

Adhesion Aspects of Levulinic-Acid-Modified Furan Polymers To Crystalline Zinc Phosphate Metal Surfaces

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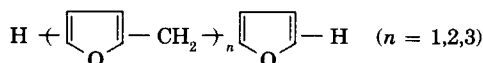
Synopsis

The nature of the interfacial interactions between functional levulinic-acid-modified furan resin coatings and crystalline zinc phosphate hydrate films deposited on carbon steel surfaces has been systematically investigated. The typical surface topography of the highly crystallized zinc phosphate films was found to be characterized by the presence of a dendritic microstructure array of interlocking triclinic crystals. This structure acts significantly to develop mechanical interlocking bonds with the functional blend polymer which penetrates into the open surface structure of the films. Both the thickness of deposition film and the polar H₂O molecules of hydrate at the outermost film surface sites play essential roles in wetting by the functional liquid resin. When the polarized furan polymers spread on the oxide film surfaces, the carboxylate groups derived from the levulinic ester and acid molecules react to form strong hydrogen bonds with the crystallized H₂O molecules on the hopeite film. This formation of hydrogen bonding was shown to be a major factor affecting the chemical intermolecular attractions. A formulation consisting of 95 parts furan to 5 parts levulinic acid was found to yield the optimum protective coating. More than 5 parts levulinic acid resulted in the transformation of the characteristics of the polymer film from hydrophobic to hydrophilic.

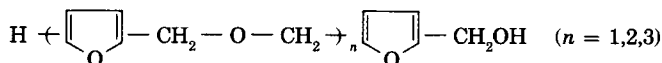
INTRODUCTION

Furan resins (FR) consisting of a mixture of furfuryl alcohol, furfuraldehyde, and copolymers of furfuryl alcohol with formaldehyde have been utilized as chemically resistant coatings for a broad range of acids, bases, and solvents.¹ The condensation polymerization of furan resin is usually accomplished by the addition of mild mineral, organic, and Lewis acid or acid-releasing initiators. The initial polymerization rate can be controlled by regulating the catalyst concentration (pH) and by cooling the reaction mixture with refluxing solvent and/or an external cooling fluid.^{2,3} The condensation reaction of furan resin to form a linear structure is propagated by intermolecular dehydration occurring between the hydroxyl group of one molecule and the active hydrogen atom in the 5 position of the furan ring. The constituents in the termination product of acid-initiated furan polymer consist of a hybrid formation of a heterogeneous compound such as furfuryl alcohol, its dimer, and higher homologs, regardless of the different acid initiators employed.^{4,5} It is generally known⁶⁻⁸ that the furan polymer compounds formed, which are a combination of those due to the furan nucleus of C₅ and to the hydroxymethyl primary alcohol group,⁹ are composed of the following four chemical structures:

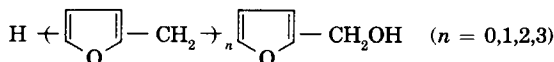
(a) homologs of difurylmethane,



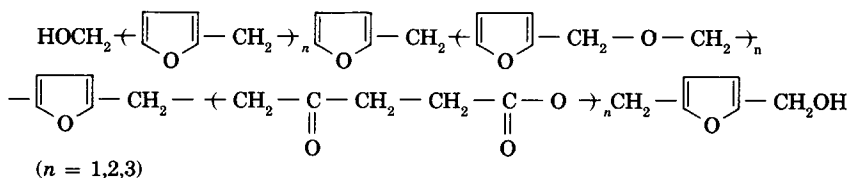
(b) homologs of difurfuryl ether,



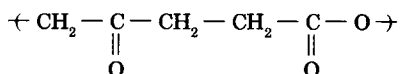
(c) homologs of 5-furfuryl-furfuryl alcohol,



(d) polyfunctional resin, HOCH₂



As mentioned above, the end groups of these oligomers are —CH₂OH and unsubstituted furan rings. The yields of each of these furan compounds can be estimated by using thin-layer chromatographic (TLC) densitometry.^{7,8,10} Quantitative analysis indicates that the major formulation in the heterogeneous product is the homolog of 5-furfuryl-furfuryl alcohol. This constitutes ~45% of the total quantity of polymeric compound. The second highest yield (~40%) is for a functional resin containing an ester of levulinic acid.



This resin results from the hydrolytic cleavage rearrangement of furan rings expressed in terms of the ring opening. It is interpreted that this ring opening is due to the hydrolytic activity of water formed during the initial condensation and ring oxygen protonation.¹¹

In recent studies,¹² the authors found that the addition of a 1.1.1-trichlorotoluene (TCT)—zinc chloride (ZnCl₂) initiator system to furfuryl alcohol diluted with a small amount of water produced a rapid reaction rate accompanied by the release of a large amount of heat. The resulting polymeric reaction product was apparently different in chemical structure from those usually formed by the use of other acidic initiators without the ZnCl₂ solution. The newly formed products were identified as zinc-furfuryl alcohol chelate compounds. It was concluded that these are formed through reactions between the divalent metallic Zn²⁺ ions dissociated from the ZnCl₂ solution used as an acid-releasing mineral initiator, and the carboxylate anions (COO⁻) formed by hydrolysis of levulinic esters. Thus, when the furan resin is applied as a protective coating to metal surfaces, it is pre-

sumed that the reactivity of the functional levulinic ester will result in great improvements in the bonding forces at the furan-metal interfaces.

On the other hand, the surface sites of oxide films deposited by immersing the metal substrates in an oxidizing solution contain polar OH groups which are strongly chemisorbed with proton-donating carboxylic acid (COOH) groups, present as a result of acid-base and charge transfer interactions.¹³ Since the number of levulinic ester configurations in the furan macromolecules can be controlled, the chemical affinity of COOH groups for the oxide films offers the potential for producing furan coatings which possess strong chemical activity.

The ideal modification of the furan polymers to obtain a high interfacial bond at the polymer-oxidized metal boundary would be to incorporate an adequate amount of levulinic acid reagent to interact with the methylol groups in alpha positions on neighboring furan rings to form a methylene-bridged polycondensate. Accordingly, the objective of the present work was to understand the fundamental physicochemical factors needed to design levulinic acid-modified furan coatings which will have strong bonding forces with crystalline zinc phosphate hydrate films deposited on metal substrate surfaces. In addition, the transformation of the polymer surfaces after exposure to chemically and hydrothermally aggressive fluids was studied to obtain basic information regarding their resistance to strong acid and base solutions and hot water.

EXPERIMENTAL PROCEDURE

Materials

Commercial-grade furan (FR) 1001 resin having a viscosity of 470 cP and a specific gravity of 1.22 at 24°C was supplied by the Quaker Oats Co. The condensation-type polymerization of the FR resin was initiated by the use of 4 wt % Qua Corr 2001 catalyst, which is an aromatic acid derivative. The gel time for a 200-g resin sample containing the initiator was ~15 min at 24°C. Commercial analytical-grade levulinic acid reagent (LA), $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$, was employed to assemble the more reactive FR macromolecules.

The metal used in the experiments was nonresulfurized mild carbon steel consisting of 0.18–0.23% carbon, 0.3–0.6% manganese, 0.1–0.2% silicon, and $\leq 0.04\%$ phosphorous. To deposit the zinc phosphate crystalline films onto the polished metal substrate surfaces, the metal was immersed for up to 24 h in an oxidizing solution consisting of 9 parts zinc orthophosphate dihydrate and 91 parts 15% H_3PO_4 solution at 60°C. The pH of this solution was ~2.0. After depositing the oxide film, the metal substrates were dried in a vacuum oven at 110°C for ~3 h to remove any moisture from the film surfaces.

Measurements

The surface topography and morphology of the chemically treated metal adherends were analyzed by AMR 100-Å scanning electron microscopy (SEM).

A Perkin-Elmer Model 257 Spectrometer was used for infrared spectroscopic (IR) analysis. To obtain basic information regarding the interfacial reaction mechanisms, IR spectra were obtained for the samples prepared in the form of KBr discs. The samples were powdered before mixing and grinding with KBr. The spectra were run at an 8 min scanning rate over the range of 4000–600 cm^{-1} .

The magnitude of the wetting force of the oxidized metal surfaces and polymer film surfaces by levulinic-acid-modified furan resin, water, and methylene iodide molecules was measured with a Contact Angle Analyzer in a 60% RH and 24°C environment.

X-ray powder diffraction (XRD) analyses were employed to identify the major oxide compound layers deposited on the treated metal surface. To prepare the fine powder samples, the deposited oxide layers were removed by scraping the surfaces and were then ground to a size of ~ 325 mesh (0.044 mm).

The lap-shear tensile strength of metal-to-metal adhesives was determined in accordance with the modified ASTM Method D-1002. Before overlapping between metal strips 50 mm long, 15 mm wide, and 2 mm thick, the 10 \times 15 mm lap area was coated with the levulinic acid–furan blend resin adhesives. The thickness of the overlapped film ranged from 1 to 3 mil. The bond strength values for the lap shear specimens are the maximum load at failure divided by the total bonding area of 150 mm^2 .

RESULTS AND DISCUSSION

Mechanical Interlocking Behavior

In general, good mechanical interlocking between a polymeric coating and an oxide substrate can be attributed to the following: (1) the nature of the surface topography and micromorphology of the deposited oxide layer, and (2) the physical properties of the adhesive and its ability to penetrate easily into the pores in the oxidized films. The former relates directly to surface activation factors, such as the highly crystallized oxide layer consisting of an open surface structure and an adequate crystal thickness. These factors lead to an increase in the magnitude of the wettability and spreadability of polymeric adhesives on the oxide films. The second element is associated with the resin's having low viscosity and surface tension.

On the basis of the above concept regarding the mechanical interlocking behavior, it is thought that the changes in the topographical features that occur during the growth of zinc phosphate crystals significantly affect the spreading and wetting behavior of the oxidized layers by the resin. Thus, it is very important to assess systematically any correlations that exist between the micromorphological nature of the aged oxide films and the adsorption rate of resin on the films. As a first attempt to obtain this information, the degree of crystallization of hydrated zinc phosphate compounds deposited on the metal surface as a function of the soaking time in the zinc phosphating solution was investigated by use of scanning electron microscopy (SEM).

Four steel panels, which were polished with ultrafine emery paper, were immersed in the $\text{Zn}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}-\text{H}_3\text{PO}_4-\text{H}_2\text{O}$ oxidizing solution at 60°C for 1, 3, 6, and 24 h, respectively. SEM photomicrographs of the treated metal surfaces (Fig. 1) show that the degree of deposition and the magnitude of the crystal growth increased with increased exposure to the oxidizing solution. The micrograph of the surface exposed to the solution for 1 h indicates many distinctive tiny rings, but no significant crystal deposition on the surface is apparent. The crystalline rings may have been produced by erosion of the metal surfaces by the chemically aggressive oxidizing liquids. Closer examination reveals that the ring sizes ranged from 100 to $400\ \mu\text{m}$ in diameter, and that the rings were slightly raised from the substrate surfaces. The microtexture of the metal surface changed dramatically from smooth to extremely rough after exposure for 3 h. Its morphological features were characterized by the formation of a block-appearing coarse crystal $\sim 280\ \mu\text{m}$ in length, which was distributed randomly on all surfaces of the modified metal sites. It appeared from the SEM image after 6 h soaking [see Fig. 1(C)] that the coarse microstructure formed at age 3 h was later converted into an almost rectangular crystal structure. As seen in the photomicrograph, the morphological features of the crystals formed at this age indicate a triclinic microstructure characterized by three unequal axes intersecting at angles oblique to each other. XRD analyses were performed to identify and clarify the major deposition products of the triclinic zinc

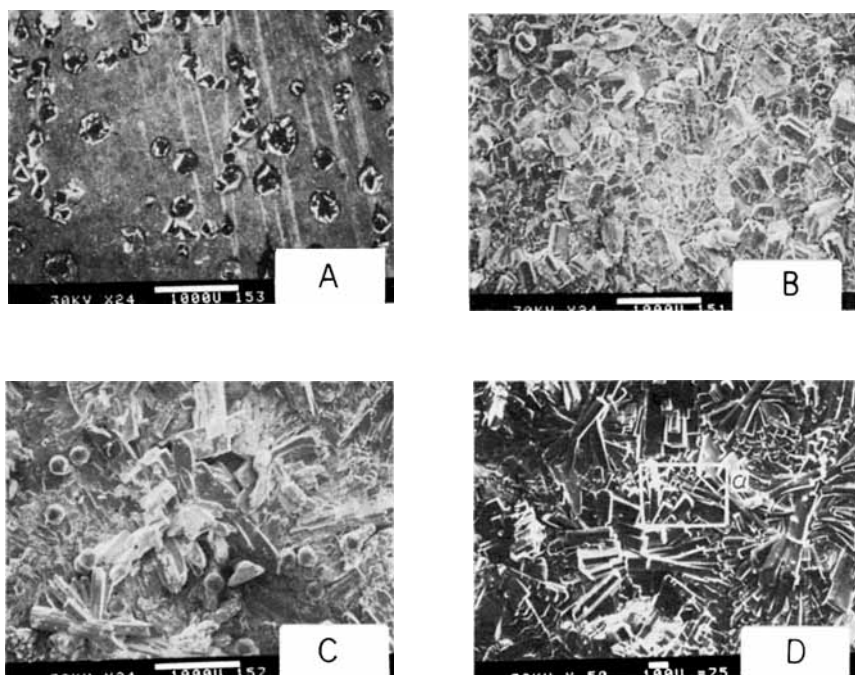


Fig. 1. Surface microstructure changes in zinc phosphage conversion crystals deposited on metal surfaces after exposure for various times in zinc phosphating solutions at 60°C : (A) after 1 h; (B) 3 h; (C) 6 h; (D) 24 h.

phosphate hydrate compound. The resultant XRD pattern in the diffraction range of 9.82–2.56 Å is given in Figure 2. The spacings of 6-h-old zinc phosphate crystals are represented by strong reflections at ~9.00, 4.51, and 2.83 Å, and weak bands at 3.99, 3.44, 3.36, 2.62, and 2.59 Å. When the line intensities of the three strong bands were compared, they were found to be almost equivalent. Accordingly, the major composition of the surface oxide film derived by immersing the mild carbon steel in the oxidizing solution for 6 h at 60°C was identified as the triclinic hopeite of $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Further exposure [see Fig. 1(D)] resulted in the formation of a pronounced dendritic microstructure of triclinic hopeite crystals. The topography of the 24-h-old hopeite film, as viewed by SEM, was comprised of a dense agglomeration of circular radiating rectangular zinc phosphate crystals.

An enlargement of section A in Figure 1(D) (Fig. 3) shows the presence of interlocked hopeite crystals $\sim 20 \times 40 \times 180 \mu\text{m}$ long. From this morphological image, it is expected that the uniformly interlocked crystals will provide a larger surface area for bonding and give sufficient mechanical interlocking with polymeric adhesives. When the adhesive penetrates into the open spaces on the interlocking surface microstructure, the rectangular crystals will become embedded in the adhesive phase and act as a reinforcement for the polymeric matrix.

SEM is particularly useful in preparing stereophotographs that can be viewed in 3-dimensional relief with the aid of a stereoviewer and, hence it can be used to determine the approximate thickness of the crystals after various exposure times. These results are illustrated in Figure 4. The data indicate that, under the conditions employed, the oxidizing solution produces a film, the thickness of which increases almost linearly with time for exposure periods ranging up to 10 h. Beyond that time, the rate of crystal deposition seems to decrease significantly. Highly crystallized hopeite layers $\sim 200 \mu\text{m}$ thick can be produced by immersing the steel plate for ~ 15 h in the phosphating solution at 60°C. From the above results, it is apparent that the prolonged exposure to the prescribed oxidizing mixture leads to the formation of highly dense interlocking crystals having an open surface structure. For a given crystal thickness, adhesion to more interlocked oxide films can be expected to be higher.

An increase in surface crystal thickness relates to an enhanced surface roughness and an increase in oxide surface area. The increased roughness will enhance the degree of wettability of the oxide film by the liquid resin and increase the mechanical interlocking at the polymer-oxide layer in-

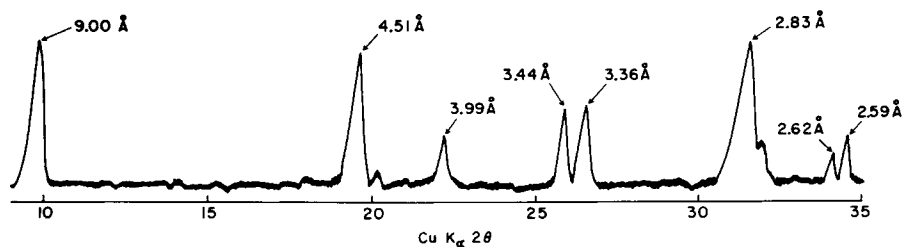


Fig. 2. Powder X-ray diffraction pattern of zinc phosphate hydrate compounds deposited on metal surfaces.

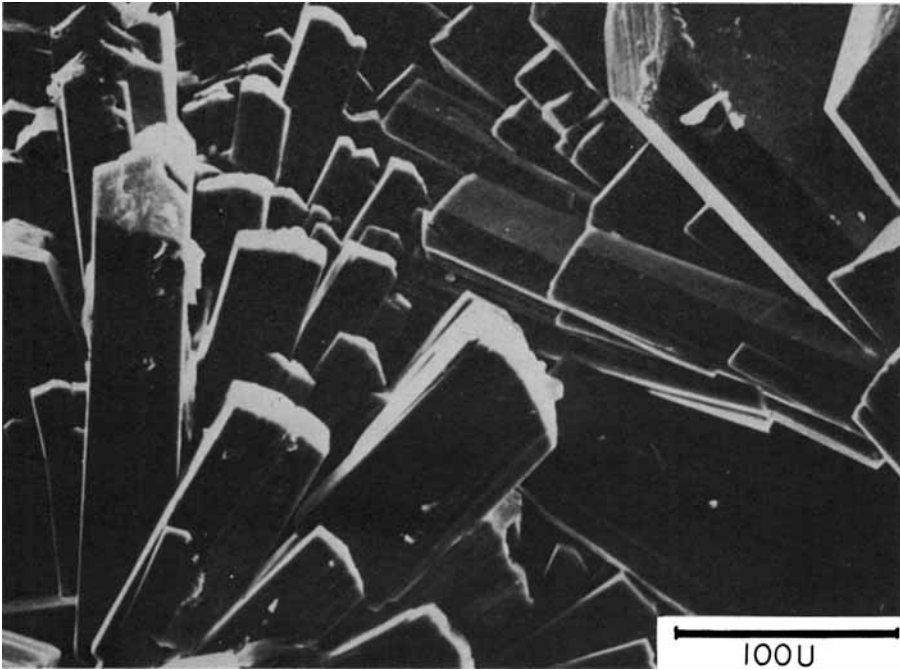


Fig. 3. Rectangular-shaped hopeite crystals. Enlargement of section (a) shown in micrograph in Figure 1(D).

terfaces. Experiments to obtain quantitative information regarding the magnitude of the wettability and the bonding forces were performed. In this work, determinations of the interfacial contact angle at the resin-oxide film boundary and the lap shear bond strength of metal-to-metal adhesives

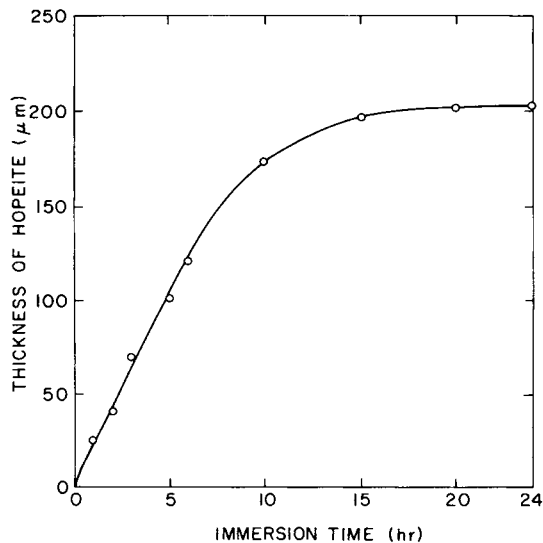


Fig. 4. Thickness of hopeite crystals as a function of immersion time in zinc phosphating solutions.

were made as a function of the immersion time for the metal substrate. A 95% furan-5% levulinic acid resin system was used in this test series. The mixture had a viscosity of 420 cP and a surface tension of 37.4 dyn/cm at 24°C. The contact angles were measured within 30 s after deposition of the liquid resin on the aged hopeite layers. Figure 5 shows the changes in the contact angle and the lap shear bond strength plotted against the extent of oxidation. It was observed that the contact angle decreases as the treatment time in the oxidizing fluid is increased up to ~24 h, after which it remains constant. Since a lower contact angle results in an increase in the magnitude of the wetting force, it appears that the wettability of the hopeite films can be enhanced by increasing the crystal thickness. The value for the contact angle for the hopeite layer produced by immersion for 24 h, corresponding to a crystal thickness of ~203 μm , was significantly lower (10° vs 30.8°) than that for an untreated metal surface. Although crystal thickness and surface roughness are major factors in the wettability of hopeite films, the unique topographical features of the dendritic structure of triclinic crystals and the facile penetration of resin into the open spaces in the interlocking rectangular crystals may also contribute.

The two curves on Figure 5 show a strong correlation between the contact angle values and the shear bond strength. The latter increases with decreasing contact angle for treatment times up to ~24 h, and then levels off as the contact angle becomes constant. The adhesion to the polished metal surface (time = 0 h) is poor because of the absence of interfacial interlocking. The failure region passes smoothly along the shear front and involves only a small amount of polymer in plastic deformation, giving a low shear bond strength of 140 psi. This low strength for the untreated surfaces can be improved by a factor of 7.4 by the zinc phosphate treatment for 24 h. An ultimate strength of 1030 psi was developed when the contact angle between the polymer and the hopeite crystal layer was 10° .

From the above results, it is apparent that the magnitude of the adhesion at the liquid resin-oxide film interface depends mainly on the area of resin contact, thereby resulting in an increase in the resin wetting capacity of

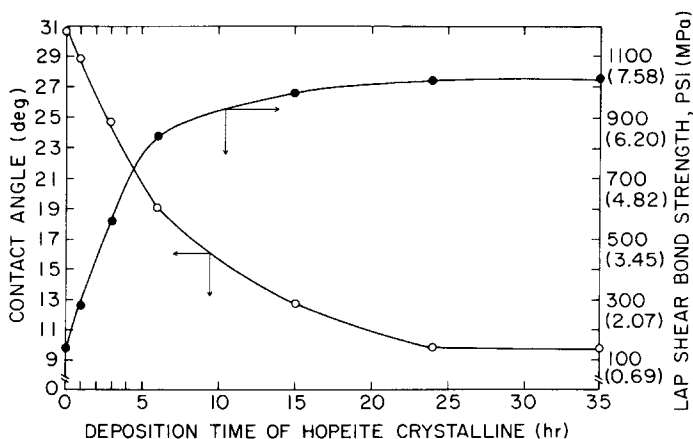


Fig. 5. Contact angles and lap shear bonding force as a function of treatment time of metal in oxidizing liquid.

the film surfaces. Thus, it is very important to estimate quantitatively the dynamic wetting feasibility which is expressed in terms of the rate of spreading. The primary objective in this work was to develop a spreading model for the wetting processes on the oxide film. A modified thermodynamic kinetics expression which may be rewritten in the following form was used to develop the model. This is as follows:

$$\frac{-d(\cos \theta_t / \cos \theta_\infty)}{dt} = k \left(1 - \frac{\cos \theta_t}{\cos \theta_\infty} \right)$$

where θ_t is the contact angle at time t , θ_∞ is the contact angle at infinite time, and k refers to the spreading rate constant. The factor $(1 - \cos \theta_t / \cos \theta_\infty)$ is defined as the rate of the contact angle fraction advanced at time t .

With this model, an attempt was made to obtain quantitative information regarding the rate of spreading on hopeite layers produced by the different zinc phosphate treatment times. Experiments were performed in which contact angles were measured as a function of time after the deposition of resin on the substrate surfaces at an ambient temperature of 24°C. Values for $\ln(1 - \cos \theta_t / \cos \theta_\infty)$ plotted against the corresponding values of t are shown in Figure 6. Straight line relationships between the contact angle

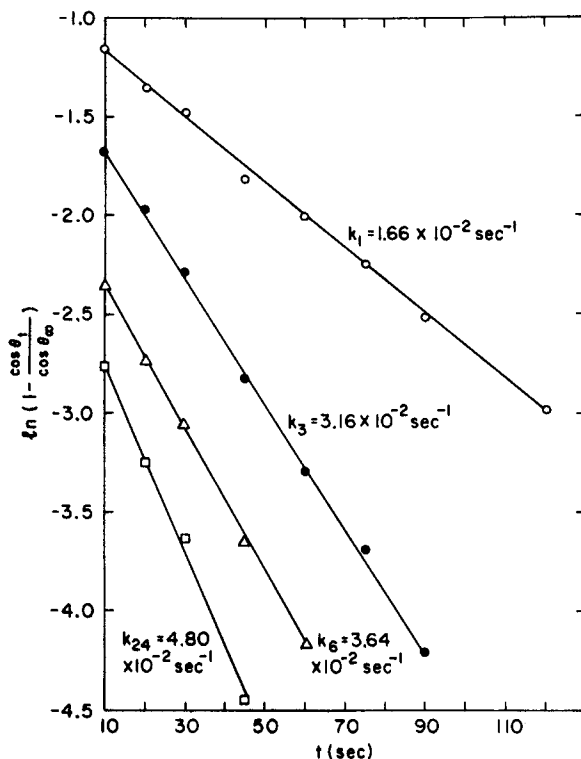


Fig. 6. Comparison of spreading rate constant of resin on hopeite films at various treatment ages; treatment time: (○) 1 h; (●) 3 h; (△) 6 h; (□) 24 h.

and elapsed time are evident. As a result, values obtained from the slopes $\Delta \ln (1 - \cos \theta_t / \cos \theta_\infty) / \Delta t$ were used as the spreading rate constant k . The influence of the surface oxide film on the spreading mobility of resins was evaluated by comparing the rate constant k for various treatment times. The data indicate that the k value increases as the treatment time of the metal surface is increased. The value of $4.80 \times 10^{-2} \text{ s}^{-1}$ after a 24 h treatment was ~ 3 times greater than that at age 1 h. This means that a film thickness of $\sim 203 \mu\text{m}$ produced during a 24-h immersion period has a more pronounced effect on the spreading processes than that produced during a 1-h exposure. It apparently verifies that the boundary of a sessile drop is significantly advanced by the growing hopeite crystal layers. Consequently, the crystal thickness and the degree of surface roughness of the oxide film appear to have major roles in the resin spreading behavior.

In summary, it was found that hopeite films contribute to a good mechanical interlocking with polymeric adhesives. The bonding is attributed to the uniform topography of the dendritic array of triclinic rectangular crystals, the thickness of the crystalline film, interlocking micromorphology, and the large open surface microstructure. Anchoring of the polymer which penetrates into the open spaces in the interlocked crystal layers also acts to enhance the bond strength at interfacial regions.

Interfacial Chemical Attraction

The presence of functional groups, such as hydroxyl, ester, and carboxylic acid, in the levulinic-acid-modified furan resin molecules may also contribute to the mobility to available adsorption polar hydroxyl (OH) groups on hopeite surface sites. The chemical treatment is intended not only to increase the rate of roughness of the metal surfaces, but also to modify the surface chemical composition. In fact, IR spectra for the fine hopeite powders removed by scraping hopeite-deposited metal surfaces exhibited a strong sharp frequency at 3560 and 3400 cm^{-1} , which represents the presence of coordinated water expressed in terms of the hydration water. These strong bands represent the stretching vibration of OH groups of hydrated water. Water of hydration is also distinguished from OH groups by the presence of the H—O—H bending motion which produces a medium band at $\sim 1620 \text{ cm}^{-1}$. This band can be taken as another important means of identifying water of crystallization, and it is very useful in the elucidation of inorganic structures. IR results suggest that water molecules in the hopeite molecular structure are present as simple water of crystallization and as coordinated water in hydrates. The fact that the highly crystallized hopeite formation contains a large number of polar OH groups in water molecules indicates that it should be possible to form strong hydrogen bonds to organic functional groups in polymeric coatings. Therefore, a study was performed to investigate the role of water in the interfacial chemical attraction between the functional resin and the hopeite layer. In an attempt to elucidate this role, composite samples were prepared by incorporating the modified furan resins with finely powdered hopeite which was removed from the metal surfaces, and then curing the mixture in an oven at 80°C for 10 h. The composition of the hopeite-filled furan resin was adjusted by

varying the concentration of the hopeite powder in the range of 0–70% by weight. After curing, the samples to be used in IR spectroscopic analyses were ground to a size of ~ 325 mesh (0.044 mm). IR analyses for these samples, prepared in the form of KBr discs, were conducted by interference techniques, using interfering discs containing various proportions of KBr and hopeite powders.

The resultant IR spectra indicate that the most pronounced changes in the peak intensity of IR absorption bands, as a function of hopeite concentration, take place in the frequency range of 1800–1350 cm^{-1} . As seen in Figure 7, the absorption spectra for bulk furan–levulinic acid-blend polymer showed a conspicuous band at a frequency of 1710 cm^{-1} and weak bands at 1560 and 1420 cm^{-1} . The prominent absorption at 1710 cm^{-1} is due to

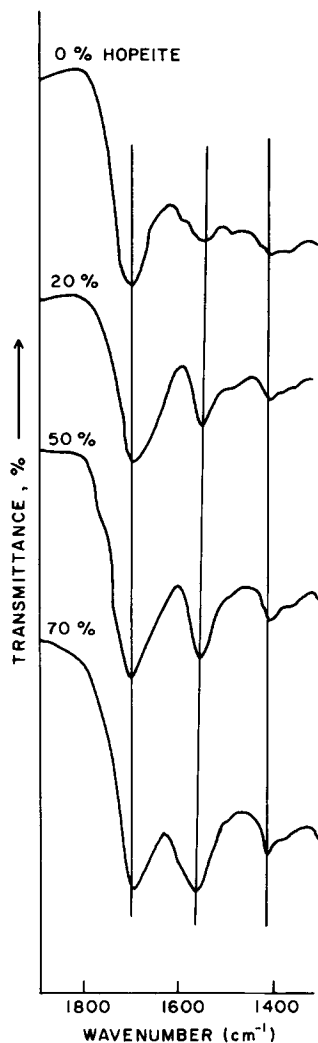


Fig. 7. Changes in IR intensity at frequency of 1710, 1560, and 1420 cm^{-1} as a function of hopeite concentration in the composite samples.

the stretch vibration of carbonyl groups (C=O) of levulinic ester formed by cleavage of furan rings and of reacted or unreacted levulinic acid. The peaks at 1560 and 1420 cm^{-1} are of approximate equal intensity and can be assigned to the asymmetric and symmetric stretching vibrations of carboxylate anion (COO^-) groups derived from the analogy of the ionized carboxyl groups. Of interest are the noteworthy changes in intensity at these frequencies that occur as the hopeite content in the composite systems is increased. As is evident from the figure, the intensities of COO^- bands at 1560 and 1420 cm^{-1} increase markedly with increased hopeite concentrations. Conversely, the C=O band at 1710 cm^{-1} tends to shorten with growth of the COO^- bands. From the viewpoint of interfacial chemical affinity, these results apparently demonstrate that OH groups on the hopeite surface can hydrogen bond with the carbonyl oxygen atom in the polymer molecules. Thus, the C=O stretching frequency of polymer decreases upon hydrogen bond formation through the carbonyl oxygen, whereas that of the asymmetrical and symmetrical stretching vibration of COO^- anion groups shifts to a higher frequency.

In practice, the rate of hydrogen bond formation between the C=O groups in the polymer and the OH groups on hopeite is directly related to the intensity of an absorption band or the absorbance at any given frequency. This bond rate as a function of hopeite content, from 0% to 70%, was quantitatively estimated by comparing the absorbance ratio of the C=O frequency at 1710 cm^{-1} with that of the COO^- at 1560 cm^{-1} . The absorbance at a given wave number can be calculated by using a Beer-Lambert law as shown below:

$$D_\lambda = \log(I_{0\lambda}/I_\lambda)$$

where D_λ is the absorbance at wavenumber λ , $I_{0\lambda}$ is the intensity of incident radiation, and I_λ refers to the intensity of transmitted radiation. For quantitative analysis by IR spectroscopy, the peak height or the area of the band is usually taken as the criterion of band intensity. Therefore, an accurate measurement of band intensity is required. The value of transmittance ($I_{0\lambda}$) at the base of an absorption band was determined by the use of the horizontal baseline connecting the two wings of the complex bands.

As shown in Figure 8, the plot of the absorbance ratio as a function of hopeite concentration exhibits a direct linear relationship. This indicates that the intensity of the band characteristic of COO^- formation becomes stronger as the C=O group band intensity decreases. Accordingly, it appears that the OH groups formed on the outermost surface of hopeite layers are accessible to electron donor-acceptor interactions to form hydrogen bonds. This fact further suggests that a large hopeite surface area, corresponding to the presence of a plentiful supply of polar OH groups on the outermost surface sites, is more strongly chemisorbed by the functional resin than a smaller surface area. This effect leads to an increase in the strength of the mechanical bonding at the interfaces.

A possible interpretation for the facile resin mobility at the liquid resin-hopeite interfacial regions can be developed from the nature of hydrogen bond mechanisms. When a resin, initially in a liquid state, is brought into

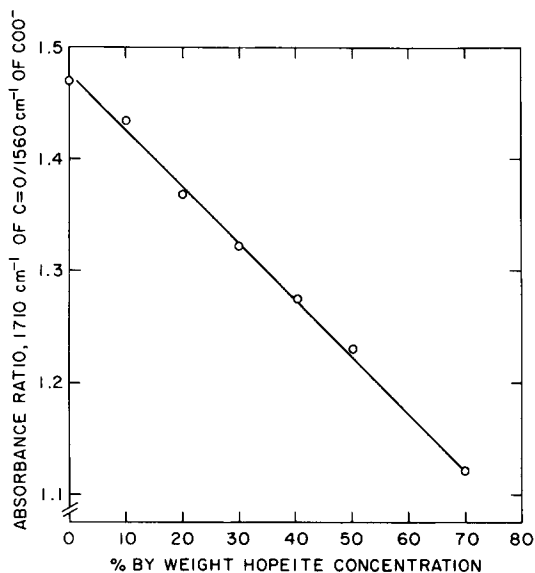


Fig. 8. Correlation between absorbance ratio and hopeite concentration incorporated in furan resin system.

contact with the hopeite films, the functional groups in the liquid resin are mobile enough to migrate to the polar OH group sites on the film where the energetics of adsorption to form the hydrogen bonds are particularly favorable. This behavior may be explained using a model for a charge transfer bonding mechanism which predicts that the functional groups will bond strongly to oxygen atom forming metal-oxygen-resin complexes. Charge transfer leading to the formation of chelate-type complexes is much more common and seems to occur on most C = O-containing resin surfaces. These C = O groups can stem from carbonyl, carboxylate, ketone, or other functional groups.

A study was conducted to elucidate the role of crystallized water, often called hydrates, in hydrogen bond behavior. The water molecules of crystallization are stable enough to remove water vapor from ordinary air at ambient temperature. As mentioned earlier, the presence of these thermally stable water molecules can be identified by the IR frequency at 1620 cm^{-1} which is assigned to the bonding vibration of water crystallization. Therefore, the rate of hydrogen bond formation of the water molecule with the C = O groups in the copolymer may be estimated on the basis of data obtained from quantitative analysis by IR spectroscopy. The analytical work was focused upon the changes in the absorbance ratio of C = O bands at 1710 cm^{-1} and H_2O bands at 1620 cm^{-1} . The samples for IR studies were prepared by mixing equal parts of initiated furan-levulinic acid blend resin and hopeite powder. To study the hydrogen bond reaction of C = O groups and H_2O groups, the concentration of levulinic acid reagent in the blend resins was varied, ranging from 0% to 40% by weight of total resin mass. IR spectra were recorded for samples prepared in the form of conventional KBr discs.

Figure 9 shows the changes in absorbance ratio which are calculated from

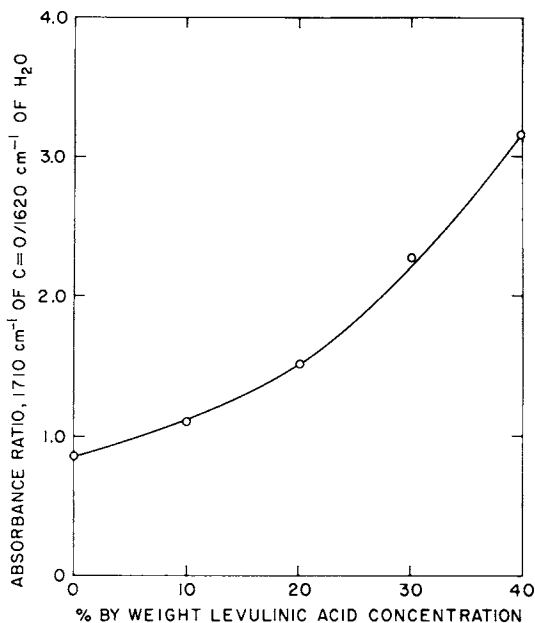


Fig. 9. Absorbance ratio obtained from 1710 and 1620 cm^{-1} absorption bands vs. levulinic acid concentration.

the peak intensities at the two frequencies (1710 and 1620 cm^{-1}), as a function of the levulinic acid concentration. The data indicate that the absorbance ratio gradually increases with an increase in the amount of levulinic acid. The absorbance ratio for the sample containing 40% levulinic acid was more than three times greater than for the sample without the levulinic acid. The reduction in the intensity of the H_2O frequency at 1620 cm^{-1} with increased $\text{C}=\text{O}$ groups is due to a lowering of the $\text{H}-\text{O}-\text{H}$ bond order by formation of the hydrogen bond, $-\text{C}=\text{O}\cdots\text{H}_2\text{O}$. As is evident from the above results, an interesting speculative possibility is that the water crystals formed on the hopeite layers play an essential role in binding the oxide film-polymeric coating units together, thereby producing good adhesion. All available crystallized H_2O at the outermost sites of the hydrated hopeite surfaces reacts chemically with the numerous functional groups modified by addition of the levulinic acid to the furan. Subsequently, the proton-donating ester and carboxylic acid groups chemisorbed strongly with the polar OH groups are converted into carboxylate anions which induce hydrogen bonding as a result of acid-base and charge transfer interactions. It should be noted that the rate of hydrogen bond formation between the functional groups and the H_2O groups can be estimated by determining quantitatively the reduction rate of the IR peak intensity at 1620 cm^{-1} .

Surface Energy of Polymer Films

Because of their strong affinity for water, functional ester and carboxylic acid groups are generally classified as hydrophilic. It was expected that the presence of a superfluous number of such hydrophilic groups in the polymer

macromolecules, except those forming hydrogen bonds with polar H₂O groups at the oxide film surface sites, would render the polymeric coating susceptible to excessive hydrolysis and consequent softening and swelling when immersed in water. Hence, the degree of hydrophilicity of polymer surfaces is one of the important factors affecting the absorption, permeability, and water resistance of coatings.

To study the transformation of levulinic-acid-modified furan polymer film surfaces from hydrophobic to hydrophilic, six different ratios of furan to levulinic acid (100/0, 95/5, 90/10, 80/20, 60/40, and 40/60) were used in a series of tests. Approximately 10-mil copolymer film samples were exposed for 7 days in an autoclave at 150°C and in 30% H₂SO₄ and 30% NaOH solutions at 80°C. Another goal of this study was to find the optimum furan-levulinic acid formulation which would yield a copolymer that is resistive to hydrothermal and chemically aggressive fluids. Usually the hydrophilic nature of polymeric coating surfaces is described as a wettability correlation between the water and the solid surfaces. The magnitude of wetting behavior can be determined by comparing the quantitative values expressed in terms of the surface free energy. As described in a previous paper by the authors,¹⁴ the energetic data were obtained by using a geometric mean expression, proposed as a natural extension of the Fowkes¹⁵ empirical formula by Owens and Wendt,¹⁶ which is especially applicable to the surface characterization of polymers. The equation, which expresses the work of adhesion (W_a) in dealing with the wettability of a liquid on a flat solid surface, was used to measure the total solid surface free energy (γ_s) which is the sum of two components, the dispersion forces (γ^d), and the dipole-hydrogen bonding forces (γ^p):

$$W_a = 2 (\gamma_s^d \gamma_l^d)^{1/2} + 2 (\gamma_s^p \gamma_l^p)^{1/2}$$

where $\gamma_s^d \gamma_l^d$ and $\gamma_s^p \gamma_l^p$ refer to the dispersion forces and polar forces in the solid and the liquid. In this equation, the values of γ_s^d and γ_s^p , which are needed to obtain γ_s , are unknown. Experimentally, they can be determined by the method of Owens and Wendt¹⁶ by measuring the contact angles with water and methylene iodide. Values of W_a for water and methylene iodide were computed from experimentally measured contact angle and surface tension values. Values for the parameters γ_l^d and γ_l^p were obtained from data reported by Fowkes¹⁷: $\gamma_l^d = 21.8$ erg/cm² and $\gamma_l^p = 51.0$ erg/cm² for water; $\gamma_l^d = 48.5$ erg/cm² and $\gamma_l^p = 2.3$ erg/cm² for methylene iodide.

Figure 10 presents γ_s^p , γ_s^d , and γ_s values plotted as a function of furan (FR)/levulinic acid (LA) ratio for films after exposure to hot water at 150°C and acid and base solutions at 80°C. For the surfaces of the film samples autoclaved at 150°C, the γ_s^p -FA/LA ratio curve indicated an interesting trend. The γ_s^p values between FR/LA ratios of 100/0 and 95/5 tend to decrease slightly with increasing LA contents and then increase progressively as additional LA is incorporated. The highest γ_s^p value of 11.0 erg/cm² obtained from the 40/60 ratio is 2.8 times greater than that obtained for the 95/5 ratio film. A possible reason for the increased dipole-hydrogen bonding force as a result of the addition of LA could be that the excess functional LA molecules configured in FR macromolecules lead to a polar

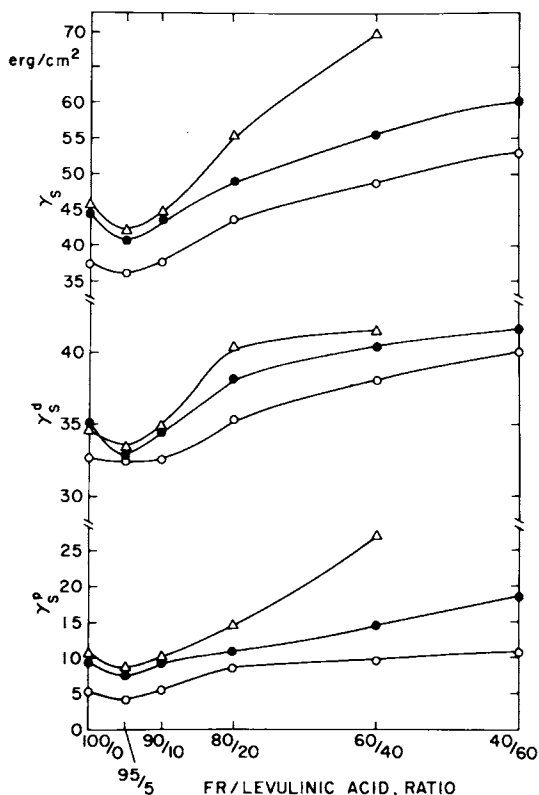


Fig. 10. Components of surface free energy as a function of FR/LA ratio for film samples (○) autoclaved at 150°C, (●) exposed to 30% H_2SO_4 , and (△) 30% NaOH at 80°C.

surface which is composed of a hydrophilic monolayer. Conversely, the lower γ_s^p value observed on the autoclaved film surfaces may be the result of a low hydrophilic density, producing a lower affinity for water.

Trends similar to those of γ_s^p were observed for γ_s^d . However, a notable difference exists in the rate of increase in γ_s^p and γ_s^d , between FA/LA ratios of 95/5 and 40/60. The shift in γ_s^d is considerably lower (23% vs. 175%) than that for γ_s^p . This suggests that autoclaved film surfaces containing large amounts of LA are more likely to have increased polarizability of their molecules. This may result from the hydrolysis of the functional groups existing on the outermost surface sites, rather than with the increase in surface roughness. Since the total surface free energy γ_s is the sum of the attractive forces γ_s^p and γ_s^d , the curve is similar to those for γ_s^p and γ_s^d . The surface energy for the FR/LA ratio of 40/60 was 52.8 erg/cm², ~47% higher than that for the FR/LA 95/5 ratio samples which had the lowest surface energy in this test series. Accordingly, it appears that, during exposure in the autoclave, the functional polymer film surfaces produced by adding a superfluous amount of LA to FR copolymer systems were converted into hydrophilic surfaces having a strong affinity for water, because of the increased surface energy.

Upon exposure to chemically aggressive fluids such as 30% H_2SO_4 and 30% NaOH at 80°C, the trends for the γ_s values as a function of FR/LA

ratio were almost the same as those for the autoclaved samples. This indicates that the acid and alkaline media at an elevated temperature act aggressively to increase the number or the accessibility of hydrophilic groups to water. This is particularly the case when samples containing high LA concentrations are exposed to NaOH. The γ_s of 70 erg/cm² obtained from the 60/40 ratio samples is 44.3% and 27.2% higher than those for the same FR/LA ratio samples after exposure to hot water and acid solutions, respectively. Thus, it was confirmed that the presence of a large quantity of functional LA reagent leads to a severe alkaline hydrolysis which increases the hydrophilicity of the film surfaces.

In order to find a possible reason for the progressive surface reactions of the polymer films by the NaOH treatment, the surfaces of films containing an FR/LA ratio of 60/40 were evaluated using attenuated total reflectance (ATR) spectroscopy. ATR is a very effective and simple method for analyzing surface layers of material by spectrophotometric techniques, usually in the infrared. Figure 11 shows the ATR spectra for the hydrothermally and chemically treated film surfaces. As is evident from the figure, the spectrum for the NaOH-treated film surfaces was characterized by the pronounced presence of two strong new frequencies at 1570 and 1380 cm⁻¹ and by the almost complete disappearance of the conventional band of C = O groups at ~1700 cm⁻¹. These absorption bands can be assigned to the asymmetrical and symmetrical stretching vibrations of carboxylate anions, COO⁻. In contrast, ATR frequencies for both the autoclaved or the H₂SO₄-treated film surfaces did not exhibit a conspicuous peak intensity at 1570 and 1380 cm⁻¹. These results clearly demonstrate that a salt complex formation consisting of COO⁻Na⁺ groups was yielded on the film surfaces by the acid-base

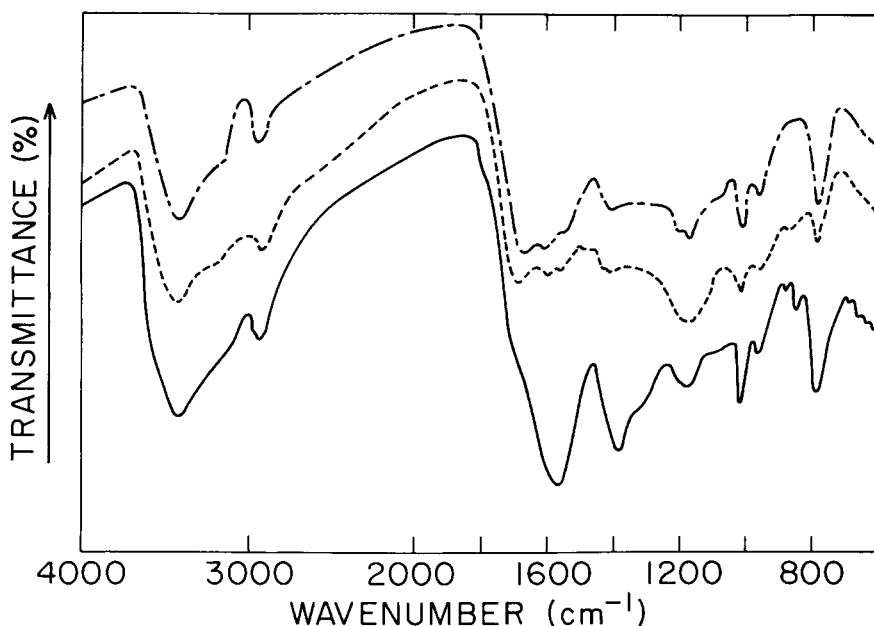


Fig. 11. Comparison of ATR spectra for (—) NaOH-treated, (---) H₂SO₄-treated, and (-·-) autoclaved film surfaces containing 60/40 FR/LA ratio.

reaction between the carboxylate anions formed by proton donor characteristics of the carboxylic acid in the LA molecules and the active nucleophilic Na^+ ions dissociated from NaOH in an aqueous medium. This surface transformation by the salt complexes formed in the superficial layers of NaOH-treated film results in the subsequent entanglement and coiling of the copolymer macromolecules. This was verified by SEM examination.

From the above results, it was found that the optimum polymer formulation for resistance to hydrothermally and chemically aggressive fluids consists of 95 parts furan to 5 parts levulinic acid.

CONCLUSIONS

On the basis of the experimental results and analysis, the following physicochemical factors significantly affect the adhesion of levulinic-acid-modified furan polymer to crystalline hopeite films deposited on metal surfaces. The nature of the interfacial attraction, which can be modified to achieve good bonding at the hopeite-film-modified furan polymer interfaces, was influenced by the following three elements: (1) mechanical interlocking bonds which are provided by the degree of the surface roughness of the substrates, (2) spreading forces of the deposited hopeite polar film by the functional liquid resins, and (3) chemical intermolecular attractions.

The highly crystallized triclinic hopeite has a considerable deposition weight, and a typical surface topography comprising a dendritic microstructure array of an interlocking rectangular crystal was confirmed. This structure was found to be the primary factor contributing to the increased mechanical interlocking forces associated with the mechanical anchoring of the polymers yielded by penetrating liquid resin into the open surface microstructure and microfissures of the films. The extent of hopeite-polymer interlocking depends mainly on the thickness of the hopeite crystals, the polar H_2O groups at the crystal surface sites, and the reactive molecular structure of the liquid adhesives. The coordinated and crystallized H_2O molecules existing at the outermost surface of the films were found to play an essential role in wetting the furan blend resin containing a levulinic acid admixture which has functional carboxylic acid groups in the molecules. Thus, the presence of a plentiful supply of polar H_2O groups on a hopeite film surface with a crystal thickness of $\sim 200 \mu\text{m}$ acts as a good spreading key in promoting mobility of the functional resins. The ability of furan coatings to interact chemically with the hopeite surfaces can be modified by incorporating an adequate amount of levulinic acid. Hopeite-to-functional blend polymer chemical affinity is due mainly to the intermolecular attraction resulting from the formation of strong hydrogen bonds, $\text{COO}^- \cdots \text{H}_2\text{O}$, between the carboxylate groups derived from levulinic ester or acid and the water molecules of hydration at the hopeite surface sites.

On the other hand, the addition of an excess amount of levulinic acid transformation is detrimental to the film properties. The characteristics of films exposed to hydrothermal and chemically aggressive fluids at elevated temperatures were observed to change from hydrophobic to hydrophilic. The greatest deterioration occurred when films containing FR/LA ratios of $< 80/20$ were exposed to 30% NaOH at 80°C . This was interpreted as a

severe alkaline hydrolysis brought about by the salt complex formation of $\text{COO}^- \text{Na}^+$ groups yielded by an ionic reaction between the carboxylate anion of levulinic acid molecules and the nucleophilic Na^+ ions released from NaOH . Accordingly, the optimum blend polymer formulation which contains enough functional groups to occupy all the available adsorption H_2O groups on the hopeite surfaces consists of 95 parts furan resin and 5 parts levulinic acid.

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