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Chemistry of the Metal-Polymer Interfacial Region

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In many polymer-metal systems, chemical bonds are formed that involve metal-oxygen-carbon complexes. Infrared and Mössbauer spectroscopic studies indicate that carboxylate groups play an important role in some systems. The oxygen sources may be the polymer, the oxygen present in the oxide on the metal surface, or atmospheric oxygen. Diffusion of metal ions from the substrate into the polymer interphase may occur in some systems that are cured at elevated temperatures. It is unclear whether a similar, less extensive diffusion occurs over long time periods in systems maintained at room temperature. The interfacial region is dynamic, and chemical changes occur with aging at room temperature. Positron annihilation spectroscopy may have application to characterizing the voids at the metal-polymer interface.

A QUANTITATIVE CHARACTERIZATION OF THE INTERFACIAL region between a metal and an organic polymer has long been a goal of surface science. Attempts to achieve this goal have reached a new degree of intensity during the past decade, as many industrial products now depend on the integrity of metal-polymer systems. Examples include metallized plastics, metal-polymer laminates such as those used in retort pouches and protective food packaging, corrosion protective coatings for metals, metal food containers with polymer linings, foil-coated products, packaged electronic components, photoresists and other products formed by lithography, and prosthetic devices. Metal-polymer adherence can be destroyed by processes such as the intrusion of water (*1*), by

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electrochemical processes at the interface (*2*), by crack nucleation and growth on the imposition of a tensile stress, and by thermal cycling. Characterization of the interfacial region should allow the design of systems that resist environmental degradation. We summarize some recent work concerning the chemical nature of the metal-polymer interfacial region and outline preliminary results on the detection of voids at or near the metal surface.

Three terms used throughout the text, interface, interfacial region, and interphase, need definition. Interface is the boundary between two phases—the metal, or the oxided metal, and the polymer. Interfacial region is the volume of material slightly below the surface of the metal and extending into the polymer, whereas the interphase is that volume of the polymer that adjoins the substrate. The thickness of this interphase is unknown and is the subject of much research, particularly in the field of composites.

Experimental Approaches

Early efforts to understand the metal-polymer interface attempted to model the system and to determine the energetics of the interaction. Two prominent approaches involved (i) measurement of the contact angle between a liquid polymer and a solid metal surface and (ii) measurement of the adsorption of polymers from solution onto a metal surface. Limited progress was made, because the experimental protocol envisioned the interface as a discrete boundary between the two solids. The experimental emphasis has now changed to studies of real as opposed to model systems. Three major approaches to studying the solid polymer–solid metal interface have received attention recently. One approach is a destructive method based on analysis of the interfacial region after separation by mechanical or electrochemical means. The second approach involves the formation of a layer 1 to 100 nm thick of one component on the second bulk component, after which the chemical species present at the interface are studied. The third method, and the one that we have used, is based on spectroscopic studies of the intact interface. None of the methods, unfortunately, yields unambiguous results, but the collective results of all of these approaches allow us to make a first approximation to a quantitative description of the interfacial region. Our focus is on the nature of the chemical bonding that has been identified in the interfacial region.

Destructive techniques. The chemical nature of the interfacial region can be inferred by studying the polymer side and the metal side after adhesive failure. One method to promote adhesive failure is to damage the coating so that the metal is exposed locally and then to apply a cathodic potential while the coated sample is immersed in an electrolyte. The disbonding that occurs is known as "cathodic delamination." A summary has been given recently of the state of knowledge of this phenomenon for steel coated with polybutadiene (*3*).

A group at Ford Motor Co. has used x-ray photoelectron spectroscopy (XPS) to determine the composition of the metal surface and the polymer surface after cathodic delamination (*4*). They studied the interfacial region, after separation, between an epoxy-ester, an epoxy-urethane, and an epoxy-amine and mild steel. They suggested that polymer degradation occurred at the interface because of the strong alkali generated by the cathodic reaction. Using phosphated steel as a substrate and a range of epoxy coatings (*5*), they confirmed the concept that coatings more resistant to attack by alkali had lower rates of cathodic delamination. As an aside, we think it is more likely that the improvement in performance is a result of lower rates of Na^+ ion transport through the coating (*6*). For epoxy-ester, they noted that the metal surface bore carboxyl moieties as well as ionic carboxylates. These facts, although subject to other interpretations, suggest that the original bonding between the steel and the epoxy-ester was through carboxyl groups.

Watts and Castle (*7*) noted that "when polybutadiene bonds to mild steel it does so by the formation of a discrete chemical interphase," basing this conclusion on the presence of Fe^{2+} in the polymer side of the interface upon cathodic delamination. The composition of this interphase was associated with the role of polybutadiene as a reducing agent for iron oxide. The presence of the reduced metal oxide species was confirmed in emission Mössbauer studies of the intact interface between cobalt and polybutadiene (*8*). Although iron was used in one study and cobalt in the other, the similar chemical properties of these two metals permitted comparison between the results obtained with the two techniques. Adhesive failure occurred during cathodic delamination of an epoxy-powder coating from steel immersed in NaCl solution, and some iron migrated into the polymer (*9*). There was no severe polymer

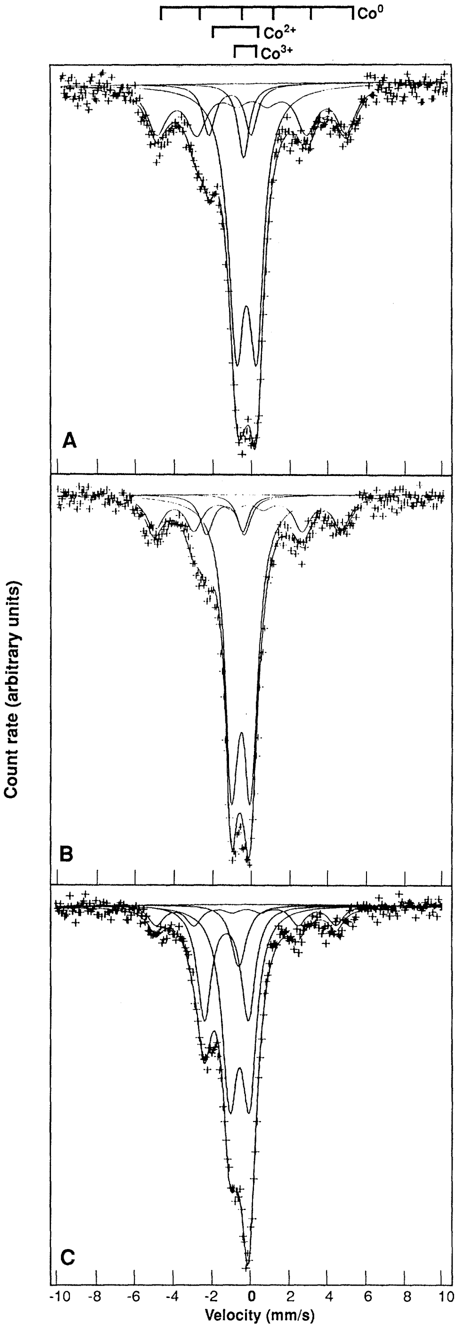

Fig. 1. (**A**) Emission Mössbauer spectrum obtained for a ^{57}Co electrodeposit on a cobalt foil at room temperature. (**B**) Spectrum obtained after coating with polybutadiene. (**C**) Spectrum obtained after coating with polybutadiene and curing for 10 min at 195°C.

modification or degradation at the interface during the disbondment. The mode of failure in this system appeared to be attack of the iron oxide in the high pH solution generated under the coating by the cathodic process.

Studies of metal-polymer fracture surfaces in a high vacuum have been used to understand better the interfacial region. Gettings *et al.* (*10*) applied an epoxy adhesive to an abraded steel surface using a final cure of 180°C for 2¼ hours and then fractured the samples inside the vacuum system of the surface analysis equipment. They proposed that fracture occurred in a region near, but not exactly at, the epoxy-steel interface. However, their data can also be interpreted in terms of diffusion of iron into the polymer with the formation of an interphase containing both iron and polymer. Iron atoms with core-electron binding energies as high as 713.4 eV were detected, and iron was found as deep as 115 nm into the polymer. The species with the high binding energy was not identified, but it was speculated to be a hydrated iron oxide.

Interfaces formed with a very thin layer of one component. Substantial evidence for polymer-metal bonding at the interface has come from measurements of the electronic structure of metals deposited in high vacuum on a polymer substrate. Burkstrand (*11*) evaporated copper, nickel, and chromium onto polystyrene and polyvinyl alcohol polymers. The following evidence obtained from XPS studies indicated that a metal-oxygen-polymer bond existed in the polyvinyl alcohol-nickel and polyvinyl alcohol-chromium systems. (i) The bulk value of the $2p^{3/2}$ core binding energy of nickel on polystyrene was reached at a coverage equivalent to 0.1 monolayer and of chromium on polystyrene was reached at a coverage equivalent to 0.04 monolayer, but the bulk value was obtained with polyvinyl alcohol only after the equivalent of a monolayer of metal was deposited. (ii) The greatest difference in the $2p^{3/2}$ core energy from the bulk value was 0.5 eV in the case of polystyrene but was approximately 2 eV for both chromium and nickel on polyvinyl alcohol. The importance of oxygen in developing the metal-polymer bond was confirmed by noting that the adhesion of copper, nickel, and chromium to untreated polystyrene was poor but was greatly improved when the polystyrene surface was treated with oxygen (*12*).

Evaporated metals adhere poorly to hydrocarbon polymers such as polyethylene or polystyrene. In the fabrication of packaging, adhesion is often improved by subjecting the polymer metal to a plasma discharge. Burkstrand (*12, 13*) subjected polystyrene to a plasma discharge in oxygen; XPS measurements showed that both singly bonded and doubly bonded carbon-oxygen bonds were formed at the surface. The formation of such a complex is consistent with an increased adhesive strength for metals deposited on oxygen-plasma–treated polymer surfaces (*14*). Thus the major type of chemical bond at the interface between a metal such as copper and a polymer involves oxygen.

The bonding of metals to polyimide is of interest because of the use of metal-polyimide systems in electronic device manufacture. Bartha and co-workers at IBM (*15*) have used ultraviolet photoelectron spectroscopy (UPS) and XPS to monitor the electronic structure of aluminum deposited on polyimide while the polyimide was maintained at 300°C during deposition. Material reaction had previously been observed by these workers at the interface for chromium, nickel, and copper. This reaction resulted in the intermixing of the metal and polymer constituents and cluster formation of metal at the interface. The nature of the interfacial bonding depended largely on the chemical reactivity of the metal, as indicated by the decreasing strength of the bonding in the order chromium> nickel>copper. For aluminum it was conjectured that carbon-carbon double bonds were severed by the aluminum to form an aluminum-oxygen-carbon complex. A substantial intermixed aluminum-polyimide zone formed, as well as metallic aluminum clusters, after deposition of aluminum equivalent to 170 monolayers. The aluminum clusters were in turn coated with a thin film that exhibited aluminum-nitrogen and aluminum-carbon bonding.

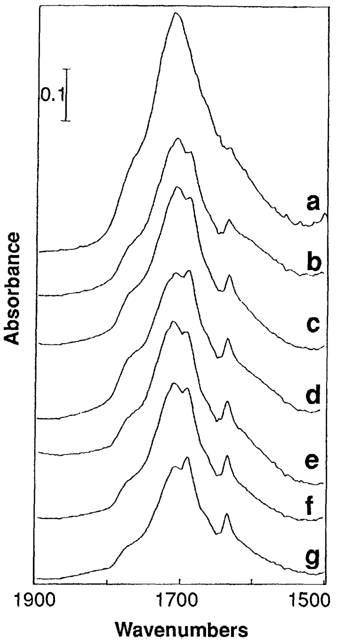

Fig. 2. Carbonyl stretch region of the infrared spectrum of polybutadiene obtained at the polymer-air interface for polybutadiene on (**a**) aluminum and at the polymer-metal interface for polybutadiene on (**b**) cobalt, (**c**) gold, (**d**) copper, (**e**) aluminum, (**f**) chromium, and (**g**) iron.

Atanasoska *et al.* (*16*) used less extreme conditions and evaporated aluminum onto a polyimide. They showed using XPS that aluminum was active at low coverages and that it bonded with carbonyl sites on the polyimide. In the initial reaction stage, aluminum preferentially occupied planar imide rings. These adsorbed atoms transferred charge to carbonyl carbon atoms through oxygen and developed a resonant hybrid state of a carbon-oxygen-aluminum complex. With increasing aluminum coverage, strong aluminum-oxygen bonds were observed and were attributed to a carbon-oxygen-aluminum complex compound.

Studies of the intact interface. Studies of the intact interface in which the metal is the substrate require that any probe signal must pass through the polymer coating or through the metal substrate. Thus the bulk polymer or the metal must not contribute to the signal, or else it should be possible to isolate the signal from the intact interface from that of the bulk constituents. As described above, some workers have avoided this problem by condensing metal vapor in low concentration on the surface of the polymer and then using surface analysis techniques within the same vacuum system to characterize the interaction between the metal and the polymer. This method is pertinent when applying the results to metallized plastics, but it is not appropriate in those cases in which the polymer is applied to a metal substrate already covered with a thin oxide.

We describe two techniques that have proven useful in our own studies: emission Mössbauer spectroscopy and internal reflection infrared (IR) spectroscopy through a thin metal film. Both techniques have their shortcomings, but they can be applied to the same systems in order to determine consistency in interpretation. Emission Mössbauer spectroscopy has the disadvantages that (i) the radioactive isotope must be concentrated at the interface and (ii) it can be applied with relative ease only to cobalt and tin. The internal reflection IR spectroscopic technique has the disadvantages that (i) it must be used with a thin metal film that may have different properties and characteristics than the bulk metal, (ii) the sensitivity to the interfacial region is a function of wavelength, and (iii)

Table 1. Extent of oxidative cure as determined by IR-FTIR for 30-μm polybutadiene applied to several metals. The values for carbonyl absorbance were reduced by dividing by the absorbance of the CH_2 bending mode at 1440 cm^{-1} and were normalized to the sum of reduced absorbances for the spectrum obtained from the outer surface of polybutadiene on aluminum. The reduced carbonyl stretch area integrated from 1850 to 1640 cm^{-1} was obtained by extrapolating the linear portion of the curve to the baseline.

Metal	Reduced carbonyl absorbance			
	1771	1719	1680	Area
Al (outer)	0.17	0.43	0.29	0.87
Au (outer)	0.16	0.42	0.26	0.87
Co	0.07	0.19	0.19	0.38
Au	0.06	0.16	0.18	0.39
Cu	0.06	0.13	0.17	0.36
Al	0.05	0.15	0.16	0.33
Cr	0.05	0.15	0.16	0.32
Fe	0.05	0.14	0.17	0.33

subtraction techniques must be used to obtain spectra heavily weighted with information from the interfacial region. Nevertheless, even with these limitations, the two techniques have provided useful information.

Mössbauer spectroscopy. This technique is dependent upon gamma ray resonance between a source and a standard absorber. In our application of the method (*17*), radioactive ^{57}Co is electrodeposited on a cobalt substrate in an amount equivalent to a monolayer so that a significant amount of the radioactive cobalt is immediately at the surface. Electron microscope studies indicated that the electrodeposit was in the form of small islands so that not all the cobalt was immediately at the surface. This material served as the gamma ray source. In some cases the metallic component was visible in the spectrum as a six-line magnetic component, whereas in other cases the deposit was largely converted to oxide upon termination of the applied potential and exposure of the sample to the atmosphere. In the latter instance, the metallic component was present only as a single paramagnetic line. The spectra to be presented are given in terms of gamma ray absorption (vertical axis) by a reference iron foil and the energy of the gamma ray (horizontal axis) given in terms of the Doppler shift of the reference in millimeters per second.

The Mössbauer spectrum arises from the deexcitation of the daughter ^{57}Fe nuclei. However, the spectrum is representative of the chemical environment of the parent cobalt nuclei because the brief lifetime of the excited ^{57}Fe is short compared with the time required for chemical reactions. However, the valence state of the nuclei from which the gamma rays originate is uncertain since aliovalent states are possible during the lifetime of the excited ^{57}Fe species. This uncertainty does not interfere with interpretations based on changes in the relative fractions of different valence state species nor with interpretations based on the magnitudes of the chemical shift and the quadrupole splitting.

Internal reflection IR spectroscopy. This technique, which uses Fourier transform procedures, has recently been reviewed by Mirabella (*18*). We placed our samples in intimate contact with either a thallium bromide iodide or silicon prism. Two identical samples were used on the two faces of the prism. The bulk polymer spectrum was determined by placing the polymer side against the prism, whereas the interfacial region was sampled by placing the thin evaporated-metal substrate against the prism. The interfacial region spectrum was determined by subtraction of the two spectra. The error range was determined by disassembling and reassembling the polymer on the prism and retaking the spectrum five to ten times.

Spadafora and Leidheiser (*19*) correlated the water disbondment properties of metal-coating systems with data from IR spectroscopy; systems that showed chemical bonding also showed excellent resistance to disbondment when the coated metal was immersed in water. These data, although not indicative of behavior of all systems, suggest that chemical bonding between the metal and the polymer reduces the likelihood of water intrusion at the interface. Baked coatings in general are more resistant to water disbondment than room-temperature–cured coatings on metals.

Reflection IR studies of the interfacial region between a solid substrate and polymer have been pioneered by Allara, who noted that carboxylate groups formed after oxidation of a thin poly(1-butene) film on copper (*20*) and that adsorbed layers of poly(acrylic) acid were bonded to an aluminum oxide surface through carboxylate ions (*21*).

Bonding in the Cobalt-Polybutadiene System

As an example of the use of these techniques, some measurements of the cobalt-polybutadiene systems will be given. An early study by Leidheiser, Musić, and Simmons (*8*) showed that reduction of CoOOH to Co(II) species occurred coincidently with the curing of polybutadiene on the metal. This experiment has been repeated with a much thinner electrodeposit to enhance interfacial sensitivity. In Fig. 1 are the spectra obtained for the substrate prior to application of the polybutadiene (Fig. 1A), after polybutadiene application but before cure (Fig. 1B), and after curing (Fig. 1C). The spectra reveal that a large fraction of the electrodeposit exists as CoOOH with minor contributions from superparamagnetic metallic cobalt and $Co(OH)_2$. The spectrum shown in Fig. 1B is little different from that of the uncoated electrodeposit, except that there is a modest increase in the trivalent species. In Fig. 1C the cured sample shows diminished intensity of the trivalent CoOOH species with a concomitant increase in the divalent species. Thus, the reduction of Co^{3+} to Co^{2+} occurred presumably in a concurrent manner with the oxidation of the polybutadiene at the interface.

A cobalt species that diffuses into the polymer would be expected to have a lowered recoil fraction and might escape detection. A spectrum of the sample shown in Fig. 1C was then taken at 78 K and revealed the presence of two divalent species. One species was practically identical to the divalent species found in the room-temperature spectrum and was identified as $Co(OH)_2$. The other species with a quadrupole split of 1.80 mm s^{-1} was consistent with values for carboxylate species, 1.72 mm s^{-1} for $CoC_2O_4{\cdot}H_2O$ and 1.55 mm s^{-1} for CoC_2O_4, as determined by Friedt and Asch (*22*). This temperature dependence suggests that the carboxylate species is largely on the polymer side of the interface.

These observations show that a chemically active cobalt surface is in contact with polybutadiene under the cure conditions used and that the most likely mode of interaction between the cobalt and the polybutadiene is through carboxylate groups on the polybutadiene. The results are consistent with those of Watts and Castle (*7*), who analyzed delaminated polybutadiene-copper interfaces by XPS and noted the presence of carboxylate groups, and those of Hammond *et al.* (*4*), who also detected carboxylate groups at the metal-polybutadiene interface.

Several investigators (*23–25*) have claimed that greater degrees of cure of polybutadiene can be obtained at the metal or metal oxide interface than for the bulk polymer. These studies, however, are not representative of practical coating thicknesses. Dickie and co-workers (*24*) studied the oxidation of 100-nm-thick coating on gold, chromium, and steel by a reflection-absorption IR technique. Gold substrates yielded polybutadiene films with the least oxidation, whereas steel promoted the oxidation with the formation of esters. Cullis and Laver (*25*) studied the catalysis of polybutadiene curing

Table 2. Percent of cation species in interfacial region between cobalt and various polymer coatings.

Coating type	As electro-deposited		After appli-cation		After curing or storage for 3 months	
	Co^{2+}	Co^{3+}	Co^{2+}	Co^{3+}	Co^{2+}	Co^{3+}
Epoxy amine	18	68	22	66	30	62
Thermoplastic acrylic	18	70	18	74	7	85
Vinyl ester	12	72	19	76	24	67
Silicone alkyd	13	76	8	78	37	50
Polybutadiene*	4	71	5	67	38	38

*Cured

Table 3. Positron annihilation measurements in four coatings.

Coating	Positrons annihilated in large voids (%)
Powder epoxy	11
Epoxy #2 (solvent)	21
Epoxy #3 (solvent)	15
Epoxy #4 (solvent)	17

by several metal oxides. They used ultrathin coatings and determined the weight gain as a function of temperature. The temperature at which the weight gain occurred was taken as a measure of the catalytic activity of the metal oxide, with lower temperature indicating greater activity. Molybdenum and cobalt oxides were the most effective catalysts.

To produce more faithfully the interfacial condition under coatings of practical thickness, we performed IR studies using thin metal films as substrates. The carbonyl region for the spectra obtained from 14-μm-thick polybutadiene films is shown in Fig. 2. An oxidative index was assigned to each of these spectra by taking the ratio of the integrated peak absorbances for the CO stretch at 1771, 1719, and 1680 cm^{-1} to that of the CH_2 bend at 1440 cm^{-1} (Table 1). The relative order of activity for cure at the substrate interface was approximately the same as that observed by Cullis and Laver (*25*), who found cobalt oxide to be very active, copper oxide moderately active, and aluminum, chromium, and iron oxides less active. These experiments confirm the active role of the substrate in the oxidative cure of polybutadiene. The presence of carboxylate at the interface was also inferred from the difference spectra.

Bonding in the Cobalt-Polyimide System

The internal reflection IR spectra obtained for polyamic acid (PAA, precursor of polyimide prior to cure) at the air and metal interfaces were used to determine a difference spectrum (*26*). Both negative and positive peaks were observed, and both interfacial spectra exhibited the stretching and bending modes characteristic of PAA. Differences between the two spectra are subtle and may arise from interaction with the metal substrate, from differences in the relative concentrations of functional groups, or from orientation effects. The difference spectrum reveals a positive peak at 1377 cm^{-1}, which is indicative of a C–N stretch for polyimide and suggests a high degree of imidization of the polymer in the interphase. Negative peaks at 1528 and 1410 cm^{-1}, which are consistent with amide and acid functionalities, also indicate that imidization is enhanced at the cobalt interface relative to the air interface. Spectra obtained on PAA-coated samples aged for 11 months at room temperature indicated increased imidization. The change in the Mössbauer spectra prior to and after the application of PAA to the cobalt substrate showed that chemical reaction occurs. The difference spectrum obtained in the IR studies also supports this conclusion.

The IR spectra generated for polyimide on cobalt clearly show that imidization occurred. Spectral features characteristic of acid and amide functionalities decreased in intensity, whereas the carbonyl stretches for imide groups increased. The spectrum recorded at the cobalt-polyimide interface revealed a shoulder at 1670 cm^{-1}. The difference spectrum revealed this shoulder as a peak at 1651 cm^{-1}, which is interpreted as a higher concentration of acid groups in the polymer in the interphase than exists at the outer surface of the polyimide. The asymmetric carboxylate stretch absorbance is noted at 1584 cm^{-1}, and a peak at 1397 cm^{-1} is attributed to the symmetric carboxylate stretch.

The concentration of isoimide at each interface may be approximated by the method of Gay and Berr (*27*) by taking the ratio of the intensities of the C–O stretches for isoimide and imide. The spectra yield isoimide concentrations of 4.8 and 3.8% by volume at the air and metal interfaces, respectively. The bulk value is 3% (*28*). The higher concentration of isoimide at the outer surface of polyimide is not inconsistent with the 8% surface concentration reported by Gay and Berr from XPS measurements (*27*).

In view of the reactivity of polyamic acid with cobalt, a thicker electrodeposit was used for studies of the interfacial region by the Mössbauer technique. These previously reported studies (*17*) give strong evidence for the presence of carboxylate species in the interfacial region, in agreement with the IR measurements.

Changes in the Interphase Region on Aging

The chemical nature of the interfacial region changes with time, since the ability to resist interfacial disbonding by water improves in some systems upon aging at room temperature. This effect may be due to the evaporation of residual solvent from the interphase, changes in the conformation of the polymer in the interphase, or the development of chemical bonding. Emission Mössbauer spectra show that changes in the chemical nature of the interfacial region occur both on curing at elevated temperature or storage for 3 months at 50% relative humidity and room temperature. A very thin electrodeposit of ^{57}Co was electrodeposited on a cobalt metal sheet. The cobalt was coated with a polymer, and the emission spectra were analyzed to determine the amount of divalent and trivalent species (i) before application of the polymer, (ii) after application of the polymer, and (iii) after curing (polybutadiene) or after storage at 50% relative humidity and room temperature for 3 months (Table 2). Note that the percentage of divalent species increased after curing or storage in four cases and decreased in one case. These data represent convincing evidence that chemical changes do occur in the interfacial region upon high-temperature cure or after room-temperature aging.

Morphology of the Polymer-Metal Interface

The comments that follow apply to a specific type of system—a polymeric protective coating on a metal. The morphology of a metal prior to application of the coating is often complex and largely dependent upon the pretreatment operations that are performed. Abrasion, sand-blasting, welding, chemical etching, and such all affect the morphology of the surface. Chemical cleaning processes, exposure to the atmosphere, and the character of the water used for rinsing all affect the chemistry of the surface. We confine our remarks to the morphology of the surface of the metal. This surface is exceedingly rough on the 1- to 100-nm scale, as indicated by electron microscope studies, and is generally also rough on the 400- to 1000-nm scale. The latter roughness is a consequence of indentations at grain boundaries, inadequate wetting between inclusions and the metal matrix, embedded abrasive particles, facets formed by preferential etching, pits formed by etching, and so forth. The ability of the polymer to wet such a surface and form an intimate bond within the crevices, pits, and indentations in the surface is determined by the rheology of the polymer and surface chemistry of the system. In many systems imperfect wetting causes small voids at the interface. Such voids may serve as nucleation sites for the condensation of aqueous-phase water when the system is exposed to high relative humidity or upon immersion in an aqueous solution. The importance of interfacial voids is recognized, but detecting and measuring them is difficult. A secondary problem is the lack of knowledge of the dimensions of the voids and a lack of knowledge of the minimum number of water molecules that constitute an aqueous phase. The latter is especially significant because electrochemical processes, such as corrosion, require an aqueous phase.

Positron annihilation measurements are remarkably sensitive to the size of vacancies within a metal matrix. Initial experiments with several commercial coatings indicated that changes in the positron annihilation spectra upon exposure of the coated metal to water correlated well with the ability of the coatings to prevent corrosion of the substrate (*29*).

The major problem with the analysis of positron annihilation spectra is the lack of knowledge concerning the mechanism by which the positron annihilates within a polymer matrix. When positrons are implanted in polymeric coatings, their lifetimes fall in three different ranges, a short lifetime (~200 ps), an intermediate lifetime (~500 ps), and a long lifetime (~2500 ps). The physical processes responsible for the two shorter lifetimes in polymeric materials are not firmly established, but the long lifetime is associated with the formation of orthopositronium (the bound state of an electron and a positron) within voids in the polymer matrix. The chemical nature of the polymer also has an important effect on the value of the mean lifetime and the values of the individual lifetimes. Data are presented in Table 3 for the percentage of positrons that annihilate with the long lifetime, that is, in the voids, for four epoxy coatings. The powder epoxy coating did not contain any solvent, and the high temperature would be expected to permit better consolidation of the coating. If this interpretation based on voids is correct, then where are they located? Are they uniformly distributed throughout the coating or concentrated at the metal-coating interface? A typical unpigmented polymer coating requires a thickness of 600 μm to cause annihilation within the polymer of almost all the positrons formed from the decomposition of ^{22}Na. Thus, for thicknesses less than this value, the annihilation spectrum is the sum of the annihilation processes in the polymer and in the substrate metal. Knowledge of the annihilation parameters for the substrate metal and an infinitely thick coating as well as of the backscatter properties of the interface permit the spectrum to be calculated for any coating thickness. In some systems the calculated spectrum and the experimental spectrum agree. In others, the calculated spectrum departs significantly from the experimental spectrum as the coating is decreased in thickness; the concentration of voids at the interface may be greater than in the polymer (*30*). Studies now under way will seek to correlate electrochemical impedance spectra of coatings with the positron annihilation with special reference to changes that occur as a function of temperature.

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