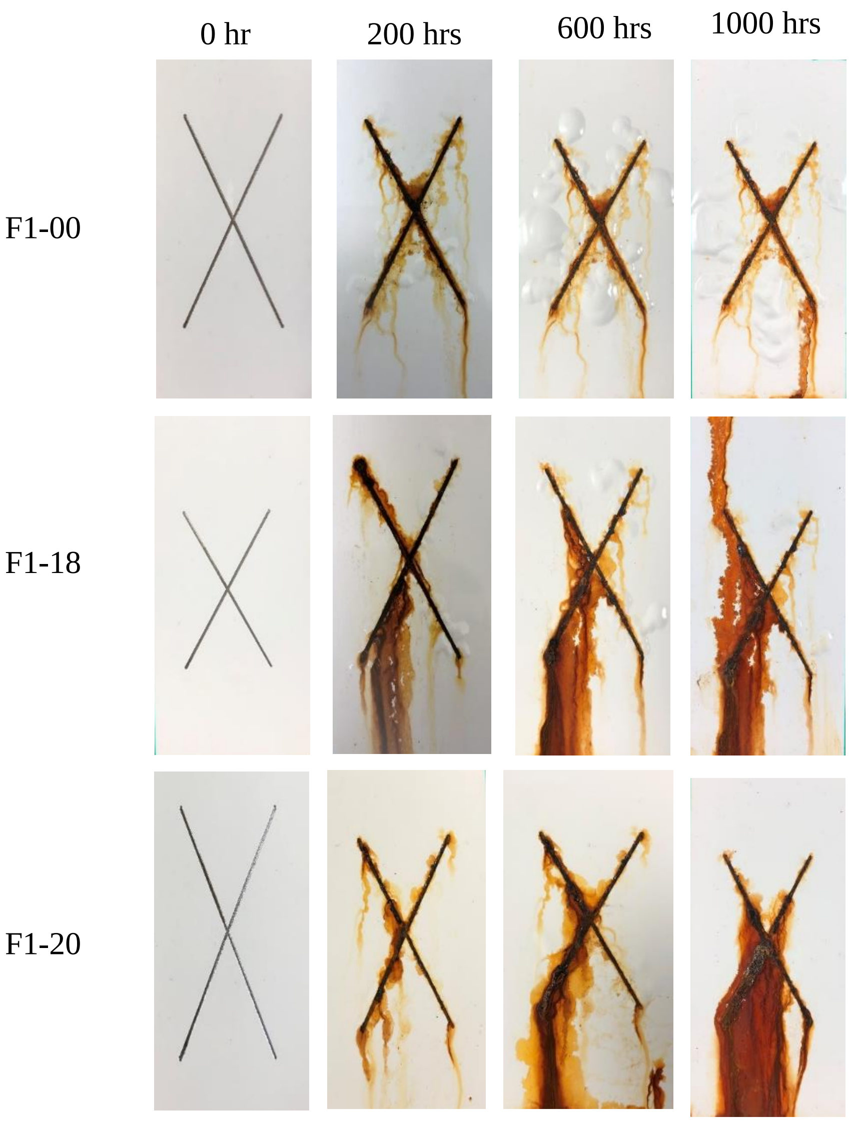


Figure 8.10. Picture of modified and unmodified epoxy primers on Fe substrate vs B117 salt spray exposure

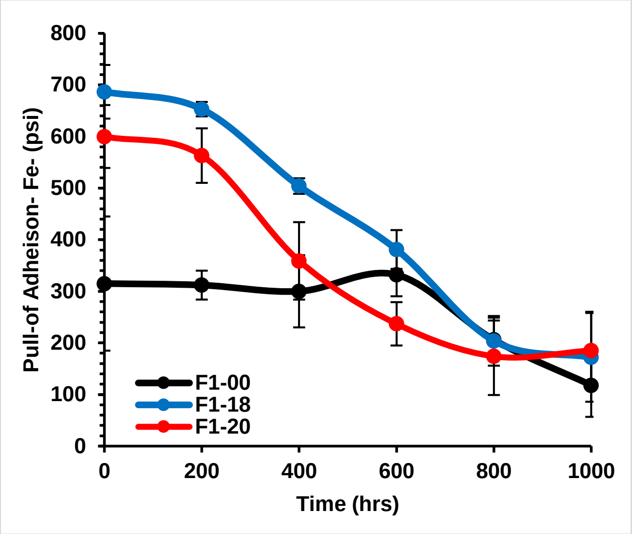


Figure 8.11. Adhesive strength of modified and unmodified epoxy coatings to Fe substrate vs B117 Salt Spray exposure time

EIS is a well-known technique to acquire parameters about the interface of coatings and metal substrates. It is commonly understood that the absolute impedance modulus of EIS at 0.1 Hz is an important parameter to evaluate the anticorrosion and barrier performance of the coating. When |Z|0.1Hz is greater than 10^6 Ω cm^2, the barrier performance of the coating is considered adequate. The Bode plot from the unscribed Fe in Fig 8.12 and the low-frequency data in 7.13 shows that for F1-00 and F1-18, the |Z|0.1Hz increases with by order of magnitude(s) from 6.05 X 10^8 to 5.44 X 10^{10}, and 8.35 X 10^9 to 3.24 X 10^{10}, respectively from 0 to 1000 h of exposure. F1-20 decreases from 1.95 x 10^{10} to 1.37 X 10^9. The observed rise barrier performance is evidence of the catalytic effect of water resulting in increased crosslinking of the epoxy and increase barrier performance.

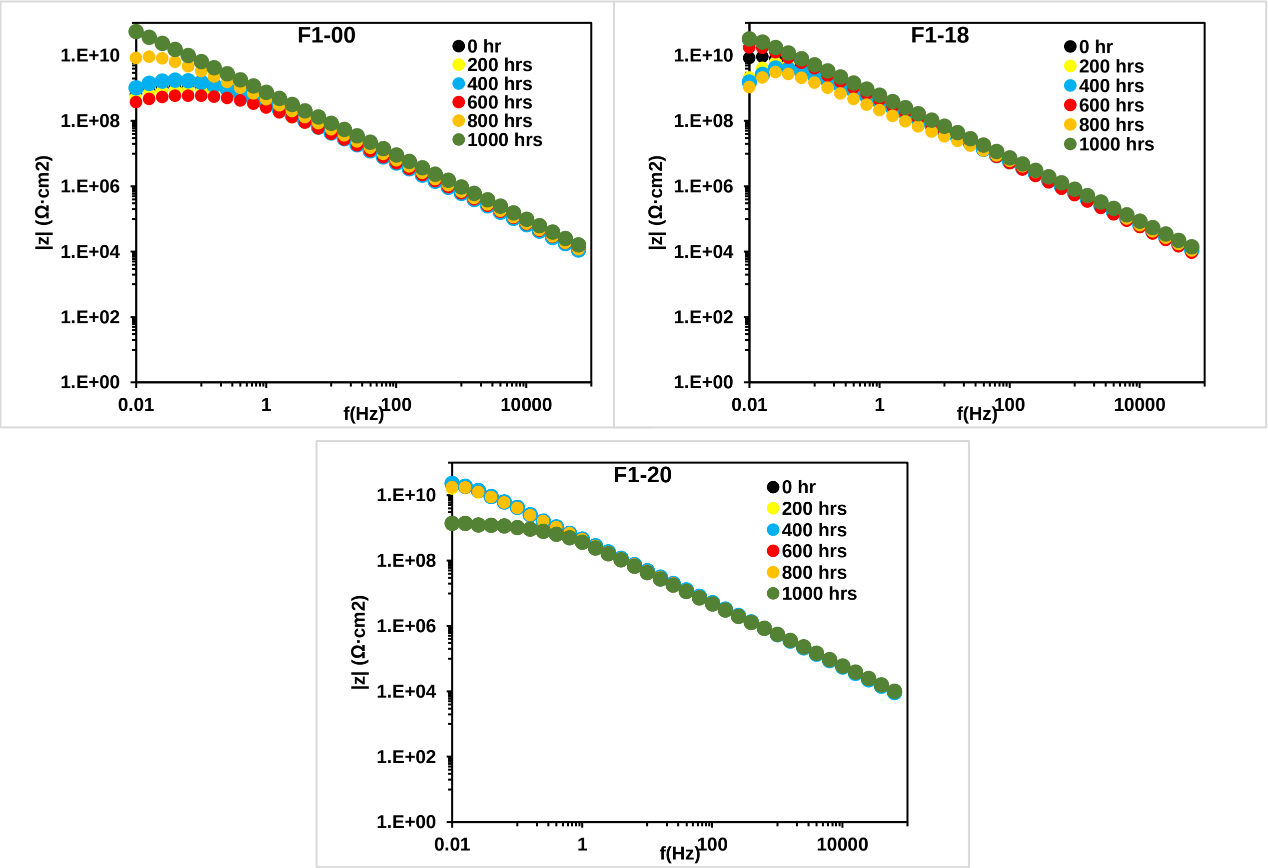


Figure 8.12. Bode plot of modified and unmodified epoxy primer on Fe substrate vs B117 exposure time

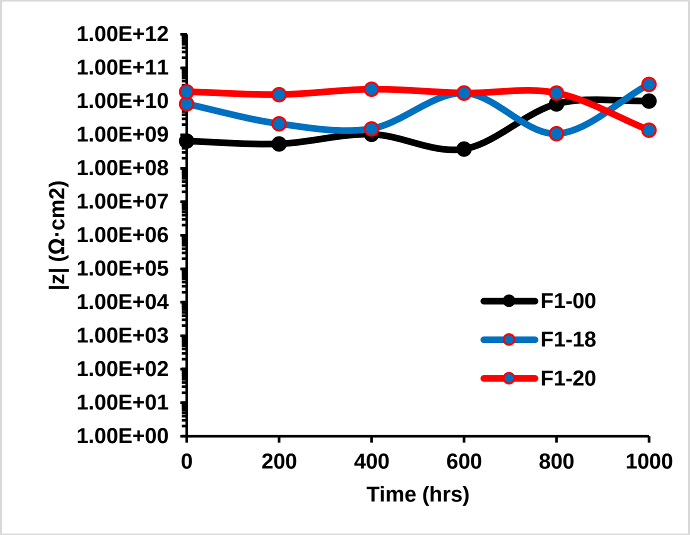


Figure 8.13. |Z|0.1Hz of modified and unmodified epoxy primer on Fe substrate vs B117 exposure time

Fig 8.14 shows the visual appearance of the modified and unmodified primers on Al substrates after salt spray exposure. No noticeable sign of blistering and corrosion byproduct was observed for primers up to 800 h. After which blister less than 3 mm in diameters were observed for F1-00 and F1-20. The blistering of F1-20 could signify that APTS and TEPS-80 are more effective adhesion promoters on Fe substrate as opposed to Al. Like Fe, the pull-off adhesion finding of the coatings on Al shown in Fig 8.15 does not reflect the visual assessment of performance. F1-00 adhesive strength to Al is stable from 0 to 400 but increased after 400 h of exposure. This increase continued for the duration of the test. This phenomenon may be associated with changes occurring at to the Al substrate due to permeation of water molecules, Na+, and Cl-. However, more work is needed to elucidate this phenomenon. The adhesive strength of F1-20 to Al is stable up until 400 h but decreases for the remainder of the exposure test. F1-18 adhesive strength remains unchanged over the 1000 h exposure period. This performance is contradictory to the performance Fe and could be explained by the higher amounts of polysulfide in F1-20 compared to F1-18. While polysulfides are known for their adhesion promoter performance, they are also hydrophilic. They contain functional groups that chemically attract and interact with water molecules via hydrogen bonding. Arundhati et al. demonstrated that as the percentage of polysulfide in an epoxy network increases the water absorption tendency was amplified.[194] Thus, with increased exposure time they could result in more water absorption leading to disruption of the polymer substrate bond.[194]

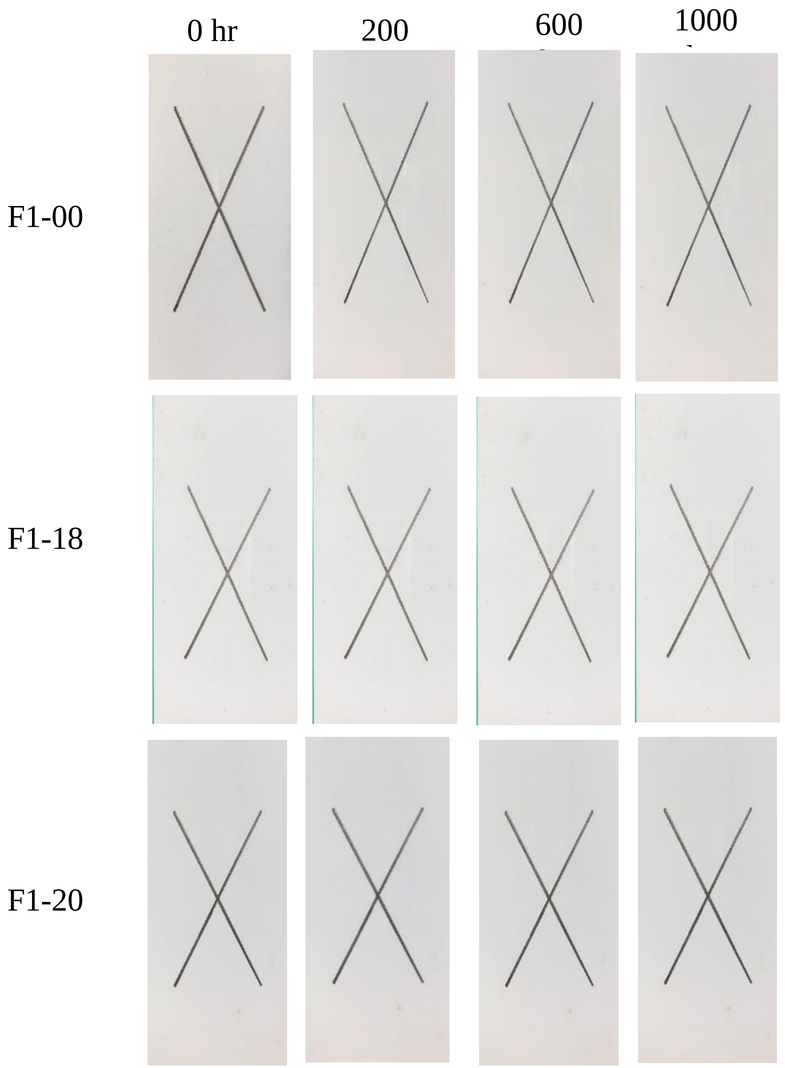


Figure 8.14. Picture of modified and unmodified epoxy primers on Al substrate vs B117 salt spray exposure

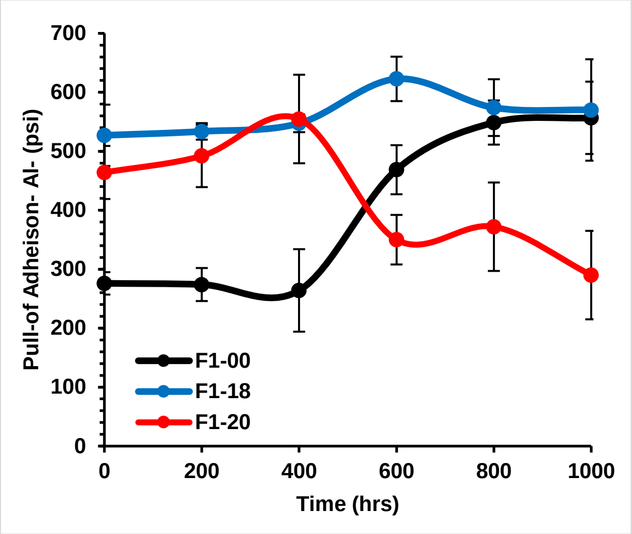


Figure 8.15. Adhesive strength of modified and unmodified epoxy coatings to Al substrate vs B117 Salt Spray exposure time

Conclusions

From the experimental results the following conclusions were obtained:

F1-20, the formulation with higher levels of polysulfide (TEPS-80) and (APTS), results in a slight decrease in flexibility due to increasing crosslinking density with exposure time. The hydrophilic nature of the polysulfide could result in higher water absorption of the polymer. The polar interactions between the water and the polymer backbone led to hydrogen bonding and the creation of secondary crosslink networks that would further restrict the molecular motion leading to a decrease in chain mobility. Since water can demonstrate both a catalytic and plasticizing effecting, the higher hydrophilicity of F1-20 also explains the decrease in barrier performances with increasing aging as well as the large quantity of red rust corrosion product observed on the scribed Fe substrate.

The lack of blistering observed in F1-20 on Fe substrate is attributed to the elevated level of adhesion promoters. APTS is known to form covalent bonds between the polymeric network and oxide layer of metallic substrates

The flexibility of F1-18 remained unchanged for the duration of salt spray exposure.

The lower level of adhesion promoters in F1-18 results in poor substrate adhesion to the Fe and blister formation during salt spray exposure. However, blistering does not affect the barrier performance of the coating. Barrier performance increases with exposure time, suggesting potential network crosslinking

After 200 h, a drastic drop in the adhesion strength of all coating to FG was attributed to matrix degradation and disbondment of the resin matrix of the composite.

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CHAPTER 9. CONCLUSIONS AND FUTURE WORK

Several approaches were explored to improve the flexibility and adhesion of bisphenol A diglycidyl ether (DGEBA) epoxy amine coatings for multi-substrate applications. Liquid rubbers, polyethers, polyethers/silane coupling agent, polysulfides, novolac resins, and 1,3-propanediol bis(4-aminobenzoate) (PBAB) were used as additives in the epoxy amine coatings and the effects on adhesion and flexibility were studied. Adhesion performance was evaluated by a pull-off adhesion test on steel, aluminum, carbon fiber reinforced plastics, and fiberglass. Flexibility was assessed by T_g, crosslinked density, pendulum hardness, elastic modulus, and indentation hardness. The additives were initially added at 1, 5, and 10 wt% of the epoxy resin.

Per T_g, hardness, and elastic modulus measurements, large molecular weight polyethers/SCA such as polytetrahydrofuran 1000 (pTHF-1000), Jeffamine® THF-170 polyetheramine (ApTHF-170), and 3-Aminopropyl-triethoxysilane (APTS) resulted in the maximum improvement in flexibility. The observed improvement was attributed to molecular mobility of the linear ether chain as well as the long bond length, large bond angle, and low barrier of rotation imparted by the Si-O-Si bond of the SCA. Per XLD calculations, PBAB and the higher molecular weight novolac resin, poly (phenyl glycidyl ether)-co-formaldehyde (PPGEF-570), resulted in the lowest XLD. These results were not reflected in other markers of flexibility such as T_g due to the branching effect and bulking aromatic groups. Improved adhesion to Al was imparted by APTS/ApTHF-170, APTS/pTHF-1000, and PPGEF-570. Adhesive strength to Fe was increased by the addition of APTS/ApTHF-170, APTS/pTHF-1000, and PBAB. SCA are known to enhance adhesion by facilitating the formation of a covalent bond between an organic polymer network the inorganic oxide layer of metal substrates. The presence of novolac resin increases the concentration of hydroxyl group within the polymer backbone resulting in increased polarity, wettability, and thus adhesion to metal substrates. PBAB performance could be attributed to greater interfacial bonding energy imparted by van der Waals force and Coulomb electrostatic force. The effect on adhesive strength due to polyether could be attributed to a slight improvement in the polarity of the coating due to the electronegativity difference between the oxygen and carbon atoms of the ether. All pull-off adhesion assessments on CF resulted in substrate failure or delamination of the composite, implying that the adhesive strength between the coatings and substrate is stronger than the cohesive strength of the matrix. Therefore, the effect of the additives could not be assessed on CF. All the additives investigated had a detrimental effect on the adhesive strength to FG compared to the control polymer, however high molecular weight polyether, and polysulfide had the least detrimental impact.

After the initial screening, six of the top-performing additives were down-selected and incorporated into a standard epoxy amine pigmented primer per a fractional factorial design of the experiment. ANOVA results demonstrated that in the presence of fully pigmented primer, high molecular weight polyether (ApTHF-170 and pTHF-1000) imparted the highest degree of flexibility by all matric of assessment. PBAB and APTS have a detrimental effect on flexibility. The detrimental effect of APTS could be attributed to the interaction of the hydrolyzable group and metal oxide pigments such as titanium dioxide, improving the cohesive strength of the coating while diminishing flexibility. PBAB's impact on flexibility is attributed to the bulking aromatic group.

Per ANOVA results, the effect of the six additives on the adhesive strength of Fe, Al, and CF was not statistically significant at the 95% or 90% confidence interval. However, a few notable formulations (F1-02, F1-18, F1-19, and F1-20) resulted in higher amounts improved adhesion on the metal substrates. Additives PBAB and ApTHF-170 had the most significant effect on the adhesive strength of the primer to FG. Of the statistically significant additives, PBAB resulted in the most detrimental effect on adhesion, while ApTHF-170 had the least detrimental effect. Overall, the addition of additives reduced the adhesive strength of the primer to FG.

Per EIS analysis on Fe, the top 6 performing modified primer and unmodified control all resulted in a $|Z|_{0.1Hz}$ greater than 106 Ω cm^2, thereby indicating suitable barrier performances per industry standard. However, the $|Z|_{0.1Hz}$ of F1-22 was an order of magnitude lower than the control. F1-18 and F1-20 resulted in the highest $|Z|_{0.1Hz}$. The barrier performance of the coatings was attributed to their adhesive strength to Fe; F1-22 had the lowest adhesive strength to Fe.

The flexibility, adhesion, and barrier performance of the modified (F1-18 and F1-20) and unmodified (F1-00) primers were evaluated over 1000 hours of B117 salt spray exposure. F1-20 had higher levels (10 wt%) of adhesion promoters, TEPS-80 and APTS, while F1-18 had lower levels of the adhesion promoters (1 wt%). Due to the rising crosslinking density with exposure time, F1-20 demonstrated a minor decrease in flexibility over time. The hydrophilic nature of the polysulfide may have resulted in higher amounts of water absorption. The polar interactions between water and the polymer backbone resulted in hydrogen bonding and the formation of secondary crosslink networks, limiting molecular motion, and lowering chain mobility. The higher hydrophilicity of F1-20 also explains the loss in barrier efficacy with increasing aging, as well as the large quantity of red rust corrosion product found on the scribed Fe substrate. Furthermore, the high amount of adhesion promoters are responsible for the lack of blistering reported in F1-20 on Fe substrate. The flexibility of F1-18 remained unchanged for the duration of salt spray exposure. The lower level of adhesion promoters in F1-18 results in poor substrate adhesion to the Fe and blister formation during salt spray exposure. However, blistering does not affect the barrier performance of the coating. Barrier performance increases with exposure time, suggesting potential network crosslinking. Minor change was observed for Al, however F1-20 and the F1-00 did start to demonstrate some filiform corrosion. This was attributed to coatings defects. After 200 hours, a drastic drop in the adhesion strength of all coating to FG was credited to matrix degradation and disbondment of the resin matrix of the composite.

In future work, it would be valuable to extend the B117 salt spray test to further monitor adhesion, flexibility, and barrier performance. Furthermore, the degradation of the primers could be monitored by more nuanced analytical techniques such as SEM, AFM, and FTIR to help elucidate the failure mechanism. Periodic water uptake measurement would also be beneficial in explaining changes in the material performances. While the design utilized in this work was advantageous for studying the effect of various additives, it would be beneficial to incorporate several layers of screening to reduce the number of additives studied in the full primer to better understand interactions. To obtain a better understanding of the adhesive effect of the substrate on the composites, it would be advantageous in future work to incorporate multiple methods of assessing adhesive strength. Another flexibility measurement such as tensile strength, and % elongation could also help characterize the performance of the additives.

Overall, the modification of bisphenol A diglycidyl ether epoxy-amine coating system for improved adhesion and flexibility for multiple substrate applications has been demonstrated. Throughout this work, multiple approaches were explored to tailor the flexibility and adhesion of epoxy coatings which results in improved performance. Incorporation of high molecular weight polyethers, SCA, polysulfide, and novolac resins in a pigmented primer showed promising results for long-term corrosion protection of multiple substrates.