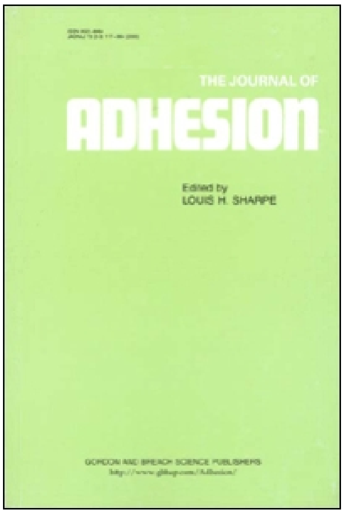

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A Study of Chemical Interactions at the Stainless Steel/Polymer Interface by Infrared Spectroscopy. Part 2: Mechanical Properties and Study of the Interphase

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A Study of Chemical Interactions at the Stainless Steel/Polymer Interface by Infrared Spectroscopy. PART 2: Mechanical Properties and Study of the Interphase

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The interaction of a thermoplastic ethylene-maleic anhydride copolymer with stainless steel has been studied by infrared spectroscopic techniques (FTIR). The aim was to improve understanding of the reaction processes at the steel/polymer interface in order to optimize the quality of assemblies in terms of adhesion and durability under the conditions which will subsequently be those of normal operation.

Steel/polymer associations have been tested after being submitted to several different conditions of treatment and aging in order to understand the various phenomena which occur at the steel/polymer interphase.

Mechanical behavior improves after heat treatment, and similar conclusions can be transposed to the structure after use, such as in domestic equipment. Modifications in interactions between stainless steel and polymer are caused first by the chemical reactivity of anhydride functions, and second by the mobility of organic chains which reorganize at the interphase.

Analysis of failure surfaces shows several correlations between the mechanical behavior and the chemical nature of residual polymer on the metal substrate. Localization of failure depends on aging conditions and can be explained by minimization of interfaical energy between the polar structure of the metal surface and the organic chains.

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

INTRODUCTION

Stainless steel/polymer combinations are currently on the increase industrially not only 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 destined for applications in domestic electrical equipment and in the building trade. Industrial manufacture is by on-line calendering.

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The aim of this study is to improve understanding of the reaction processes at the stainless steel/polymer interface in order to optimize the quality of the assemblies in terms of adhesion and durability under the conditions which will subsequently be those of normal operation. Such optimization can be achieved either by acting upon treatment conditions, or by selecting functional polymers with better performances.

In Part 1 of this study (see previous paper, this issue), analytical procedures were established for the interaction processes at the reactive stainless steel/polymer interface. The study used a model molecule of succinic anhydride deposited onto steel surfaces in very thin layers to simulate the behavior of maleic anhydride. Maleic anhydride is wedely used by grafting or copolymerization to improve adhesion of polyolefins on metal substrates.

In this second part, stainless steel/polymer assemblies were studied. The purpose was to study the mechanical behavior of the interface as a function of treatment and aging conditions, in order to understand the chemical and physical processes generated in the stainless steel/polymer interface. The polymers used were ethylene copolymers and polar monomers which make polyolefins reactive with steel.[1, 2]

To quantify adhesion and characterize the failure pattern, specimens underwent T-peel tests, and failure surfaces were analyzed by infrared reflection absorption spectroscopy. The FTIR spectra could be exploited best, as indicated by the results obtained during testing with a model molecule; thus it became possible for the conditions of preparation and aging of assemblies to be correlated with their mechanical behavior and the physical and chemical nature of the interphases.

EXPERIMENTAL

Materials

The substrate used for the mechanical peel tests was an austenitic stainless steel 304 RB with a thickness of 0.19 mm and was supplied by Ugine S.A., France. The chemical composition of this stainless steel was given in the previously published Part 1 of this study.

The polymer used was a 200 μm thick Lotader 3410 film. This terpolymer is produced by copolymerization of ethylene, acrylic ester (15%) and maleic anhydride (3.5%), and has a softening point of 63°C (VICAT 9.81 N). Its glass transition temperature is lower than 0°C. The polymer was supplied by the Atochem Research Center in Serquigny, France.

Preparation of Peel Specimens

The peel specimens were made in a press with heated plates to the dimensions as defined by various Standards (NFT 76 001, ASTM D 1876, ISO 4578), that is, 25 mm × 200 mm. Assembly pressure was 2 MPa, and the temperature measured on the substrates was 200°C. The press was preheated to 230°C which means that the temperature build-up time of the specimen was 100°C/min. As soon as a temperature or 200°C had been reached, pressure was applied for 30 seconds or 10 minutes, according to test requirements. The specimens were kept either at 20°C ambient temperature, or at 70°C in an oven for 10 days, before being tested. The various specimen production cycles are given in Table I. Four peel specimens were made for each production cycle.

Mechanical Tests

T-peel tests were performed on a tensile machine at a loading speed of 100 mm/min. The peel strength resulting from the test is the average peeling load per unit of specimen width required to separate the two materials progressively. This average is computed on the force/displacement curve, corresponding to a steady crack propagation over 100 mm. The peel strength thus measured not only balances the adhesive forces, but also the forces linked to a viscoelastic dissipation energy within the polymer as well as the forces used to bend and unbend the stainless steel strips.[3] However, this peel strength can be considered as a function of the adhesive force, and be correlated to a chemical analysis of the interface.

Failure Pattern Characterization

Since failure is in the interfacial region, failure patterns have to be observed by fine analytical methods, such as infrared spectroscopy,[1] suitable for identifying polymer residues thinner than one micron. The failure surfaces were analyzed using FTIR at a grazing angle of 84°, and with a beam polarized parallel to the incidence plane (mode p) over a specimen length of about 30 mm, which gives a representative result of the adhesive behavior of the assembly.[4] The spectrophotometer was a Nicolet FTIR 740 with an MCT detector, with a resolution of 4 cm^{-1} and an analysis time of 6 min.

RESULTS

IRAS Analysis of Failure Patterns

Figure 1 shows characteristic spectra between 1350 and 1900 cm^{-1} of the samples after peeling and for different aging conditions. Moreover, a reference spectrum of a thin layer of polymer is given at the bottom of the figure. The film thickness is estimated to be 200 nm by the method used in Part 1 of this study. So the average thickness of all residual polymer film left on the surface after peeling can be considered to be below

TABLE I
Thermal treatment conditions

Experimental conditions	Heating Time (s) at 200°C	Aging Temperature	Aging Time
A	30	20°C	1 day
B	600	20°C	1 day
C	30	20°C	10 days
D	600	20°C	10 days
E	30	70°C	10 days
F	600	70°C	10 days

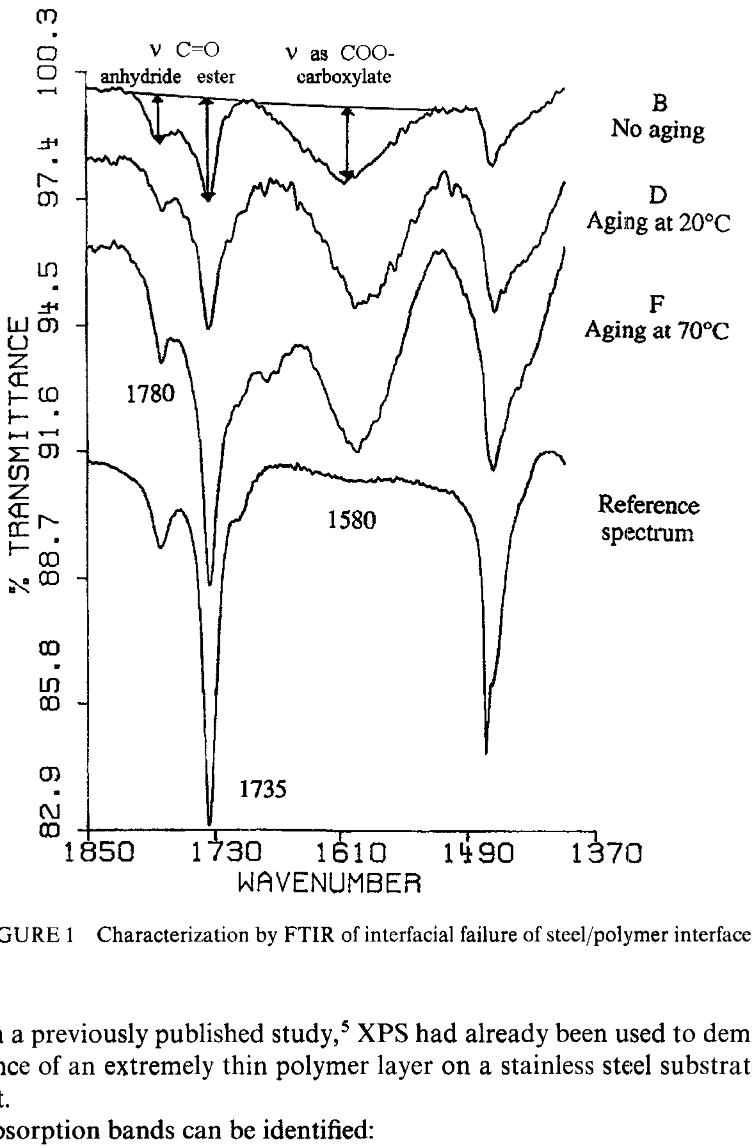

FIGURE 1 Characterization by FTIR of interfacial failure of steel/polymer interface.

200 nm. In a previously published study,[5] XPS had already been used to demonstrate the existence of an extremely thin polymer layer on a stainless steel substrate after a T-peel test.

Four absorption bands can be identified:

- an absorption band at 1780 cm^{-1} due to the anhydride function
- an absorption band at 1735 cm^{-1} related to the presence of acrylic ester (carbonyl),
- an absorption band at 1580 cm^{-1} typical of an asymmetric stretching band of carboxylate bonds (COO—)
- an absorption band at 1450 cm^{-1} due to a symmetric stretching band of carboxylate bonds and also to CH_2 bonds, which make it difficult to analyze.

The forming of carboxylates, observed with succinic anhydride and 304L polished stainless steel in Part 1, is thus detected in the same manner at the stainless steel/polymer interface. On each spectrum four parameters can be correlated to the mechanical peel strength as a function of assembly preparation conditions; they are:

- $\Delta R/R$ anhydride ($1780\,cm^{-1}$)
- $\Delta R/R$ carboxylate ($1580\,cm^{-1}$)
- $\Delta R/R$ ester ($1735\,cm^{-1}$).
- $\Delta R/R$ anhydride/$\Delta R/R$ ester

As a first approximation, the relative absorbance of the ester band is correlated with the thickness of the polymer film. The ester level within the polymer is assumed to be homogeneous. The anhydride proportion at the interphase is estimated by computing the absorbance ratio of the $1780/1735\,cm^{-1}$ bands. Surface adsorption or chain migration can change the ester content within the interfacial layer; however, looking at the small concentration of maleic anhydride (3%) relative to the ester concentration (18%) and noting that the ester absorbance varies by a factor 8, while maleic anhydride absorbance due to the enrichment at the interface varies by a factor 3, the estimation of the film thickness using the ester band can be taken as reasonable.

Carboxylate species may come from the ester groups, and this is particularly true with metals such as copper. However, interactions of ester groups on stainless steel surfaces have not shown any formation of carboxylate species. It is also known that adhesion of a polymer such as EVA with no acid functions is very low. The intensity of the ester band near $1735\,cm^{-1}$ was measured and it remains constant at around 10%.

IRAS Analysis of the Failure Pattern on Mechanical Specimens

Table II shows the average results for each aging condition. The mechanical behavior of stainless steel/polymer assemblies in relation to the maleic anhydride concentration within the interphase is given in Figure 2. The peel strength decreases as the relative maleic anhydride quantity measured at the interphase increases. As can be seen, the maleic anhydride concentration at the interphase is far higher than that in the adhesive film, which is 0.22 before coating the steel substrate. The various aging treatments at 20°C and 70°C tend to lower the quantity of maleic anhydride at the interphase.

Figure 3 shows that the peel strength increases with the increase of the carboxylate content, which is facilitated by aging at 20°C and 70°C.

Figure 4 shows the peel force as a function of the relative absorbance of the carbonyl bonds of the ester. At low $\Delta R/R$ values the failure tends to be of the adhesive type and

TABLE II
Effect of temperature on adhesion measurements and interface compounds

Experimental conditions	Peel strength N/mm	$\Delta R/R$ (%) Ester	$\Delta R/R$ (%) Anhydride	$\Delta R/R$ (%) Carboxylate	Ratio Anhydride/Ester
A	0.53	1.5	0.6	0.7	0.38
B	1.25	1.6	0.8	1.6	0.47
C	1.77	6.2	1.8	2.35	0.29
D	1.98	4.5	1.5	3.1	0.33
E	2.55	7.3	2.3	3.4	0.31
F	2.96	7.7	2.3	3.1	0.30

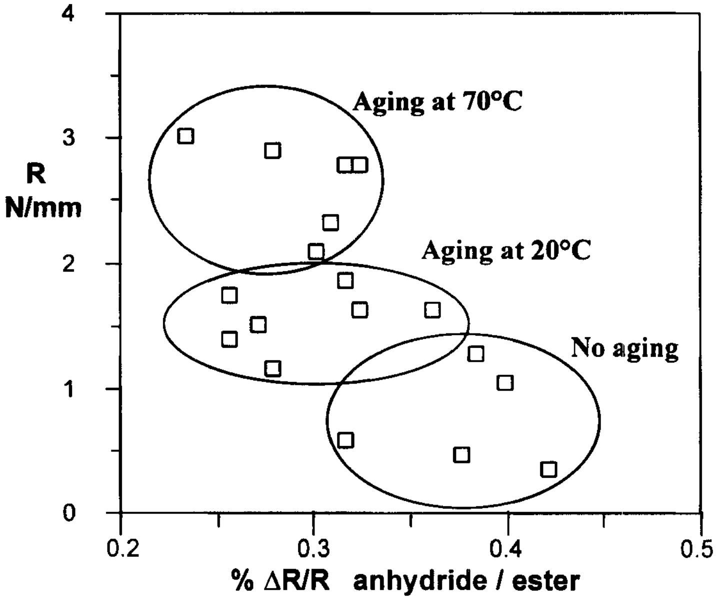

FIGURE 2 Mechanical behavior of stainless steel/polymer interface as a function of anhydride concentration at the interphase (initial anhydride/ester ratio in the adhesive film is 0.22).

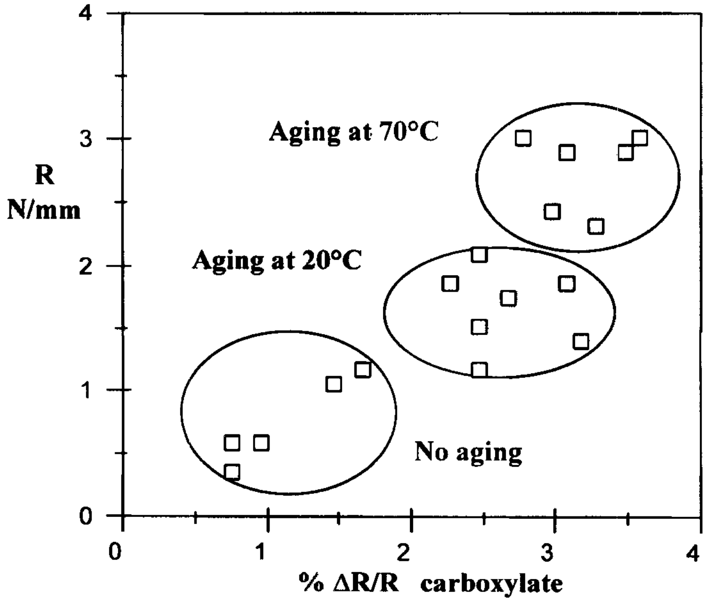

FIGURE 3 Mechanical behavior of stainless steel/polymer interface as a function of carboxylate formation at the interphase.

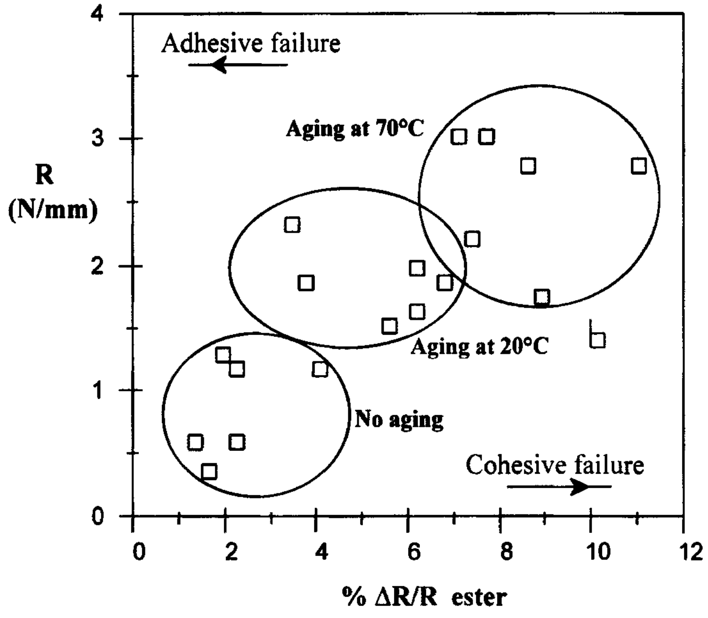

FIGURE 4 Effect of aging on failure of stainless steel/polymer assembly.

the peel force is small while at high $\Delta R/R$ values the failure tends to be of the cohesive type and the peel force is higher. It can be noted that aging increases the quantity of polymer left on the stainless steel substrate. This effect gains in strength as the aging temperature is raised. Good correlation can further be established between increased peel strength and the thickness of the polymer deposit remaining on the substrate after failure.

DISCUSSION

Reaction Phenomena of Succinic Anhydride on Stainless Steel

Identification of absorption bands in the FTIR spectra obtained from the analysis of a thin coating of succinic anhydride on a polished 304 steel substrate has been studied as described in Part 1 of this study. The reaction includes two main steps:

- anhydride hydrolysis and formation of acid groups on the metal surface
- reaction of acid groups and formation of carboxylate anion (—COO) groups.

During carboxylate formation, a phenomenon of molecular reorientation at the substrate surface can be observed as a function of time, pointing to a steric hindrance and, consequently, increasing interactions between molecules. This leads to reorientation of the carboxylate group as shown by FTIR. Reaction of chemical functionalities with the metal is not immediate; that tends to show that assemblies would evolve after pressing at 200°C.

Reaction Phenomena in Stainless Steel/Polymer Assemblies

First of all, carboxylate formation is noted to be high and only compares with the quantities observed for succinic anhydride reaction on stainless steel if the specimens have been heat treated at 200°C. A first explanation is that the oxide is modified by heating at 200°C. We know[6] that this treatment induces a chemical change (Cr/Fe ratio) of the oxide composition, desorption of surface contamination or modification of the oxide roughness. A second hypothesis is that the reactivity of the anhydride is enhanced by heating at 200°C. This is less probable because results show also an enhancement of the relative absorbance of carboxylate bands during aging at 20°C and 70°C.

The specimens showing the highest anhydride concentration exhibit the lowest strength and were peeled off without aging. After 10 days at 20°C this anhydride concentration has considerably diminished while strength increased. The highest strength values can be measured after 10 days at 70°C (Fig. 2). It can further be noted that longer treatment at 200°C (10 min instead of 30 s) leads to higher mechanical strength as shown in Table II.

The higher maleic anhydride concentration found at the interphase, than within the coating, shows that during treatment at 200°C polar anhydride functions are attracted by the metal surface with which they may react. This phenomenon can be explained by the minimization of interfacial energy between the polar structure of the metal surface and the organic chains.[7]

During this exchange the anhydride functions integrated into the macromolecular chains will carry the latter along to the substrate; at 200°C such migration will be much higher if lasting for 10 min than for 30 s. These functionalities do not all react with the substrate at 200°C, and the assembly strength remains low. After 10 days, however, those functionalities close to the substrate have reacted and mechanical strength is much higher. The higher the aging temperature (70°C), the more mobile the polymer chains and the higher the adherence. Diffusion and chain migration are helped by the high temperature curing while chemical interactions take place during aging at 20°C or 70°C at longer time.

This hypothesis is confirmed by evaluating the thickness of the polymer remaining after failure. Since the anhydride functions have reacted, their concentration in the interphase is lower (Fig. 2). The number of carboxylate bonds is higher (Fig. 3) after aging, and increases with temperature, so that the peel strength increases in relation to the number of carboxylate bonds. Failure location is further removed from the substrate as strength increases (Fig. 4). Once the carboxylate bonds have formed, the rupture spreads beyond the macromolecular chains which are "anchored" to the substrate into a low cohesive strength region.[8, 9] Failure propagation before and after aging is shown graphically on Figure 5.

If bonds have not formed (before aging), failure spreads within an interfacial area where some macromolecular chains are and some are not yet "anchored" by anhydride reaction. The anchored ones remain bonded to the substrate while the unanchored ones, which are not bonded to the substrate but only interlaced into a polymeric amorphous structure, make up the crack propagation area. The coating remaining on the substrate is very thin, and it shows an anhydride enrichment since macromolecular chains have migrated and anhydride functions have not yet reacted. The chains which

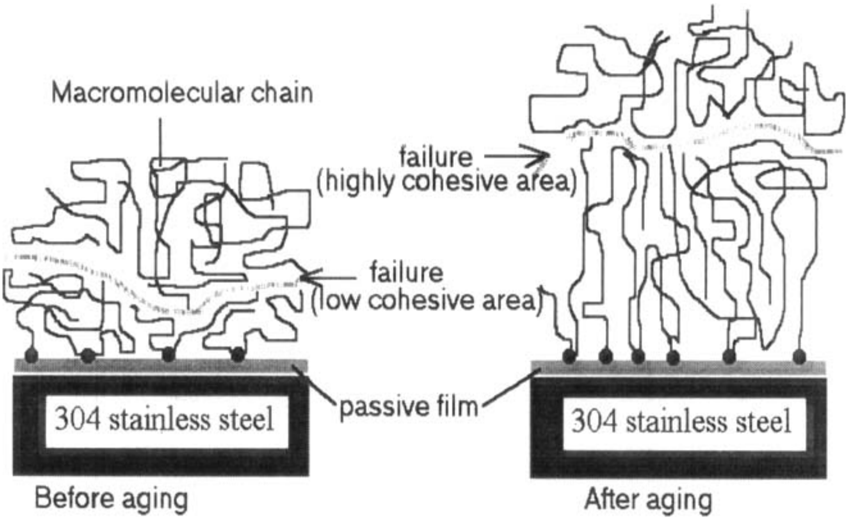

FIGURE 5 Physical and chemical interaction processes at the stainless steel/polymer interphase.

have easily migrated during the first moments of heating are the shortest ones; consequently, the enrichment which can be observed might be faster, though leading to a coating of low cohesive strength, which explains why failure is very close to the substrate. Short chains make a thin but strongly cohesive coating between the substrate and the weakly cohesive polymer.

Table II also shows that the differences in mechanical strength due to the 200°C treatment time (*i.e.* 30 s or 10 min) can also be found after aging, which suggests that the migration phenomenon at 200°C does not end after 30 s.

Figure 5 shows the macromolecular structure at the interphase and highlights a phenomenon of chain orientation which would explain the high adhesion area. All chain segments do not migrate, only those carrying an anhydride function. As a consequence, and although we did not see anything on the CH_2 wag vibrations between 1350 and 1150 cm^{-1}, we suggest that chains stretch out and that orientation occurs during the cure, leading to an orientation normal to the substrate surface due to the polar graft motion. Up to now, lack of crystallinity in this structure has prevented confirmation of this hypothesis by X-ray diffraction analysis. However, it can be assumed that polymers with a high molecular mass lead to higher failure levels, or at least to crack propagation located further away from the substrate, corresponding to a cohesive failure whose strength depends on polymer cohesiveness.

Figure 6 shows that after aging anhydride enrichment in the polymer layer left on the substrate after peeling decreases while the thickness of this layer increases. These results confirm the previous hypothesis, illustrated in Figure 5, highlighting the progressive reaction of anhydride functionalities which come into contact with the stainless steel surface and the formation of an increasingly thicker high-cohesion coating.

Mobility of grafted chains brings about reactions at the interface, related to the concept of adhesion, on the one hand, and an increase in polymer cohesion close to the

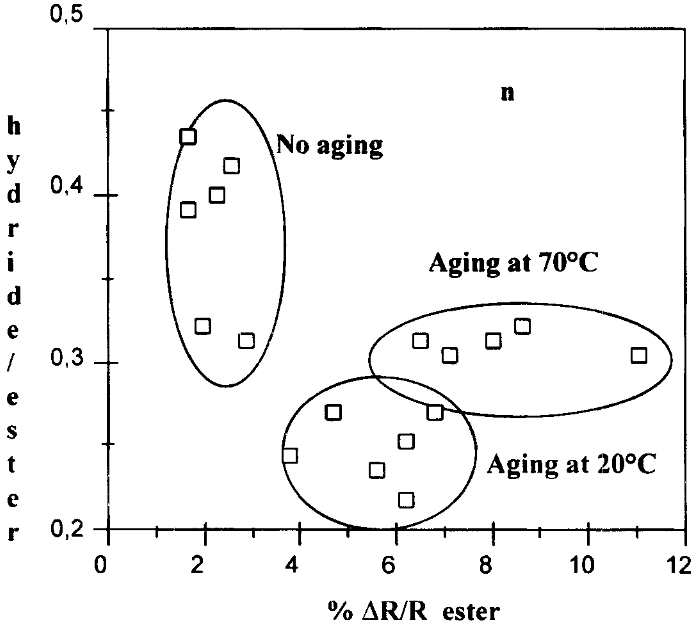

FIGURE 6 Effect of aging on anhydride enrichment as a function of the polymer thickness left on the steel substrate after peeling.

metal substrate, related to the concept of mechanical assembly behavior, on the other hand. Both concepts are different and affect two different areas of the assemblies studied, since failure is never in adhesion from a microscopic point of view.

CONCLUSIONS

Stainless steel/polymer interactions were studied on the basis of IR spectrometric analysis of the behavior of a model succinic anhydride/polished stainless steel interface as a function of time and temperature. With this methodology, the various reaction steps were defined more precisely and the stability of the bonds formed was characterized. First migration and orientation of organic chains occur, followed by chemical interactions. The interaction process of this functional group within the polymers can be broken down into two main phases, namely: opening of the anhydride ring at the contact with the water layer adsorbed to the stainless steel surface, and carboxylate formation from the acid resulting from hydrolysis.

These tests highlight the evolution of a steel/polymer compound during aging as a function of temperature, and its improved mechanical properties. The interaction process can be schematically divided into two parts:

- Diffusion phenomena and migration of chains grafted with maleic anhydride to the metal surface. This phenomenon occurs during treatment at 200°C.

- Chemical reactivity of anhydride functionalities with the oxidized surface and formation of strong bonds of the carboxylate type. Such reactivity is strong at 200°C and continues to occur more widely during assembly aging at ambient temperature or 70°C. During aging, the mechanical strength of the assembly increases and failure location moves further away from the substrate, leading to a cohesive type failure.

Considering the analytical techniques utilized, this multi-field approach has been particularly facilitated by the nature and surface state of stainless steel, and it can be applied to other steel/polymer compounds..The first phase consists in simulating and validating chemical and physical interactions which may exist between a steel and a polymer. The second phase is to study how these interactions change as a function of various parameters such as temperature or humidity, so as to know the durability of the bonds formed. To understand the reaction processes, the analytical results have to be compared with mechanical test results and with the thermal treatments of the assemblies characterized.

Polymer modification due to chains grafted by polar groups and migrating to the steel/polymer contact area has been demonstrated in this study, thus confirming the minimization principle of interfacial energy whereby materials in contact change so as to reduce the difference between their surface energies. The assemblies studied here have no adhesion problem but may show improved mechanical behavior if polymer cohesion is increased at the contact with steel. The consequences of damp aging should, however, be investigated. This will be the subject of our next study.

References

1. T. Hjertberg, J. E. Lasko, *J. Appl. Polym. Sci.*, **37**, 1228 (1989).
2. L. Ulren, T. Hjertberg, H. Ishida, *J. Adhesion.*, **31**, 117 (1990).
3. M. Mantel, F. Descaves, *J. Adhesion. Sci. Technol.*, **6**, 357 (1992).
4. H. F. Webster and J. P. Wightman, *Proceedings of the 15th Annual Meeting of the Adhesion Society*, F. J. Boerio, Ed., Hilton Head, SC, USA (1992), pp. 187–190.
5. D. Macarinelli, M. Mantel, B. Baroux, N. S. Prakash, M. Charbonnier and M. Romand, *Proceedings, Euradh'92, European Adhesion Congress*, Dechema, Karlsruhe (Sept. 1992), pp. 470–477.
6. M. Mantel and J. P. Wightman. *Surf. Interface Anal.*, **21**, 595–605 (1994).
7. J. Schultz, L. Lavielle, A. Carré and P. Comien, *J. Mater. Sci.*, **24**, 4363 (1989).
8. J. J. Bikerman, *Ind. Eng. Chem.*, **59**, 40 (1967).
9. J. Schultz, A. Carre and C. Mazeau, *Int. J. Adhesion Adhesives.*, **4**, 163 (1964).