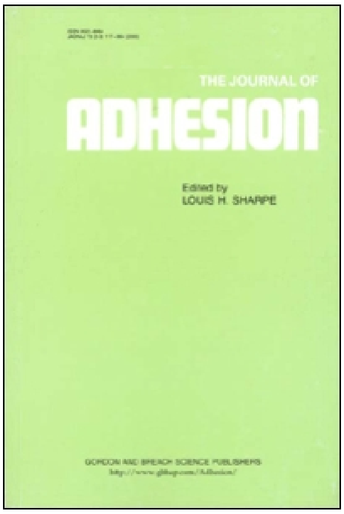

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A Study of Chemical Interactions at the Stainless Steel/Polymer Interface by Infrared Spectroscopy. PART 1: Interaction Mechanisms Between Succinic Anhydride and 304 Stainless Steel

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In order to study, by infrared spectroscopy techniques (FTIR), the interfacial interaction of a polymer functionalized by maleic anhydride, with stainless steel, an analytical methodology has been established. Interfacial chemical interactions of maleic anhydride with stainless steel are simulated through a thin layer of succinic anhydride on a polished metal surface. FTIR spectroscopy (grazing angle) permits a direct access of the interphase for identifying new bonds between organic and metallic compounds. Interaction of succinic anhydride with the polar OH groups of the oxidized metal surface followed a reactional mechanism which can be described by two steps:

- opening of the anhydride ring for reacting with adsorbed water and formation of an acid group (—COOH),
- reaction of the acid group with the hydroxylic function of the metal surface and formation of carboxylate anion (—COO—) groups.

Thermal stability of carboxylate groups is good but the effects of water, studied on thin layers of organic products, show an evolution of the chemical bonds at the reactive interphase. These results have to be compared with the observations of the interactions of polymer on the stainless steel substrate.

KEY WORDS: Interface; stainless steel/polymer interaction; FTIR; durability; failure surfaces; ethylene-maleic anhydride copolymer; model system; effects of moisture; reactions at interfaces.

INTRODUCTION

Stainless steel/polymer combinations are currently on the increase industrially for coatings, but also for sandwich structures where the polymer is used between two sheets of stainless steel. This product possesses good acoustic properties and is chiefly

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destined for applications in domestic electrical equipment. Industrial manufacture is by on-line calendering.

The aim of this study is to improve understanding of the reaction mechanisms occurring at the stainless steel/polymer interface, in order to optimize the quality of the assemblies in terms of adhesion and durability under conditions which will subsequently be those of normal service. The first part of this study shows interaction mechanisms at the reactive interphase, and the second part concerns mechanical properties and interaction products at the steel/polymer interface.

The polymers used are polyolefins copolymerised or grafted with polar groups, giving the polymer the reactivity towards steel necessary to obtain strong bonds. But the procedure described below can, indeed, be applied to any steel/polymer reaction system. In fact, the interactions are studied using monomers having the same reaction functions as the polymers, and the adhesion mechanisms of a complex polymer can be broken down to study the contribution of each reaction.

Maleic anhydride (MA) is often used for the adhesion of polyolefins on a metal substrate, and its part in the process repays close study. This chemical function was, therefore, chosen for the study of interactions with steel. A model was established using succinic anhydride on highly polished 304L stainless steel.

This study takes the stability of the bonds formed between succinic anhydride and stainless steel as a means of studying the longevity of the connections. Two different treatments were applied: the first (200°C in the absence of oxygen) representing the calendering of the polymer between the stainless steel sheets and the second (40°C in a damp atmosphere) representing aging of the sandwich structure during use.

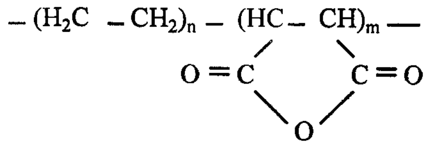
1 EXPERIMENTAL

Materials

The steel employed is a highly polished 304 austenitic stainless steel supplied by Ugine S.A., France. The chemical composition, designation and structure of the 304 stainless steel are given in Table I.

To simulate the functions possessed by polymerized MA, the monomer employed was succinic anhydride.

Ethylene/MA copolymer

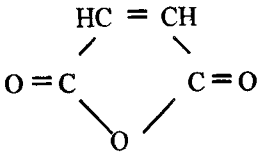


$$-(H_2C-CH_2)_n-(\underset{O=C-O-C=O}{HC-CH})_m-$$

TABLE I
The chemical composition (bulk), designation and structure of the 304 stainless steel.

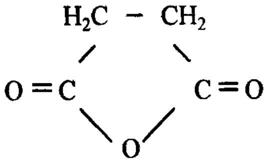
Designation	Structure		Chemical Composition						
			Fe	Cr	Ni	Mn	Si	Mo	C
AISI 304 (18/8)	Austenite	wt%	72	17.4	8.42	1.37	0.49	0.17	0.06
		at. %	71	18.5	7.90	1.37	0.96	0.10	0.23

Maleic anhydride



The double bond of maleic anhydride disappears on polymerization. Its hydrogenated derivative, succinic anhydride, is consequently a better simulator of the active function of the copolymer.

Succinic anhydride



Sample Preparation

The polished surface of the substrate offers a passive layer of a few nanometers thickness whose chemical nature may be defined by reference to the composition of the metal. This passive layer consists mainly of chromium and iron oxides.[1]

The samples were prepared by polishing with 1200 silicon carbide paper and then with diamond paste to obtain a mirror-finish surface with a roughness less than 0.01 µm. This surface preparation was used to provide the highest possible quality of observations by infrared spectroscopy. The sample was then rinsed with THF in an ultrasonic tank.

Thin layers were made by casting dilute solutions of succinic anhydride onto stainless steel surfaces. The succinic anhydride (SA) was deposited on the steel surface from a solution of SA in tetrahydrofuran. The solvent employed is not adsorbed onto the surface of the metal and evaporates rapidly. The thickness of the product was estimated on the basis of the volume of solution deposited on the stainless steel, and its concentration. In this way thin layers from around 1 to over 100 nm can be produced. The relative absorbance of C—H groups (0.1%) is in good agreement with the estimated thicknesses.

IR Analysis

The products of interaction between SA and stainless steel were analyzed by infrared reflection absorption spectrometry. The spectrometer employed was a Nicolet FTIR 740 equipped with an MCT detector. The angle of incidence was 84° and the IR radiation was polarized in the plane of incidence. Two methods of acquisition were employed:

Long acquisition (duration = 6 min)

- 1,000 coadded scans
- 4 cm^{-1} resolution

Fast acquisition (duration = 10 s)

- 32 coadded scans
- 16 cm^{-1} resolution

The second method was used for kinetic observations (1 point every 10 seconds). The spectra obtained showed a fairly high proportion of noise, but were nevertheless usable for our purpose. For both methods, the reference employed was the high polished stainless steel before the deposition of SA.

RESULTS

Identification of the Succinic Anhydride/Steel Interactions

To identify the products of interaction formed at the interface, reference spectra were taken of the acid and the succinic anhydride in solution in tetrahydrofuran to determine the exact position of the vibration bands of the carbonyl group as shown in Figure 1. It is a fact that, according to Do and Baerns[2, 3] who have carried out infrared studies of the interactions of MA on Al_2O_3, the formation of acid is to be expected by opening of the anhydride ring, followed by reactions with the substrate to form a metallic succinate complex. Looking to the IR spectrum of sodium succinate, it is possible to determine the vibration frequencies of the carboxylate bonds (1563 and 1438 cm^{-1} for both antisymmetric and symmetric components).

A layer of succinic anhydride was deposited on a highly-polished 304 L stainless steel surface. Both absorbance modes of succinic anhydride at 1863 cm^{-1} and 1788 cm^{-1} are no longer present but a band appears at 1726 cm^{-1} indicating a carbonyl stretching band of an acid group. This carbonyl stretching band corresponds to the opening of the anhydride ring, which results in the formation of COOH acid functions similar to those of succinic acid, whose vibration band is found at 1737 cm^{-1}. On the other hand, two

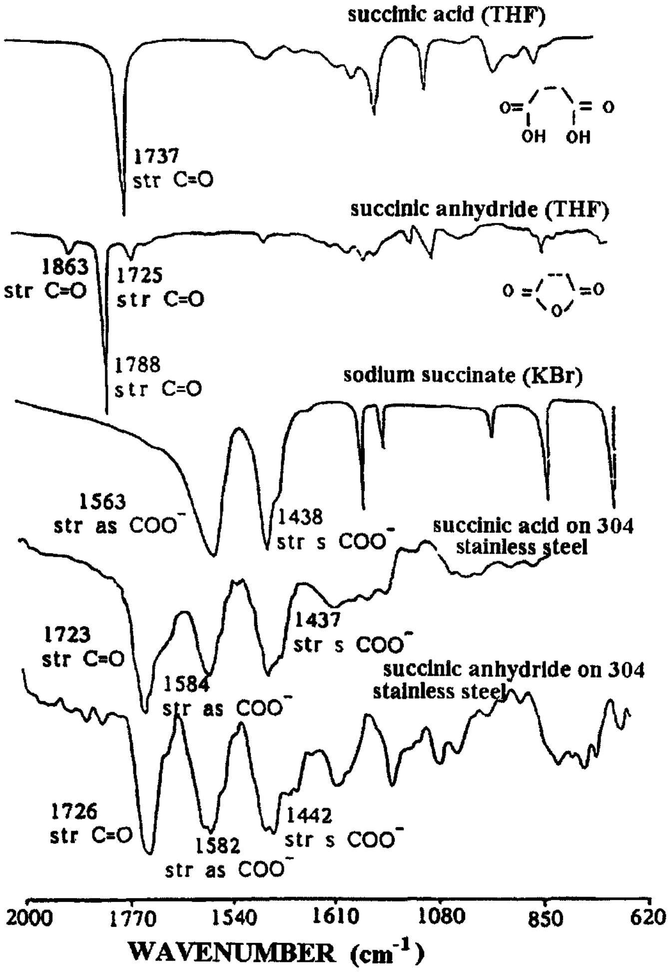


FIGURE 1 Analysis of succinic anhydride/304 stainless steel interactions by FTIR.

peaks appear at 1582 and 1442 cm^{-1} corresponding to the antisymmetric and symmetric stretching bands of carboxylate groups, due to the chemisorption of acid groups on the metal surface.

Deposition of a thin layer of succinic acid on the same substrate was followed by the same interactions characterized by absorption bands at 1584 and 1437 cm^{-1}, which prompts the supposition that the succinic acid may be an intermediate product between the succinic anhydride and the carboxylate.

An absorption band at 1685 cm^{-1} may be connected with the adsorption (hydrogen bond) of the diacid on the substrate. This slide towards low frequencies, already observed by Lorenzelli[4] and Buckland[5] would be typical of an intermolecular bond between the free electrons of the oxygen in the carboxyl and the metallic substrate (coordinate bond). These bonds would not be as strong as the carboxylate bonds.

Kinetic Study of the Interaction between SA and Stainless Steel Surface

In order to improve the understanding of the successive reactions occurring between the succinic anhydride and the stainless steel, the interface was observed over a period of time by IR spectroscopy as soon as the thin layer had been formed. As shown in Figure 2, the first spectrum obtained shows the presence of succinic anhydride, but we observe in the first thirty seconds a slight decrease of the anhydride band at 1785 cm^{-1}, while a vibration band at 1724 cm^{-1} corresponding to the stretching mode of the acid increases. At lower wavenumbers the spectra show the symmetric stretching band of the carboxylate at 1445 cm^{-1}. The antisymmetric vibration rises after a few minutes and remains constant after 5 minutes. The development of the bands for succinic anhydride (1785 cm^{-1}), acid (1724 cm^{-1}) and carboxylate (1585 cm^{-1}) are given in Figure 3, and are associated with an initial thin layer of 1, 5 and 10 nanometers.

Thermal Stability of the Bonds formed

After a thin layer of a few nanometers of succinic anhydride had been deposited on the high-polished stainless steel, the sample was placed in a chamber with a helium atmosphere and heated to 200°C.

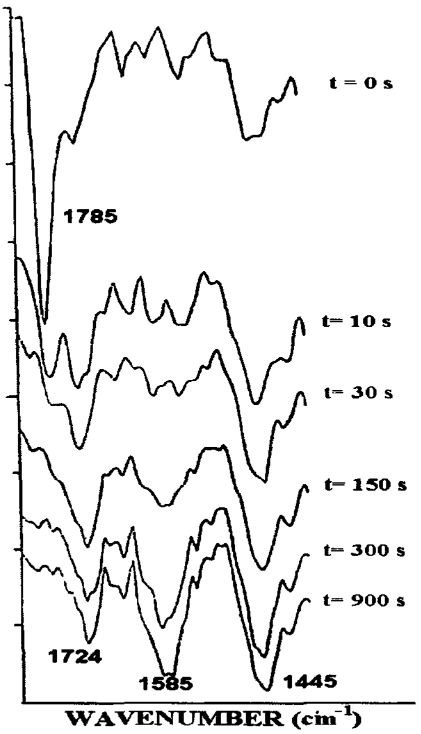


FIGURE 2 Reflection-absorbtion infrared spectra from a 1 nm layer of succinic anhydride absorbed on 304 stainless steel surface as a function of time.

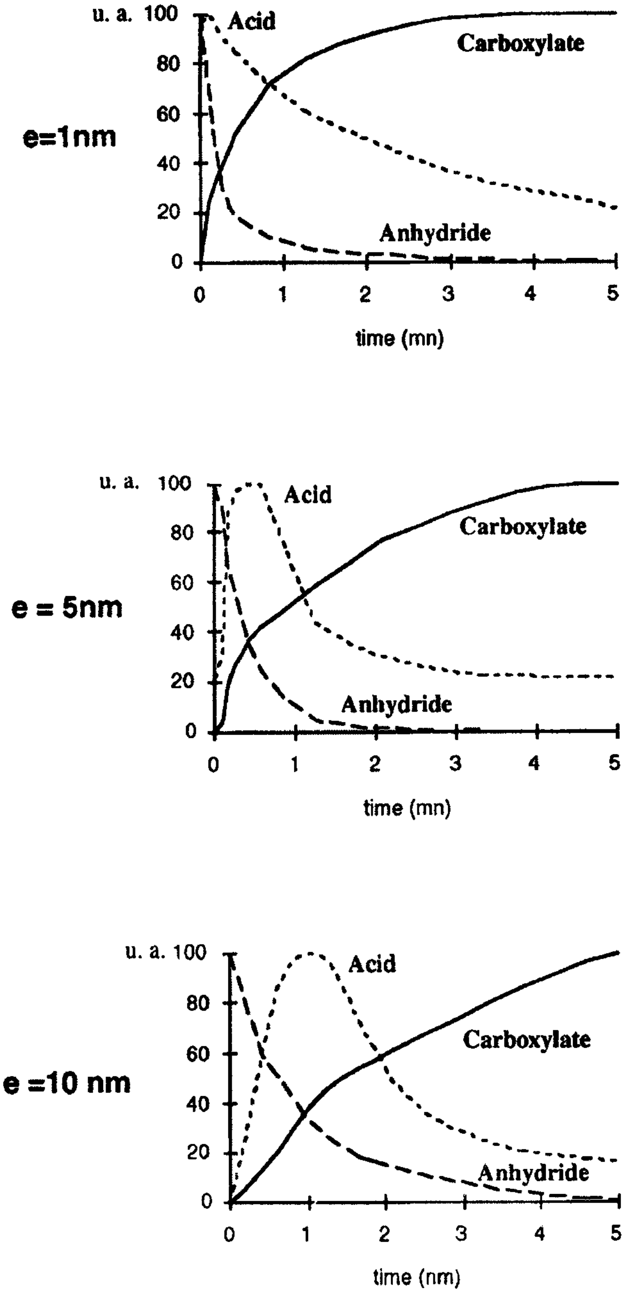


FIGURE 3 Evolution of chemical groups for different succinic anhydride layer thicknesses on 304 polished stainless steel surface as a function of time.

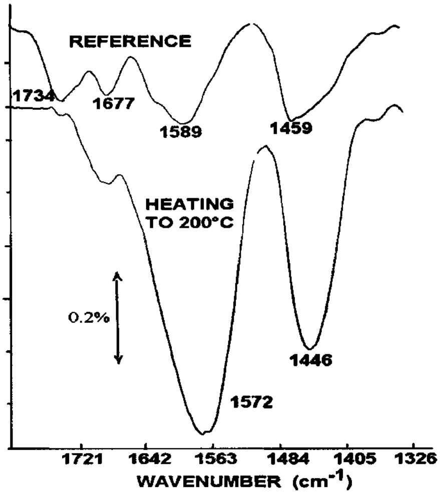


FIGURE 4 Evolution of chemical groups in a thin layer of succinic anhydride on 304 stainless steel after heating to 200°C.

FTIR observations carried out before and after heating are given in Figure 4 and show a complete disappearance of the acid functions and an intensification of the carboxylate bands.

Bond Stability in a Damp Environment

The thin layers of succinic anhydride on stainless steel were subjected to the action of water at 40°C in a damp environment. The different spectra as a function of time are given in Figure 5. The acid forms present disappear very quickly, whereas the carboxylate bonds remain stable for several hours. Then these products disappeared and an absorption band at 1682 cm^{-1} and an OH band (3200–3600 cm^{-1}) increased.

DISCUSSION

The results confirm the hypothesis, previously formulated in the literature,[6] that the anhydride ring opens in proximity to the surface to react with physisorbed water, and leads to the formation of carboxylate bonds with the metallic elements. Indeed, after a few minutes of reaction, the film formed by the deposition of about 1 nm of succinic anhydride on the highly-polished stainless steel is identifiable by three main infrared bands:

1726 cm^{-1}	$\nu C=O$ dissociated acid
1582 cm^{-1}	ν antisymmetric band COO—
1442 cm^{-1}	ν symmetric COO—

The anhydride function has disappeared in favor of acid functions which have not all reacted with the surface. The reaction takes place in two main stages, hydrolysis of the

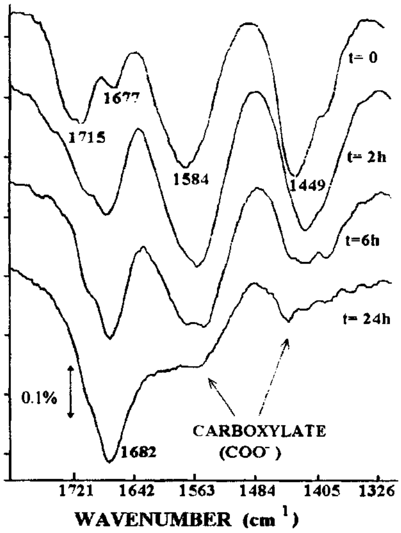
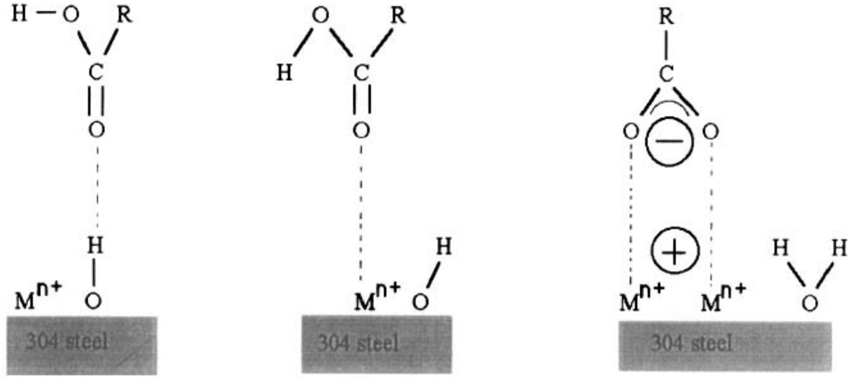


FIGURE 5 Evolution of chemical interactions of succinic anhydride on 304 stainless steel as a function of time at 40°C in a damp atmosphere.

anhydride, then reaction of the acid groups with the metallic oxide. Figure 6 describes in a simplified manner the reaction sequence. The first step is acid adsorption on the surface. Such a bonding will result in a weakening of the O—H linkage of the acid and render it liable to complete rupture. The compound formed by this reaction is a carboxylate, with the two oxygen atoms bonded on the surface in identical configuration. In the case of a metallic oxide, the rupture of the O—H linkage occurs by a simple acid-base reaction. The metallic cation acts as an acid and the oxygen as a base.



physical adsorption coordinated state dissociated chemisorption

FIGURE 6 Reactivity of acid groups with the stainless steel oxide/hydroxide surface.

Do and Baerns[2, 3] studied the adsorption of maleic anhydride on an aluminum substrate and found similar results. Nevertheless, aluminum substrate behavior is different from chromium. Boerio[7] observed physisorbed acid on aluminum after a long contact time. That is not the case with chromium which dissociates acid functions very quickly to form salts at the metal surface.

The film obtained is composed of succinic acid which has not reacted with the surface and of carboxylates, whose frequencies of vibration ($1582\,cm^{-1}$ and $1442\,cm^{-1}$) are very close to those obtained on numerous metals.[8] To determine the metallic elements which are the source of the reaction, and constitute active sites, several "pure" metals have to be tested. However, similarities with the results of Boerio *et al.*[7] on chromium and aluminum substrate are noted. In particular, the same significant shoulder at $1427\,cm^{-1}$ is observed with the chromium, the interactive behavior of which is very different from that of aluminum. So, it seems that several different carboxylate structures are present and may be due to the different metallic elements present at the surface of the polished stainless steel. Ashton *et al.*[9] studied anhydride on nickel using HREELS and attributed the $1420\,cm^{-1}$ band to coordinated species "OCOCO" with the surface.

IR-spectroscopy can discriminate three groups of different interactions:

- monodentate bonding where single and double bonds are clearly distinct
- bridging where each oxygen is bonded to different metallic ions (bridged bidentate)
- monometallic bidentate

There is a difference of $140\,cm^{-1}$ between the frequencies of vibration of the antisymmetric and symmetric constituents of the carboxylate bond. This interval is characteristic of a bridged bidentate.[10, 11, 12]

In the context of the surface dipole selection rule, only vibrational components normal to the surface appear strongly in the spectra. Transition moments for the antisymmetric stretching mode are parallel to the surface and perpendicular for the symmetric stretching mode. It means that if the twofold axis of the carboxylate is normal to the surface, then the symmetric band intensity is much stronger than the antisymmetric one, otherwise the group must be inclined with respect to the surface. For this reason, the ratio between the symmetric and antisymmetric bands allows us to determine the orientation of the group with respect to the surface.

Coming back to Figure 2, showing the formation of carboxylate groups as a function of time, a strong evolution in the relative peak intensity ratio is seen, indicating the changing orientation of the carboxylate groups. As the reaction takes place, the antisymmetric transition rises in intensity. This observation indicates that the twofold axis of the carboxylate group, C_{2V}, should be perpendicular to the surface during the first few seconds and then becomes more inclined as shown in Figure 7. This phenomenon was demonstrated by Allara and Nuzzo[13] and by Dubois[11] *et al.* and is connected with the reorganization of the molecules with the increase of steric hindrance and, hence, interaction between the molecules. It corresponds to a reorientation of the carboxylate group.

The delta frequencies ($\nu_{as} - \nu_s$) remains constant and equal to $140\,cm^{-1}$, so there is no conversion of the bridging structure as a function of time.

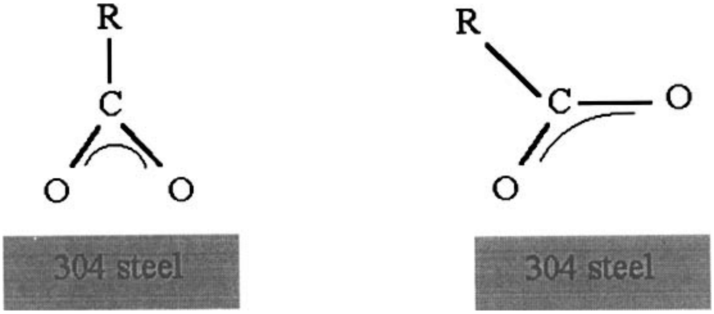


FIGURE 7 Reorientation of carboxylate groups at the stainless steel surface as a function of time.

The kinetics and evolution of chemical groups for these phenomena depend on the initial thickness of the deposit. As shown in Figure 3, the thicker the deposit, the slower the phenomenon of hydrolysis, but the kinetics, of the formation of carboxylates seems to remain constant. This may mean that hydrolysis of the anhydride is a phenomenon occurring throughout the thickness of the film, while the formation of carboxylates is purely interfacial and its kinetics could be limited by the accessibility of available active sites. The residual film after 15 minutes of reaction for different thicknesses shows that the number of sites occupied at 15 minutes, as well as the quantity of residual acid, increases with the thickness of the initial deposit and so grows with the probability of acid encountering a site. However, the intensity of the acid function adsorption band generated by a 10 nm residual film is too weak in relation to the quantity of anhydride deposited. Further experiments have shown that succinic anhydride sublimes on the surface of the metal, at a speed which depends on the thickness of the deposit.

These results considered together enable us to describe the different stages in the evolution of the anhydride. After deposition, the fastest reaction is hydrolysis of the anhydride. The quantity hydrolyzed depends on the thickness, but its duration is limited. This limit may be due either to the presence of a definite quantity of water on the surface or to the fact that the anhydride which is not hydrolyzed sublimes very quickly.

The acid groups react with the metallic surfaces to form carboxylate bonds. The kinetics of this reaction is slow and seems to be limited by the accessibility of active sites on the metal. The acid groups which have not reacted remain on the surface. The carboxylate bonds formed, with energies of 600 to 1,100 kJ/mol[14] are strongly ionic in character. This high bonding energy accounts for the thermal stability of carboxylates.

Experience indeed shows that the carboxylate formed is stable at 200°C. The temperature of decomposition of carboxylates depends on the type of bond formed. For a bridged bidentate structure, Davidov[15] cites the case of the acrylate/vanadium complex, which is stable up to 300°C. In Figure 4, it is shown that after heating to 200°C no absorbancies in the normal carbonyl region are found, indicating disappearance of acid groups. The disappearance of the acid groups as well as an increase in the intensities of the carboxylate bands, which reach a $\Delta R/R$ of 0.7%, suggests that new active sites could be liberated at high temperatures and enabled to react with the acids present. Another explanation for the increase in intensities of the carboxylate bands is related to a change of the oxide layer. Heating to 200°C allows iron oxide to grow and, as the reaction proceeds, more carboxylate species would form and diffuse into the film. The lower vibrational frequencies for both symmetric and antisymmetric stretching bands after heating also indicates a stronger interaction with the oxide surface.

As the aging time at 40°C in a damp environment increases, we observe in Figure 5 a complete shift of the vibrational band from 1715 to 1677 cm^{-1} and a disappearance of both symmetric and antisymmetric modes of carboxylate groups. The progressive disappearance of carboxylate bands as a function of time is due to an hydrolysis phenomenon occurring with carboxylates. However, a peak with an enhanced absorbance at 1680 cm^{-1} associated with OH groups (3200–3600 cm^{-1}) remains after 24 hours. A first explanation for the enhanced adsorption at 1680 cm^{-1} is that dissociated adsorbed acids transform to less stable coordinatively bonded groups. This is a manifestation of a displacement of the acid-base reaction towards the coordinated acid form, and a destruction of the ionic metal/acid bond. Another explanation is that the metal surface develops an hydroxide layer during aging which absorbs IR radiation at the same frequencies. Nevertheless, carboxylate bonds are destroyed in any case after one day in a damp atmosphere at 40°C.

CONCLUSION

The method adopted for the study of steel/polymer interactions was to study by infrared spectroscopy the interfacial reactions as a function of temperature and aging in water of a model interface between succinic anhydride and highly-polished stainless steel. This approach made possible the determination of the different stages in the reaction and the stability of the bonds formed.

Interaction of succinic anhydride with the polar OH groups of the oxidized metal surface followed a reaction mechanism which can be described by two steps:

- opening of the anhydride ring, and subsequent reaction with adsorbed water on the steel surface and formation of two acid groups (—COOH)
- reaction of the acid group with hydroxylic function of the metal surface and formation of carboxylate anion groups (—COO—).

The formation of carboxylates necessitates access to active sites, and this access and their saturation at 20°C takes more than 15 minutes in the case of a small molecule like succinic anhydride. This means that in a polymer, the diffusion rate of the grafts is a significant parameter governing reactivity and adhesion. Assembly of the steel and polymer at high temperatures will favor mobility of the grafts by reducing the viscosity and allow them to react on the active sites whose number can grow with temperature.

Thermal stability of carboxylate groups is good but the effects of water studied on thin layers of organic products show an evolution of the chemical bonds at the reactive interphase. These results have to be compared with the observations of the interactions of polymer on stainless steel substrate.

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