

Factors Affecting Improvement in the Flexural Modulus of Polyacrylic Acid-Modified Crystalline Films

T. SUGAMA, L. E. KUKACKA, N. CARCIELLO, and J. B. WARREN,*
*Process Sciences Division, Department of Applied Science, Brookhaven
National Laboratory, Upton, New York 11973*

Synopsis

When high-molecular weight polyacrylic acid (PAA) macromolecules are incorporated into phosphating solutions, they significantly increase the stiffness and ductility of zinc phosphate conversion crystal films deposited on metal substrate surfaces. The degree of improvement in these mechanical properties depends primarily on the thickness and fineness of the highly dense PAA-complexed zinc phosphate crystals that are formed. The presence of this complexed PAA polymer at the outermost surface sites on the crystal layer plays an essential role in promoting adhesion with polymeric topcoats by the formation of polymer-polymer chemical bonds. The use of low-molecular weight PAA results in a poor interfacial adhesion because of a high degree of alternation in chain conformation caused by charge-transfer reactions between the proton-donating COOH groups and the nucleophilic Zn^{2+} ions in the acidic aqueous medium. In addition, the protective polymer topcoat overlaid on the complex precoat surfaces increases the flexibility of the crystalline precoat itself. The most important factors controlling the flexibility of the precoat were low elastic modulus, high tensile strength, and elongation of the topcoat systems. These characteristics are more important than the magnitude of interfacial adhesive bonds at topcoat/precoat joints.

INTRODUCTION

As noted in an earlier paper,¹ the introduction of water-soluble polyacrylic acid (PAA) macromolecules (MW, 104,000) into zinc phosphating liquids, significantly improves the controlability of the crystal dimensions, the degree of crystallinity, and the coating weight of conventional zinc phosphate conversion films deposited on cold and mild carbon steel surfaces. From the results of the surface micromorphological and spectroscopical analyses, it was speculated that the converted PAA-zinc phosphate crystal composite layer is composed of a bulk PAA polymer and complexed PAA continuously overlaying a uniform array of fine dense zinc phosphate crystals. This specified structure profile of the conversion crystal layers contributes significantly to improved stiffness and ductility properties, when compared with those of conventional conversion layers. Quantitatively, the inclusion of 2% PAA increased the flexural modulus and maximum strain by factors of 2 and 1.4, respectively, as compared to the non-PAA-containing

*Instrumentation Division

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controls. The plasticized complex layer seems to play an essential role in increasing the stiffness and ductility of the conventional crystal layers. However, the reasons for the property enhancement have not been clearly elucidated to date. The ductility and toughness properties of the crystalline conversion film itself are of considerable importance when the physical deformation characteristics of the metal substrates are considered. For instance, increased thickness of the deposition film layers makes the film increasingly brittle, thereby enhancing the potential for failure during flexure or other deformation. Generally, deformation failures of the layers having a low stiffness characteristic relate directly to the development of micropores and fissures which reduce the effectiveness of corrosion-resistant coatings. Accordingly, an aim of the present study was to obtain knowledge regarding the physicochemical factors which are responsible for increasing the stiffness and ductility properties of the crystalline conversion coatings.

The complex conversion films are generally applied as a protective pre-coating system to improve the corrosion resistance of the metal substrate surfaces, and also to increase the physical and chemical adherent forces with subsequently applied polymeric topcoatings. It was found experimentally that the surface of compatible precoat films has a significant ability to promote adhesive bonds at polymeric topcoat-complex precoat joints. This improved interfacial adhesion will lead to an enhancement of the durability of the joints and arrestment of crack initiation of precoat layers at certain loadings. Thus, a better understanding of the mechanical behavior in the topcoat-precoat interfacial regions is very important. To find the mechanical and adhesive elements of polymeric topcoats governing the crack-arresting properties of precoat layers, elastomeric polyurethane, and glassy furan topcoating systems were used in this study.

EXPERIMENTAL

Materials

The metal used in the experiments was nondesulfurized mild carbon steel consisting of 0.18 to 0.23% C, 0.3 to 0.6% Mn, 0.1 to 0.2% Si, and $\leq 0.04\%$ P. Fine crystalline polyacrylic acid (PAA) complexed zinc phosphate hydrate films were deposited onto the metal substrate surfaces. The zinc-phosphating liquid consisted of 9 parts zinc orthophosphate dihydrate and 91 parts 15% H_3PO_4 and was modified by incorporating a PAA polymer at concentrations ranging from 0 to 4.0% by weight of the total phosphating solution. Commercial PAA, 25% solution in water, having an average molecular weight in the range of 5×10^2 to 5×10^5 , was supplied by Scientific Polymer Products, Inc. The PAA-zinc phosphate composite conversion film was deposited on the metal substrates by immersing the metal for 10 h in the modified zinc-phosphating solution at 60°C. After depositing the composite conversion films, the substrates were left in a vacuum oven at 150°C for ~ 5 h to remove any moisture from the film surfaces and to solidify the PAA macromolecules.

Commercial-grade polyurethane (PU) M313 resin, supplied by the Lord Corporation, was applied as an elastomeric topcoating. The polymerization of PU was initiated by incorporating a 50% aromatic amine curing agent

M201. Furan (FR) 1001 resin employed as a glassy topcoating system was supplied by the Quaker Oats Company. The condensation-type polymerization of the FR resin was initiated by the use of 4 wt% QuaCorr 2001 catalyst, which is an aromatic acid derivative. These initiated topcoatings were cured in the oven at a temperature of 80°C.

Measurements

In an attempt to evaluate the mechanical properties of the layers, the stress-strain relation and modulus of elasticity in flexure were determined using computerized Instron Flexure Testing Systems, operating at deflection rates of 0.5 to 0.05 mm/min. The determination of the stress-strain curve was made on the tensile zones of metal plate specimens, 6.2 cm long by 1.3 cm wide by 0.1 cm thick, subjected to three-point bending at a span of 5.0 cm.

The approximate thickness of the complexed precoat layers deposited on the metal substrate surfaces was measured by AMR 100-Å scanning electron microscopy (SEM) observation of the edge view of sliced sections. SEM was also used to observe the crack-initiation and -arrestment regions of fractured surfaces of polymer-topcoated precoat layers.

Modulus of elasticity, tensile strength, and elongation tests for the cured topcoat polymers were performed on dumbbell-like samples 7.0 cm long and 0.5 cm wide at the narrowest section. Stress-strain diagrams were obtained with a tensile tester having a crosshead speed of 0.5 mm/min. All strength values reported are for an average of three specimens.

Peel strength tests² of adhesive bonds at the polyurethane topcoat-modified metal substrate interfaces were conducted at a separation angle of ~180° and a crosshead speed of 5 cm/min. The test specimens consisted of one piece of flexible polyurethane topcoat, 2.5 by 30.5 cm, bonded for 15.2 cm at one end to one piece of flexible or rigid substrate material, 2.5 by 20.3 cm, with the unbonded portions of each member being face to face. The thickness of the polyurethane topcoat overlaid on the complex crystal surfaces was ~0.95 mm.

The lap-shear tensile strength of metal-to-metal rigid furan adhesives was determined in accordance with the modified ATM method D-1002. Prior to overlapping between metal strips 5.0 cm long, 1.5 cm wide, and 0.2 cm thick, the 1.0- × 1.5-cm lap area was coated with the initiated furan adhesive. The thickness of the overlapped film ranged from 1 to 3 mil. The Instron machine was operated at a crosshead speed of 0.5 mm/min. The bond strength values for the lap shear specimens are the maximum load at failure divided by the total bonding area of 1.5 cm².

RESULTS AND DISCUSSION

Elastic Behavior of PAA-Complexed Precoat Layers

Figure 1 is a typical stress-strain diagram for control and 2% PAA-complexed zinc phosphate layers deposited on metal surfaces. The stress was computed assuming elastic behavior of the flexural member, and the strains were computed from the deflection measurements.

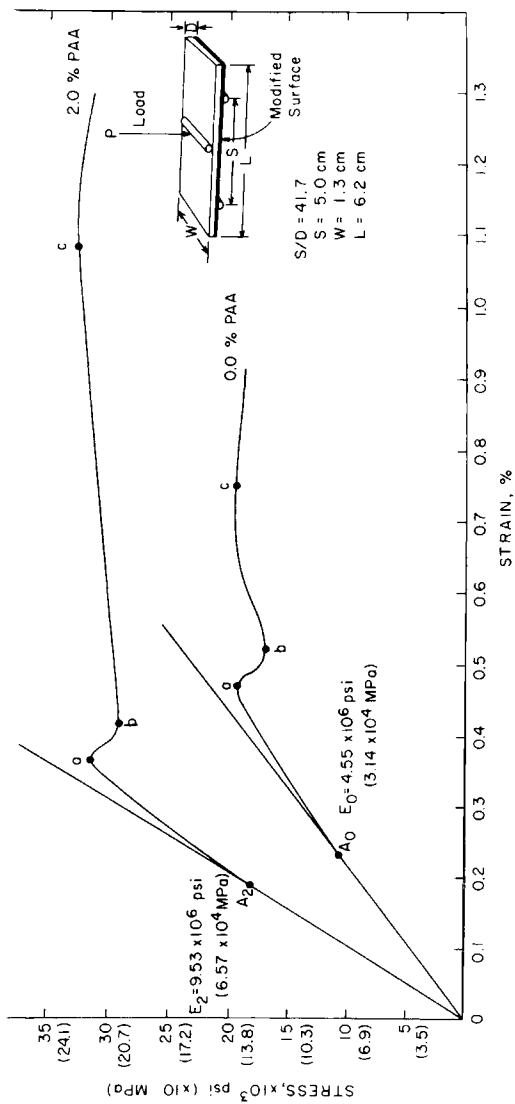


Fig. 1. Flexural stress-strain relations for unmodified and 2% PAA-modified zinc phosphate crystal conversion coatings.

In the figure, the elastic region is the straight-line portion of the stress-strain curve from zero strain to the strain at point A.³ The elastic behavior implies the absence of any permanent deformation, so that point A is termed the proportional limit of the material. The slope of the line from the origin to A is the elastic modulus E. Physically, E represents the stiffness of the material to an imposed load. The resultant flexural modulus for PAA-complexed layers was computed to be 9.53×10^6 psi (6.57×10^4 MPa), corresponding to a value more than twice that of the control specimens. This suggests that the stiffness of conventional crystal layers can be improved significantly by the incorporation of PAA.

The stress associated with the yield point of a layer is represented by the position of the line ab in Figure 1. The flexural stress at the yield point for the control was increased by a factor of 1.7 by adding a 2% concentration of PAA. In addition, the stress of the complexed layer during yielding increased somewhat with an extended strain, and an ultimate stress of 33.6×10^3 psi (232 MPa) was obtained at 1.08% strain. Further increases in strain resulted in stress reduction. In contrast, the control exhibited no increase in stress after the onset of yielding deformation was noted. The deformation takes place at an essentially constant stress of 19.2×10^3 psi (132 MPa) until the stress reduction occurs around 0.75% strain.

The magnitude of the relative toughness of the materials can be obtained from the stress-strain curves by drawing perpendicular lines from the ends of the curves to the strain coordinates and then measuring the total area under the curves. The area for the complex specimens was considerably greater than that for the control specimens. This apparently verifies that the deformation nature of the conventional crystal deposition can be made more ductile by the formation of a complex structure with PAA macromolecules.

Figure 2 shows the flexural modulus plotted against PAA concentration. The curve indicates that in the PAA concentration range from 0.4 to 3.0%, the modulus increases progressively. The maximum flexural modulus of 99.0×10^5 psi (68.2×10^3) was obtained at a 3.0% concentration, which is an improvement of more than a factor of 2 over specimens without PAA. Further PAA additions result in modulus reductions. Similar trends were observed from the results of stress at the yield points of these specimens. A yield stress of 18.1×10^3 psi (125 MPa) for the control specimens was increased by a factor of 1.7 by the modification with 3.0% PAA.

On the other hand, changes in thickness and fineness parameters of the deposited complex crystals appear to have a direct effect on the stiffness and toughness of the crystalline layers. Therefore, changes in these parameters resulting from variations in the PAA concentration over the range of 0 to 4.0% were assessed from SEM images. Factors which appeared to affect the mechanical properties of the crystals were then correlated with flexural modulus values for the coatings.

The average thickness of the crystal as a function of PAA concentration is given in Figure 3. It is apparent that the thickness decreases dramatically with an increase in the PAA content in the conventional phosphating liquid. Over a PAA concentration range from 0 to 4.0%, the thickness varied

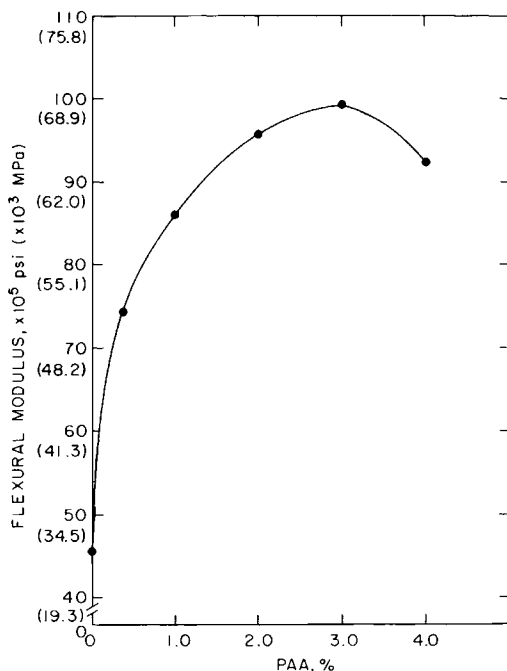


Fig. 2. Changes in flexural modulus of conversion layer as a function of PAA concentration.

between ~ 120 and $35 \mu\text{m}$. The presence of 4.0% PAA in the solution reduced the thickness to less than 30% of that produced with the conventional liquid. It was not possible to deposit a coating on the metal substrate when 7% PAA was added. Results discussed earlier (see Fig. 2) indicated that the conversion layer with the maximum flexural modulus occurred when the PAA concentration was 3%. From these data and those in Figure 3, it can be concluded that a crystal thickness of $\sim 50 \mu\text{m}$ will yield the maximum modulus.

Since the PAA overlays can be removed with an organic solvent rinse, considerable attention was given to the contrast between the relative crystal fineness of the conversion coatings under the PAA. Metal surfaces used in this test series were treated with 0, 0.5, 2.0, and 4.0% PAA-modified phosphating liquids, and then washed with acetone to remove any PAA polymer. The plates were then rinsed with water and dried in a vacuum oven at 150°C . Resultant SEM photomicrographs are presented in Figure 4. Visual comparison of these micrographs confirms that the dimensions of the deposited crystals decrease as the quantity of PAA in the conventional phosphating liquid is increased. The micrograph for the surface treated conventionally [see Figure 4(A)] indicates a dense agglomeration of rectangle-like crystals $\sim 420 \mu\text{m}$ in length. This crystal length was reduced by half by the addition of 2.0% PAA [Figure 4(C)]. With 4.0% PAA, the conversion formation consisted of short rectangularly shaped coarse crystals ranging in size from ~ 180 to $\sim 20 \mu\text{m}$.

From the viewpoint of surface topographical features, the SEM images

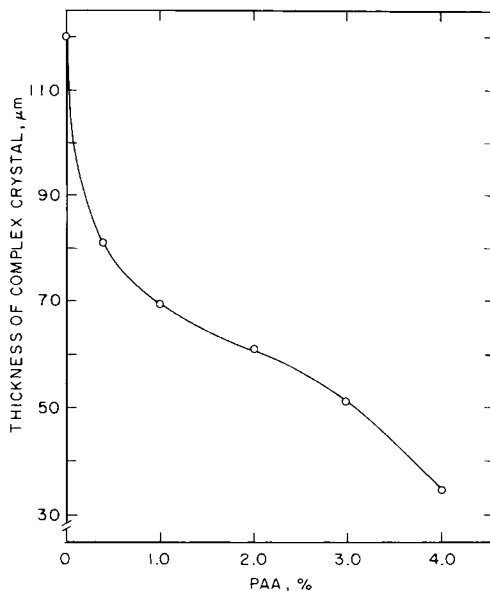


Fig. 3. Thickness of complex crystal vs. PAA concentration.

indicated that the uniformly distributed conventional zinc phosphate crystal is converted into randomly distributed fine crystals as the PAA concentration is increased. Thus, the dense arrangement of very fine crystals formed irregularly on the substrate surfaces resulted in a modulus somewhat lower than that for layers having a desirable crystal size. The most effective crystal length to achieve the high modulus was consequently noted to be in the range of ~ 200 to $60 \mu\text{m}$. The optimum crystal formation, therefore, appears to be a highly dense agglomeration of complex crystals $\sim 50 \mu\text{m}$ thick and ~ 60 to $200 \mu\text{m}$ in length.

The increase in the stiffness of the layers is not only due to the thickness, fineness, and density of the plasticized conversion formations, but also is associated with the average molecular weight of the PAA. The effect of the PAA molecular weight (MW) on the flexural modulus of the precoat layers was investigated over a MW range of 5×10^2 to 2.5×10^5 . In these studies, the complex precoat layers were derived from a mix solution prepared by incorporating a 3% concentration of the various PAA polymers into the conventional zinc phosphating solution. Figure 5 shows the correlation between the flexural modulus and the molecular weight of the PAA. The curve indicates that the modulus related directly to the molecular weight. The use of PAA with a molecular weight of 2.4×10^5 resulted in the formation of crystal layers having a modulus 1.6 times greater than that of the layers produced with PAA of MW 5×10^2 . The layers derived from acrylic acid monomer exhibited a modulus of 58.3×10^5 psi (40.2×10^3 MPa), $\sim 7\%$ lower than that from MW 5×10^2 . These results suggest that the MW of the PAA polymer plays an important role in increasing the stiffness of the complex conversion layers. This increase in stiffness also increases the ductility.

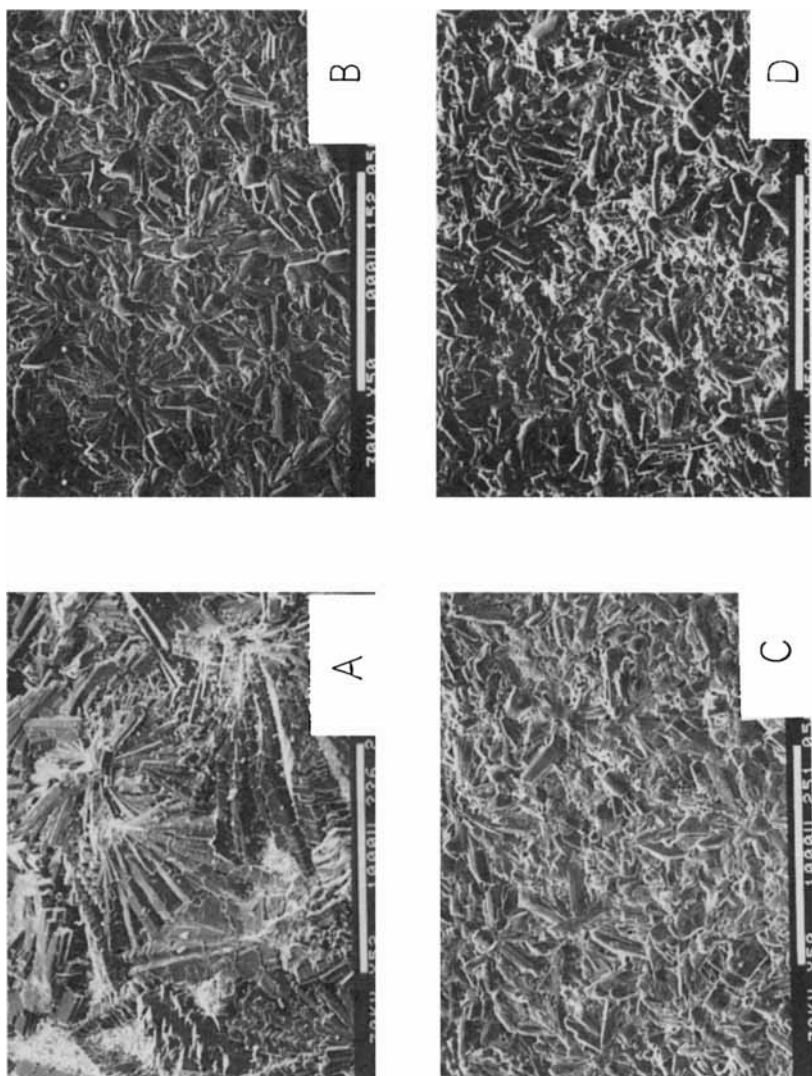


Fig. 4. Alteration in the conventional crystal size by PAA polyelectrolyte macromolecules: (A) 0% PAA, (B) 0.5% PAA, (C) 2.0% PAA, and (D) 4.0% PAA.

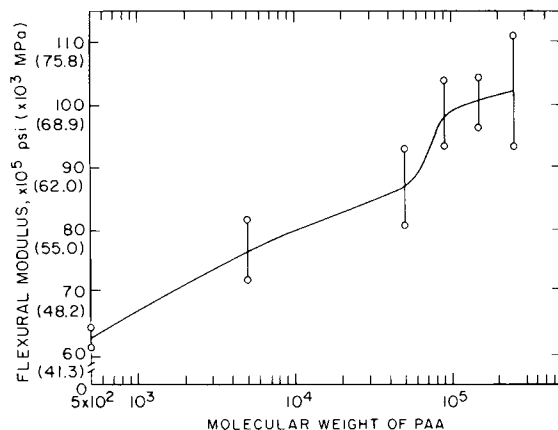


Fig. 5. Effect of molecular weight of PAA on the flexural modulus of conversion crystal layers.

Adhesion at Topcoat/Precoat Interface

As reported earlier,¹ necessary properties for the complex conversion films are chemically and physically attractive surfaces which promote adhesion to organic polymer topcoatings, and the ability to form corrosion-resistant protective coatings on metal substrate surfaces. With regard to the former, the presence of the functional PAA polymer on the complex pre-coating surface results in a film which acts in a manner similar to a primer for conventional polymer topcoats. This primer formation displays an ability to promote bonding forces at the interfaces between the complex pre-coating and the polymer topcoating materials. The interfacial adhesive mechanism was inferred to be due primarily to polymer-polymer chemical affinity. Hence, it can be expected that the elastic behavior of the pre-coating sites in the chemically bonded interfacial region depends primarily on the mechanical and adhesive characteristics of the organic materials employed as the topcoating system. These properties include the modulus of elasticity, tensile strength, and elongation for the polymer topcoat materials and the bond strength at the topcoat-precoat interface.

A study was conducted to understand the interplay between the topcoat and precoat in improving the stiffness and ductility of the crystal conversion layers. The two different topcoating systems described in the Materials section, polyurethane (PU) classified as an elastomeric polymer and furan (FR), a glossy polymer, were used in the study. Some mechanical properties of these polymers are given in Table I. As is indicated in the table, the modulus of elasticity for the FR polymer was 2.28×10^5 psi (1.57×10^3 MPa), greater by an order of magnitude than that of the PU polymer. The tensile strength and elongation values for the elastomeric PU are considerably higher than those of the glassy FR polymer. The extremely high elongation of 1040% for the PU is three orders of magnitude greater than that for the FR polymer (1%).

The adhesive characteristics for the elastomeric PU topcoat to the precoat surfaces were evaluated on the basis of 180° peel strength tests. The test specimens used to determine the bonding force at the PU-precoat interface

TABLE I
Mechanical Properties of Glassy Furan and Elastomeric Polyurethane Polymers Used as Topcoating Systems

Topcoating	Modulus of elasticity, psi (MPa)	Tensile strength, psi (MPa)	Elongation, %
Furan	2.28×10^5 (1.57×10^3)	1820 (12.5)	1
Polyurethane	1.47×10^4 (1.01×10^2)	3390 (23.4)	1040

were prepared by overlaying an initiated PU polymer onto the metal substrate surfaces that had been modified with the zinc-phosphating solutions containing up to 4% PAA polymer (MW 104,000). Overlaid specimens were then left in a vacuum oven at 80°C for ~10 h to cure the PU polymer. The 180° peel strength tests were performed at room temperature and the results presented in Table II, indicate that over the PAA concentration range of 0 to 3%, the peel strength increases progressively with increasing PAA content. In the absence of PAA, the bond strength was 3.88 lb/in. (0.70 kg/cm). The addition of 3% PAA increased the value by a factor of 2.6. Further increases in concentration up to 4.0% resulted in a strength reduction.

The failure surfaces generated by peeling were microscopically inspected to obtain information regarding the failure mode and failure locus. These observations indicated that although the PU topcoat for the control specimens without PAA delaminated from the rough crystal surfaces, the failure was clearly cohesive since a considerable amount of the PU polymer remained on the precoat surfaces. This was probably due to the strong mechanical interlocking produced by anchoring of the topcoat as a result of PU resin penetration into the open spaces in the interlocked crystal layers.⁴ After testing, all of the PU-overlaid complex precoat specimens, except for the one containing 4.0% PAA, exhibited very rough surfaces on both the peeled PU and precoat sides. This led to extensive plastic deformation and fibrillation which represent cohesive failure in the ductile topcoat. This cohesive failure can be interpreted as a well-made joint. It is apparent that the highly stable nature of the interphase region is due to direct chemical bonding between the PU and PAA.

Inspection of the peeled surfaces of the specimens containing 4.0% PAA indicated that they were much smoother than the surfaces of the other specimens and the extent of plastic deformation was much less. This implies

TABLE II
180° Peel Strength of Polyurethane Complex Crystal Coating Interfaces and Lap Shear Bond Strength of Complex Substrate-to-Furan Adhesives

PAA, %	Peel strength, lb/in. (kg/cm)	Lap shear bond strength, psi (MPa)
0	3.88 (0.70)	640 (4.41)
1.0	5.63 (1.01)	920 (6.34)
2.0	9.41 (1.68)	1160 (7.99)
3.0	10.25 (1.84)	1130 (7.79)
4.0	8.41 (1.51)	950 (6.55)

that the failure may have been through a mixed mode of cohesive and adhesive failure.

In addition to being affected by the reactive surface nature of the PAA-complexed precoat layer, the peel strength at the interface was also found to be dependent upon the average molecular weight (MW) of the PAA polymer used to restrain crystal growth. Figure 6 illustrates the variation in peel strength of PU/precoat interfaces resulting from changes in MW up to 5×10^5 . A PAA macromolecule concentration of 3% was used to prepare the conversion precoating systems in this test series. The data indicate that the interfacial bonding forces increase notably with increasing MW over the range of 1×10^3 to 1.5×10^5 . The maximum strength of 10.45 lb/in. (1.87 kg/cm) was attained with a MW of 1.5×10^5 . Further increases in MW up to 5×10^5 seemed to have little effect on the bond strength. Although the results are not shown in the figure, the precoat surfaces derived from PAA monomer yielded a peel strength of only 3.71 lb/in. (0.66 kg/cm). A speculative explanation for the effects of MW on peel strength is as follows: when the polyacid macromolecule is introduced into the zinc-phosphating liquid system, an appreciable number of divalent Zn ions dissociated from $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are preferentially taken up by the functional carboxylic acid (COOH) pendent groups in the PAA molecular structure which appear to act as a miniature ion-exchange system. A salt complex formation consisting of $\text{COO}^- \text{Zn}^{2+}$ coordinated groups could be yielded as a result of the charge-transfer characteristics of the COOH groups and the active nucleophilic Zn^{2+} ions.⁵ Thus, the formation of the complex structure, which involves intramolecular pairs of COO^- groups associated

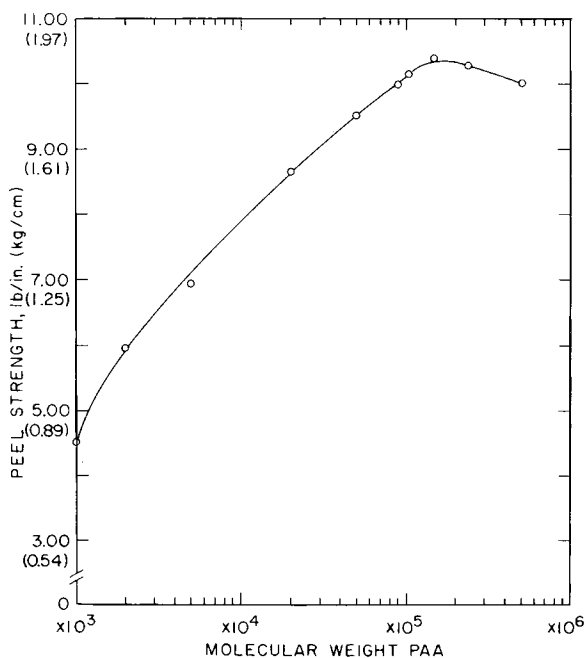


Fig. 6. 180° Peel strength of PU-complex precoat joints as a function of PAA molecular weight.

with Zn ions, would result in the intermolecular entanglement and coiling of the PAA macromolecules.⁶ The extent of the entanglement is commonly associated with an increase in the degree of neutralization. The loss of functional groups at available absorption sites for the highly neutralized PAA polymers leads to a decrease in the magnitude of the dispersion and wettability forces on the complex film surfaces by PU resin, thereby decreasing the interfacial adhesive bonds. A high MW PAA, which is comprised of long chain units, will act to suppress the extent of the coil-up and entanglement of molecules. A lesser alteration of the chain conformation will result in a regularly oriented configuration of PAA polymer containing a plentiful number of functional groups, therefore, resulting in an increase in mobility of PU resin at the interfacial regions.

The theoretical explanation given above was tested experimentally by measurements of the interfacial contact angles at the PU resin-complex precoat boundary. The Zn-complexed PAA salt formations which are yielded at the outermost surface sites of the crystal precoat layers were made by overlaying 3% PAA-modified zinc-phosphating solutions. The MW of the PAA was varied from 5×10^3 to 2.5×10^5 . The overlaid samples were then heated in a vacuum oven at 110°C to solidify the complex salt films. The contact angles were determined within 30 s after deposition of uninitiated liquid PU resin on the complex film surfaces, and the results are given in Table III. The data indicated that small decreases in the contact angle occurred as the MW was increased. Since a lower angle corresponds to an increase in the magnitude of the wetting forces, the wettability of the complex film surfaces by PU resin appears to be enhanced by incorporating a higher MW PAA. The facile resin mobility at the interfacial areas is developed from the nature of primary covalent bond mechanisms. When a topcoating resin is brought into contact with the oriented high-MW PAA overlayer, the resin is mobile enough to migrate to the functional group sites on the layer where conditions for the formation of covalent bonds by chemisorption are particularly favorable. This formation of polymer-polymer covalent bonds, which is primarily responsible for the molecular orientation, contributes significantly to the development of the interfacial adhesion forces. The use of a low-MW PAA produces a greater amount of coiled-up molecules, which are most likely to result in the formation of a weak boundary layer which gives poor adhesion at the interfaces. Therefore, controlling the extent of entanglement is one of the important factors in promoting mobility of the resins.

TABLE III
Contact Angle of Various PAA-Modified Complex Film Surfaces by PU Resin

PAA molecular weight	Contact angles, degree
5,000	59.7
50,000	55.8
100,000	53.1
150,000	51.5
250,000	50.7

The adhesion aspects of glassy rigid-type FA polymer topcoats to complex precoat systems were studied by performance of lap shear tensile strength tests. As seen in Table II, the effect of the PAA concentration on the bond strength of the FR polymer is similar to that on the PU. Namely, the bond strength increases upon the addition of PAA up to a 3% concentration. The strength of 1130 psi (7.79 MPa) at 3% concentration was $\sim 80\%$ higher than that of the control specimens. At a 4% concentration, the strength declines to 950 psi (6.55 MPa).

Elastic Behavior of Polymer-Overlaid Precoat Layer

Tests were performed to obtain stress-strain diagrams for the topcoat-precoat composite layers. In this work, ~ 1.5 -mm thick PU and FR polymer topcoat systems were placed on complex precoat surfaces which were modified with 3% PAA having a MW of 1×10^6 . Differences between the flexural modulus computed from the stress-strain relation were then used in an attempt to relate the stiffness of the precoat layer with the mechanical behavior of the topcoats. Typical stress-strain diagrams and the computed flexural modulus for these specimens are shown in Figure 7.

These interesting results indicated that the flexural modulus of the PU-topcoated composite layer specimens is 10.31×10^6 psi (7.10×10^4 MPa), corresponding to an improvement of $\sim 20\%$ over that of the specimens without the topcoating. In contrast, the modulus for FR-coated composite specimens was $\sim 12\%$ less than that of the control. Further, the yield stress of the precoat specimens was improved $\sim 10\%$ by overlaying with PU polymer, whereas a stress reduction of $\sim 16\%$ was noted for FR-overlapped layers. The features and mode of the fracture-initiating cracks at the yield

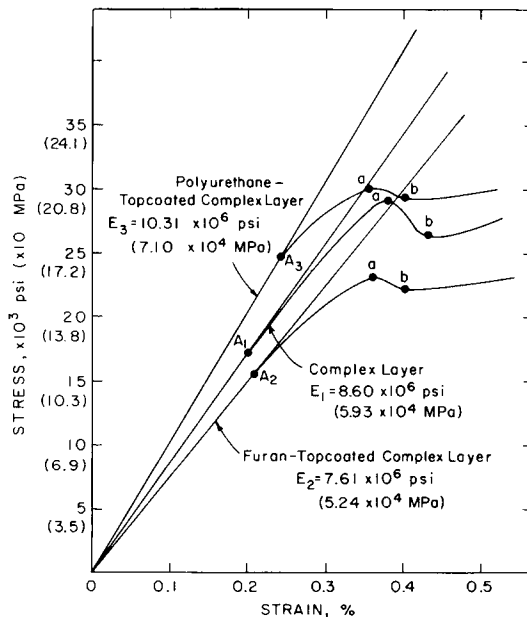


Fig. 7. Stress-strain diagrams for uncoated and PU- and FR-topcoated complex layers.

stress for the untopcoated and FR- and PU-topcoated composite surfaces were investigated using SEM. These fractographs are given in Figures 8 to 10. For the untopcoated precoat surfaces, it is of considerable interest to determine the mode of fracture and whether cracking occurs through or around the coarse crystal. Arrows on the figures, as seen in Figure 8, signify the direction of crack growth in a bent specimen surface. As expected, it was confirmed from the diverging crack pattern that the microcrack propagation is diverted around a bulky coarse crystal rather than passing through it. The width of the microcrack, which is very difficult to identify, was $\sim 4 \mu\text{m}$. The small size of the flaw produced at the yield stress suggests that the complex precoat layers possess a high degree of flexibility and stiffness.

When compared to the untopcoated specimens, the fracture origin under tension of the FR-topcoated specimens was completely different. This is microscopically discernible in the fractograph shown in Figure 8 and Figure 9(a), respectively. A linear cracking pattern, resulting in failure of the glassy FR polymer is apparent in the topcoated specimen. Figure 9(b) shows the crack initiation area of the FR polymer overlayer at a higher magnification. As is evident from the micrograph, the failed section exhibits a relatively smooth face. Thus, the fracture of the brittle FR topcoat was probably due to poor plastic deformation in connection with a rapid progression of crack growth. The size of the flaw was determined from the SEM fracture micrographs to be $\sim 30 \mu\text{m}$, more than seven times larger than that in the failed precoat layer with the topcoat system.

In contrast, no signs of cracking were detected for the composite layer surface containing the elastomeric PU topcoat (see Figure 10). These results apparently verify that the FR glass topcoat, characterized by its high elastic modulus, extremely low elongation, and good bond strength, acts to promote crack propagation at the interfacial regions. Although some nonlinear stress distribution is observed prior to the deformation failure, the fracture of FR-precoat composition systems occurs almost immediately following the formation of a visible tensile crack. The initial cracking of this composite occurs through the FR polymer-precoat stress, whereby load is transferred from the brittle FR to the ductile crystal layers. For the PU superposition, it was microscopically observed that growth of the interfacially generated initial crack is more likely to be associated with the crystalline precoat sites than with the PU polymer sites. The most significant effect of the use of the high tensile and elongation and low modulus PU topcoat is, therefore, to delay and control of the onset of tensile cracking of the precoat layers. The interfacial bond failure occurs after the precoat layer reaches its yield point. Thus, the crack-arresting properties of elastomeric topcoats are found to play the major role in improving the mechanical behavior of the precoat layer during interfacial failure processes.

On the other hand, the effect of the adhesive bonds at the topcoat/precoat interfaces on the elastic behavior of the composite layers cannot be fully ascertained from the experimental data. To gain additional information, precoat surfaces were exposed to a 100% relative humidity (RH) atmosphere at 24°C for up to 10 days before application of initiated PU and FR resins.

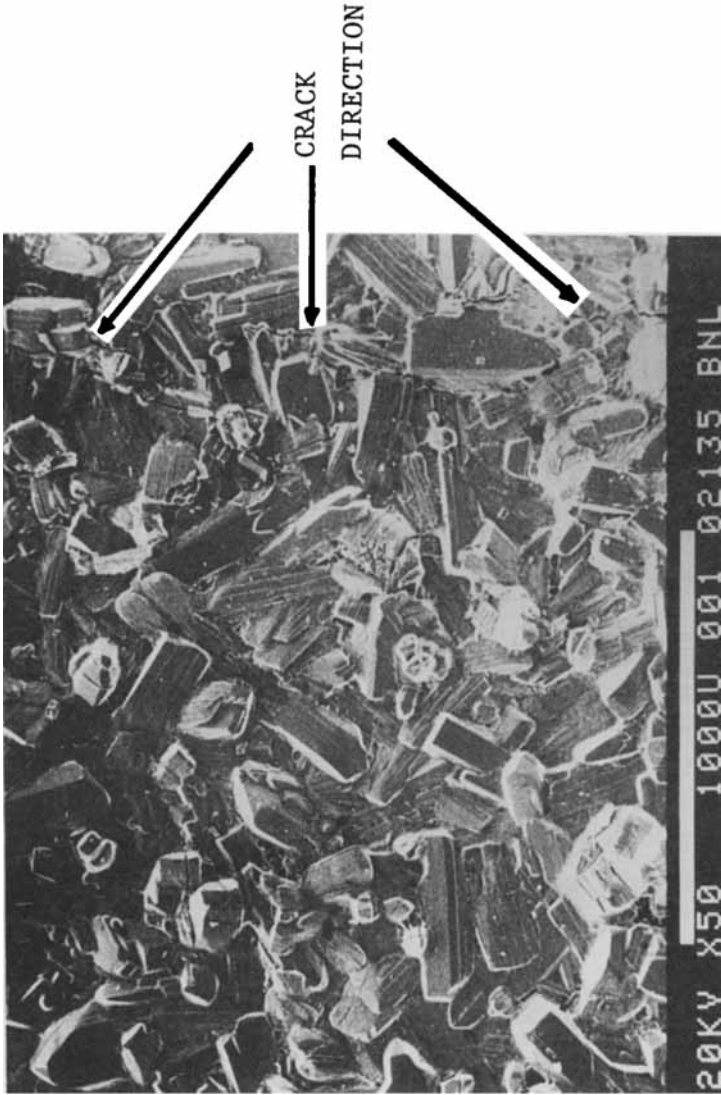


Fig. 8. Diverging microcrack pattern of a bent complex conversion precoat.

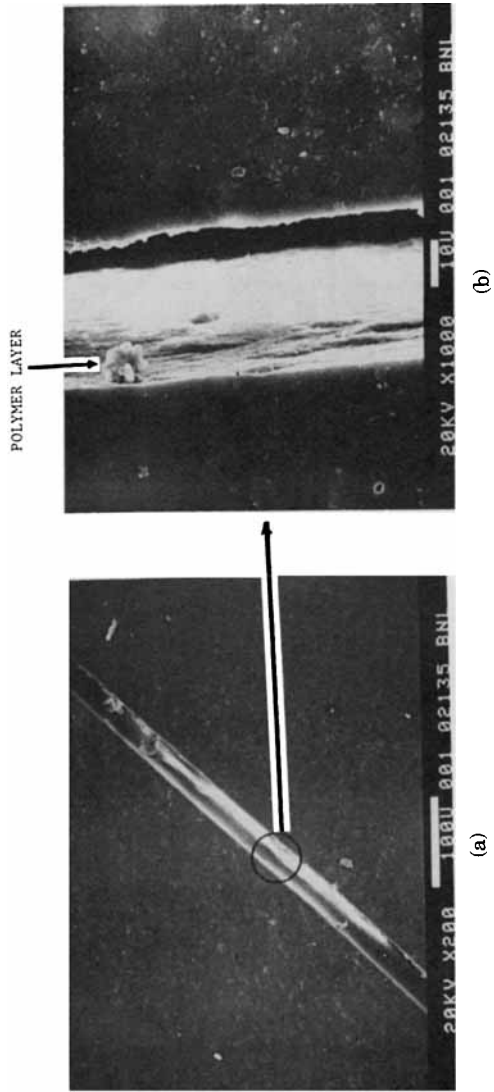


Fig. 9. SEM micrographs of glassy FR-topcoated composite layer surface at failure; (a) linear-cracking pattern of failed FR polymer, and (b) enlargement of section shown in (a).

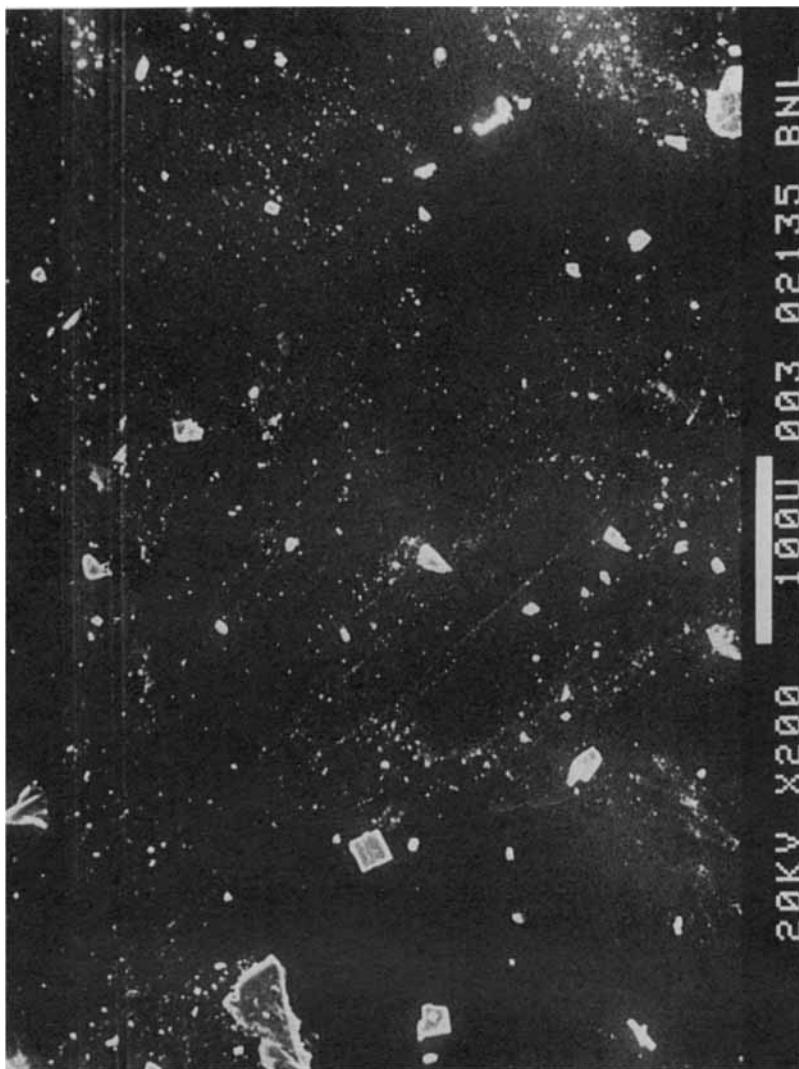


Fig. 10. Surface micrograph of PU-topcoated sample at yield stress.

The presence of any moisture on the substrate surfaces would result in a decrease in bonding force with these adhesives. The humidity also reduced the curing rate of the polymeric topcoat in the vicinity of the wetted precoat surfaces. This reduced polymerization rate relates directly to a decrease in elastic modulus of topcoating materials.

Curves showing the flexural modulus for PU- and FR-topcoated composite layers prepared after exposure of the precoat surfaces to 100% RH for various periods of time are shown in Figure 11. These data suggest that the presence of a certain amount of moisture on the precoat surfaces may increase the flexural modulus of the composite layers. Surfaces overlaid with PU after 24-h exposure to 100% RH exhibited the maximum modulus of 125×10^5 psi (86.13×10^3 MPa). This corresponds to an improvement of $\sim 20\%$ over that of the unexposed surfaces. Extending the exposure time for up to 10 days resulted in a modulus reduction, but the value was still higher than that from the dry surface. For the FR-topcoated systems, the data indicate that the modulus increased with exposure times up to ~ 5 days to an ultimate modulus of $\sim 100 \times 10^5$ psi (68.90×10^3 MPa). Beyond that time, the modulus declined to a value of $\sim 91 \times 10^5$ psi (62.70×10^3 MPa) after 10 days of exposure. From the above findings, it can be concluded that when the resins in the curing propagations are contiguous to moisture, their polymerization rate is suppressed by the humidity existing on the substrate surfaces. This suppression of polymerization acts to produce a rubbery polymer possessing a low elastic modulus and high elongation properties. Thus, even though the interfacial bonding forces are actually reduced by the presence of surface moisture, the decreased modulus of the polymer topcoat at the interface contributes to an increase in the flexural modulus of the crystalline precoat layers. This enhances the stiffness of the composite layers. The results further suggest that the interfacial stress transfer is of major importance in the topcoat-precoat composite systems. For instance, the enhanced brittleness at the interface, when a glassy FR topcoat is used, tends to result in a more rapid decrease in the interfacial stress transfer

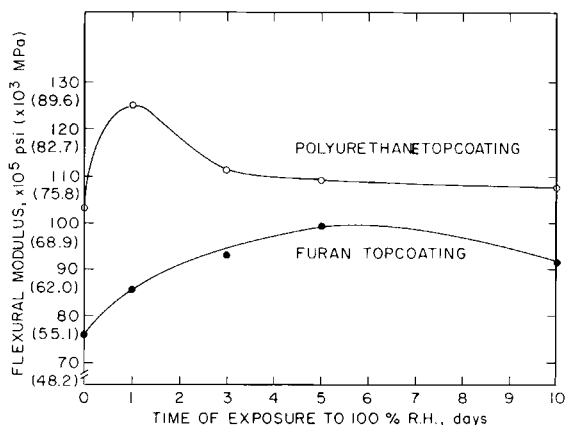


Fig. 11. Changes in flexural modulus of PU- and FR-topcoated complex crystal layers as a function of time of exposure to 100% RH.

because of an increased rate of compaction. The increased flexural modulus of the composite layers containing moisture at the interface is associated with an increase in interfacial stress transfer which is due to the absorption of a certain amount of energy by the rubbery topcoat prior to the initial cracking of the precoat layers. Accordingly, the interfacial adhesive bonds were found to have a lesser effect on the crack-arresting behavior and stiffness characteristics of the composite layers.

CONCLUSIONS

A ~3% concentration of PAA macromolecules used as a controllable admixture for crystal growth significantly enhanced both stiffness and ductility of brittle zinc phosphate conversion crystal layers deposited on metal substrate surfaces. The flexural modulus of 3% PAA-complexed crystal layers was more than two times greater than that of the conventional crystal layer without PAA. The physicochemical factors governing the mechanical behavior of the conversion complex crystal layers depended primarily upon the thickness, fineness, and density of the layers, and the average MW of the PAA. With a high MW of 1×10^5 , the most effective complex crystal formations and dimensions for achieving the ultimate flexural modulus were a uniform array of fine dense crystals ~5 μm thick and ~60 to 200 μm in length. The ductile complex crystal layer and surface not only provide a corrosion barrier on the substrates, but also possess the ability to promote adhesive bonds with polymeric topcoat systems because of the thin complex PAA polymer existing at the outermost surface sites of the crystal layers. The increase in adherent forces of the complex PAA overlayers results in a lower magnitude in the degree of coil-up and entanglement of the macromolecules brought about by the complex reaction between the proton-donating PAA polymer and the nucleophilic Zn^{2+} ions released from the $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ in a low pH aqueous medium. The use of high MW and an adequate amount of PAA contributes to a reduced alternation of chain conformation and the presence of a large number of functional COOH groups, thereby enhancing the magnitude of wettability of the complex precoat surfaces by the resins.

The mechanical characteristics of the polymeric topcoating in the topcoat-precoat composite layers play a key role in improving the stiffness, the postcracking ductility, and the flexural crack-arresting properties of the precoat layers. The improvement of these characteristics is more likely to be associated with a low elastic modulus, high tensile strength, and extremely high elongation properties of the topcoats, rather than the interfacial adhesive bonds. In fact, the flexural modulus for the elastomeric polyurethane-superposed composite layers was ~36% higher than that for the glassy furan polymer composite layers. Furthermore, no cracking of the polyurethane surfaces was detected microscopically at the yield stress of bent composite layers. This suggests that the interfacial bond failure occurs after the precoat layer reaches its yield point. In contrast, the initial cracking of the brittle furan polymer composite layers occurred through the polymer-precoat stress, whereby a load was transferred from the brittle polymer to the ductile layers.

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