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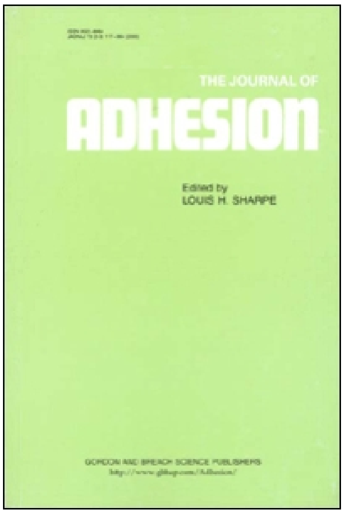

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Adhesion in Polymer/Steel Sandwiches*

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Polymer/steel sandwiches are able to reduce the nuisance due to vibrations and noise in automotive applications, for example. Thin layers of polymer are inserted between two metal sheets. The deformation of the polymer is responsible for the damping properties of the sandwiches and, therefore, the viscoelastic behavior of the polymer is of major importance. However, adhesion between the two materials is also required. The polymer studied in the present work is a copolymer of ethylene and vinyl acetate (EVA) containing 28 wt% of vinyl acetate grafted with maleic anhydride (1 wt%). A wedge test is used to measure the interfacial strength and the durability of the adhesive bond. The influence of the surface treatment of the steel substrate on the adhesive behavior and the effect of water has been studied. FTIR surface analysis after cleavage helped us to identify the nature of the interfacial bonds.

KEY WORDS: Polymer adhesion; wedge test; nature of interfacial bonds; ageing; maleic anhydride grafted ethylene/vinyl acetate copolymer (EVA); durability; sound damping sandwich; locus of failure.

INTRODUCTION

Today life requires suppression or reduction of noise in many areas. In general, steel transmits vibrations very well whereas polymers are known for their damping properties due to their viscoelastic behavior. The steel industry decided about 10 years ago to take up the challenge by combining these two materials in order to produce a competitive new material which presents most of the mechanical properties of the steel substrate and also good damping characteristics. The objective has been reached by introducing a thin layer (40–80 μm thick) of polymer between two sheets of steel. During shear deformation of the sandwich, the viscoelastic properties of the polymer are responsible for the dissipated energy. The damping behavior of the sandwich can be related to the measured loss factor for the sandwich. It is obvious that the viscoelastic properties of the polymer are of major importance.[1] However, adhesion to the steel substrate is also required. The polymer/metal interactions determine the strength of the interface and, consequently, the potential maximum deformation of the polymer layer. The effect of the surface treatment of the steel, such as anticorrosion coatings, therefore, needs to be studied.

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Several methods can be used to evaluate the fracture energy of a polymer/metal joint.[2] The advantage of the wedge test[3] used in the present study lies in the fact that the joint can be submitted to stresses which allow one to obtain a good correlation with the performance of the product in service. Moreover, high energy of adhesion can also be measured and this test is well adapted to study ageing.

Poly(vinyl acetate) and copolymers are widely used as damping materials especially when their glass transition temperature is near room temperature.[4] Moreover, ethylene-vinyl acetate copolymers (EVA) present good vibration damping properties for the foreseen applications for which the frequency range is 100–500 Hz. It has been shown by Chen *et al.*[5] that the damping efficiency at room temperature of laminated steel sheets is higher for a copolymer based on polyethylene and acrylic acid than for polyvinyl butyral. In this work, we have used EVA copolymer containing 28% of vinyl acetate (VA). However, this copolymer does not sufficiently adhere to metal substrates even though polar vinyl acetate groups are present. Different treatments of the polymer surface are possible: flaming, corona discharge, chemical oxidation, etc. Reactive groups of the acrylic or methacrylic type can also be introduced into the polymer chains to obtain good adhesive properties.[6] Grafting of maleic anhydride onto polyethylene[7] or polypropylene[8] by a peroxide-catalysed reaction has also been used. It increases the interfacial strength for both polymer/polymer and polymer/metal interfaces. Moreover, the interactions established increase the stability of the interface in agressive media.[9]

One steel substrate with different surface treatments was chosen in order to evaluate, by a wedge test, the adhesive strength of the EVA/steel assemblies. Durability of these joints in the presence of water is especially important. Determination of the locus of failure and nature of the interfacial bonds was obtained by Fourier Transform Infra-Red Spectroscopy after failure.

EXPERIMENTAL

Materials

Three steel substrates with different surface treatments, provided by SOLLAC (USINOR-SACILOR group, France), were considered:

- mild steel S_0 of high elastic limit,
- S_1:S_0 steel submitted to a phosphatizing bath containing zinc followed by a chromium post-rinse;[10] this treatment is known to be beneficial for corrosion protection,
- S_2:S_0 treated with a commercial anti-corrosion solution containing chromium, phosphorus and silicon among other elements.

The steel surfaces were examined by scanning electron microscopy. The S_0 and S_2 surfaces look very smooth but the typical crystal microstructure of the phosphate coating appears clearly on the S_1 surface. No chromium was detected with energy-dispersive X-ray spectroscopy (EDXS). Nevertheless, this element was seen by X-ray photoelectron spectroscopy in agreement with observations made by Fedrizzi and

Marchetti.[11] Therefore, chromium is present in the top surface layer. Roughness measurements were not sensitive enough to distinguish between the three metal surfaces ($R_a = 0.5\,\mu m$).

S_0 and S_1 substrates were cleaned before assembly by immersion for 5 minutes in an ultrasonic bath containing trichloroethane, then dried for half an hour at 120°C. No cleaning of the S_2 surface was made, in order to avoid partial elimination of the treatment by the cleaning solvent as shown by IR analysis and wettability measurements.

The EVA copolymer (ELF-ATOCHEM, France) contains 28 wt% of vinyl acetate and is grafted with maleic anhydride in the amount of approximately 1 wt%. The steel/polymer/steel sandwiches were obtained under pressure (180°C, 1.5 MPa for 5 min). The platens of the heated press were cooled down by circulating water.

Wedge Test

The joint was submitted to a deformation in mode I (Fig. 1) by introducing a wedge. The rupture propagates up to equilibrium. If the deformation of the substrate is purely elastic and if no energy is stored in the adhesive layer, the equilibrium is reached when the rate of loss of elastic energy by the substrates is equal to the failure energy, R, per unit area of the joint.[12]

R can be written as:

$$R = \frac{3Eh^2e^3}{16l_0^4}$$

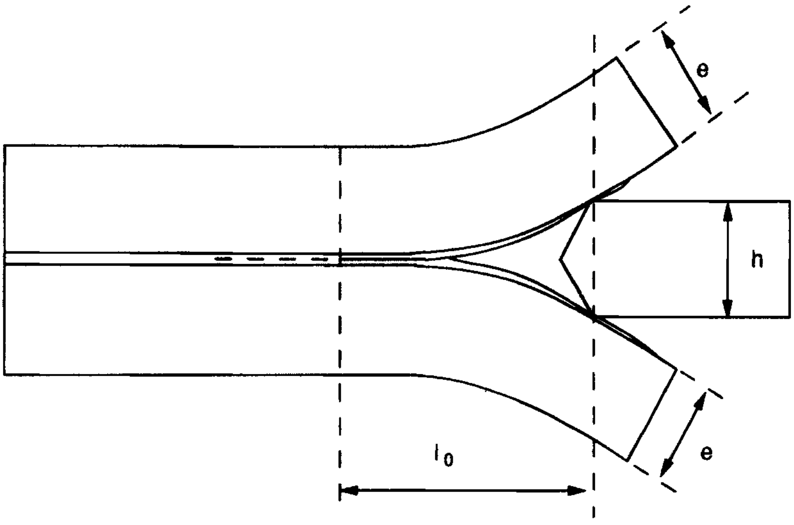

FIGURE 1 Wedge test configuration.

with:

- E = Young's modulus of the substrate
- e = thickness of the substrate
- l_0 = length of the crack
- h = height of the wedge

Dimensions defined by Cognard[12] were applied: length and width of the joint equal to 40 and 10 mm, respectively, thickness of the wedge equals to 1 mm.

The plastic deformation of the substrates is minimum when using one-millimeter-thick steel of high elastic limit. It can be assumed that the Young's modulus of the steel is not affected by the surface treatment. The wedge test was performed at 20°C in air. The propagation of the fracture as a function of time was followed and has shown that the quasi-equilibrium is quite rapidly reached. Therefore, the measurements were made half an hour after introduction of the wedge. The crack length at equilibrium was measured with a low-power microscope. Average values of about 10 measurements are given.

The ageing behavior of the samples in water was studied. The wedge was introduced into the assembly in air. The length of fracture was measured at equilibrium. Then, the assembly in which the wedge is inserted was placed in distilled water at 20°C and the propagation of fracture was followed as a function of time of immersion.

Surface Analysis

Steel surfaces were analysed after failure by Fourier Transform Infra-Red Spectroscopy (IFS 66 spectrometer from Brüker) by the diffuse reflectance technique using a mirror as a reference. Spragg[13] has shown that this technique is also adapted to the study of polymers deposited onto substrates.

RESULTS AND DISCUSSION

The fracture lengths, l_0, are given in Figure 2 as a function of the polymer thickness for the three steel substrates. Due to the fact that the steel substrates only differ in their surface treatment, it can be considered that their elastic moduli are identical. Therefore, it is possible to compare the crack lengths. The length of fracture is reproducible as seen by the uncertainty bars shown on the figure. S_2 sandwiches always lead to shorter cracks whatever the polymer thickness. However, it is seen that the influence of the thickness is not identical for the three laminates. The variation of l_0 is quite small for sandwiches made with S_2 (about 1 mm over the studied thickness range). A slight increase is observed with S_0 (about 2 mm) and it is much more significant with the phosphated surface S_1 (about 4–5 mm). The microstructure of S_1 may play a role although the roughness ($R_a = 0.5\,\mu m$) is low compared with the polymer thicknesses. Mechanical anchoring is not the only parameter influencing l_0 as shown by the behavior of the two other sandwiches.

The failure occurs apparently in the interfacial region for almost all cases, no visual traces of polymer being present on the metal surfaces. Scanning electron microscopy

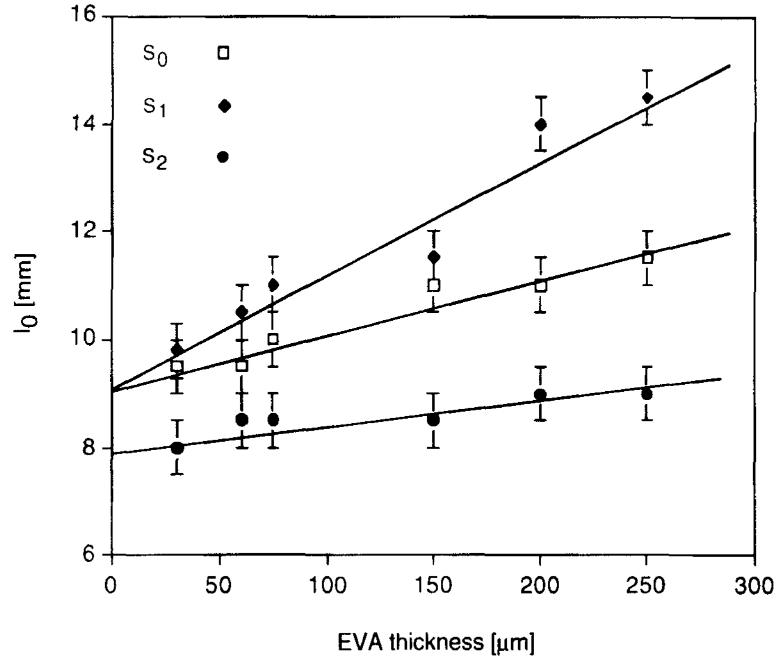

FIGURE 2 Evolution of the length of the crack function of the EVA thickness for the different liminates.

(SEM) leads to the same conclusion. However, it has been checked by SEM analysis associated with energy-dispersive X-ray spectroscopy and infra-red spectroscopy, as will be seen later on, that a thin layer of polymer of homogeneous thickness remains on the steel surfaces. It should be noticed that a clear cohesive failure is only observed in the following conditions: a thin polymer layer 30–40 μm thick in steel sandwiches made with bare steel S_0.

The theoretical analysis of the wedge test does not take into account the thickness of the polymer layer, nor the bulk properties of the polymer. Moreover, the EVA deformation is not purely elastic. However, dissipation effects which may occur in the polymer should lead to a lower length of failure when the thickness of the layer increases. Nakano *et al.*[14] have shown that the interfacial stress is higher when the thickness of the polymer is lower. This effect, also, should lead to an increase in l_0 for thinner layers. The different behavior (length and locus of failure) as a function of the substrate in contact is in agreement with the modification of the polymer/metal interactions and/or induced modifications of the polymer properties in the vicinity of the polymer/steel interface.

The efficiency of the surface treatment in the ageing behavior is shown in Figure 3, where the length of fracture is plotted as a function of time of immersion in distilled water at room temperature for sandwiches in which the thickness of the polymer is equal to 40 μm. Delamination of S_0/EVA sandwiches is observed after less than 10 hours in water, whereas the two other laminates are almost insensitive to the water

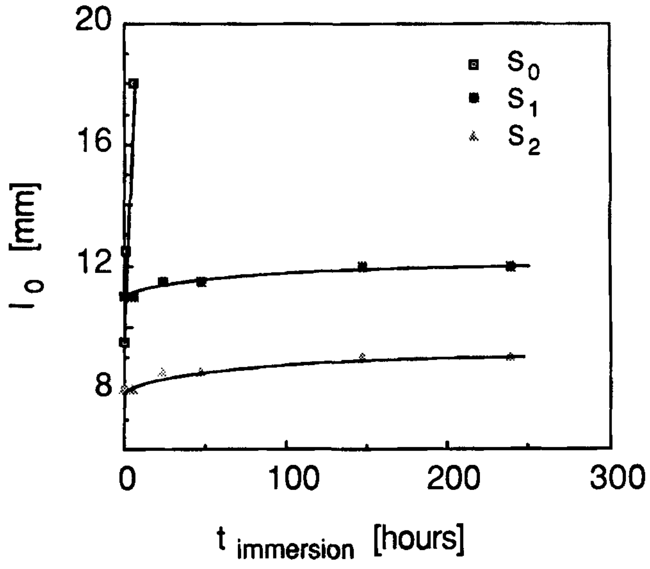

FIGURE 3 Evolution of the length of fracture as a function of immersion time in water (thickness of EVA layer ≈ 40 μm).

environment for at least 10 days. Moreover, for S_0, the failure which initially propagates cohesively within the polymer moves closer towards the interface and then becomes partly cohesive in the oxide layer of the metal. Although the bulk properties of the polymer layer are slightly affected by the presence of water, as shown by the small increase of the length of fracture observed for S_1 and S_2 sandwiches, the interfacial properties are the most important parameters in the ageing behavior in water. The plasticization effect of the polymer leads, however, to a failure occurring deeper in the adhesive layer in the case of both S_1 and S_2. The behavior of S_0 sandwiches can be explained by the corrosion of the substrate. Cathodic delamination[15] may be responsible for the low strength of the joint in water as shown by the influence of the acid or base character of the solution. Indeed, the immersion of S_0 sandwiches in acid solutions (0.01 M HCl in water) slows down the delamination which occurs after 24 hours compared with 10 hours in pure water. On the contrary, only about 4 hours are necessary to reach the separation in a base solution (0.1 M KOH in water). The surface treatment protects from cathodic delamination as shown by the behavior of the sandwiches made with S_1 and S_2 steel, which are stable in water.

These results show clearly that different bonds are present at the interface between the metal and the polymer. EVA copolymers do not adhere well to metal surfaces. The grafting of polar species such as maleic anhydride increases the adhesive properties of polyolefins[4] toward aluminum *via* formation of chemical bonds by reaction of the grafted carboxylic groups with the aluminol groups of the substrate. The steel surfaces have a very complex composition and many species (metals and oxides) are present at the surface. The reactivity of maleic anhydride was checked for two elements (iron and zinc) which are two major components in the surface composition of the substrates.

Maleic anhydride was melted at 90°C on plates of iron (99.5% purity) and zinc (99.95% purity) (Goodfellow, Cambridge, UK), and the excess of product was rinsed off by trichloroethane.

Figure 4 shows the FTIR spectra of the zinc and iron plates treated with maleic anhydride in the diffuse reflectance mode. New peaks, which do not belong either to the steel surface or to the anhydride molecule, appear in both cases and can be attributed to carboxylates. Formation of carboxylates can be explained by the reaction of the carboxylic groups (obtained by opening of the anhydride rings) with Zn and Fe. On iron, the reaction with carboxylic functions leads to three characteristic peaks at 1601, 1543 and 1439 cm^{-1}. For zinc, three new peaks are also observed (1551, 1450 and 1352 cm^{-1}). The interpretation of these spectra is quite complex although many references can be found. For example, Paul *et al.*[16] reported that the typical bands of ferric acetate are seen at 1600, 1540 and 1452 cm^{-1}. Rochester *et al.*[17] have also found different structures for iron carboxylates. The reaction of acrylic or methacrylic acid copolymers with zinc leads to tetracoordinated and hexacoordinated carboxylates and zinc acid salts in the range of 1563–1585 cm^{-1} as shown by Coleman *et al.*[18]

Others[19-20] have also studied the reaction of carboxylic groups with several metals. Due to the complexity of the steel surfaces, on the one hand, and to the different carboxylates which may be obtained, on the other hand, it has not been judged useful to continue the study of the reaction of maleic anhydride with other elements of the steel surface. However, maleic anhydride is deposited in the same way on the steel substrates. The formation of the carboxylates can also be assumed although, as expected, the vibrations do not correspond precisely with those observed with Fe or Zn carboxylates.

On Figures 5, 6 and 7 are compared the IR spectra obtained after failure in air of the sandwiches and after reaction with maleic anhydride for S_0, S_1 and S_2 surfaces, respectively.

EVA remains on the S_0 substrate as attested by νC-H and νC-O vibrations shown on Figure 5. Moreover, a band around 1590 cm^{-1} which does not belong either to the polymer or to the steel and which could correspond to a carboxylate group appears after failure.

As for the S_0 substrate, the failure is not truly interfacial for the S_1/EVA assembly, bands characteristic of the polymer being detected as seen on Figure 6. However, the rupture occurs very close to the metal surface because the νP-O vibrations typical of the phosphatization treatment appear on the spectra between 900 and 1200 cm^{-1}. Again, the symmetric and asymmetric vibrations of the carboxylate appear at 1540 and 1645 cm^{-1}.

For the last studied sample (S_2/EVA assembly), the thickness of the remaining layer is very small as shown by the low intensity of the bands (Fig. 7) and no accurate analysis can be given.

Therefore, in all cases, the failure occurs in the polymer near the interface, in a zone called the interphase, where the properties are different from those of the bulk. However, the thickness of the remaining polymer layer on the substrate is not identical. Moreover, the interactions between the polymer and the steel surfaces are different as shown by the results of the infra-red analysis and mechanical testing which are slightly, but significantly, different for the three substrates.

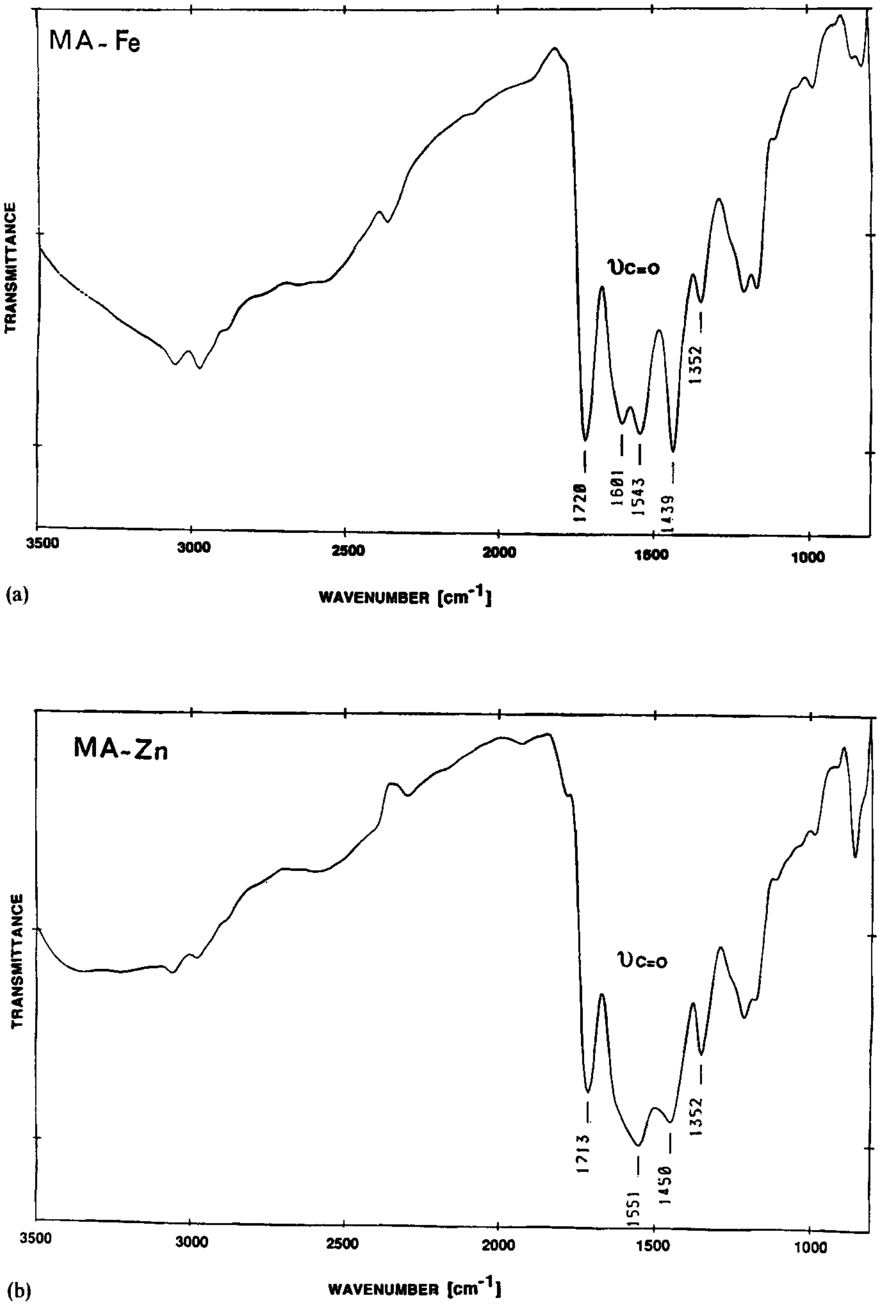

FIGURE 4 FTIR spectra of maleic anhydride (MA) melted on zinc and iron plates.

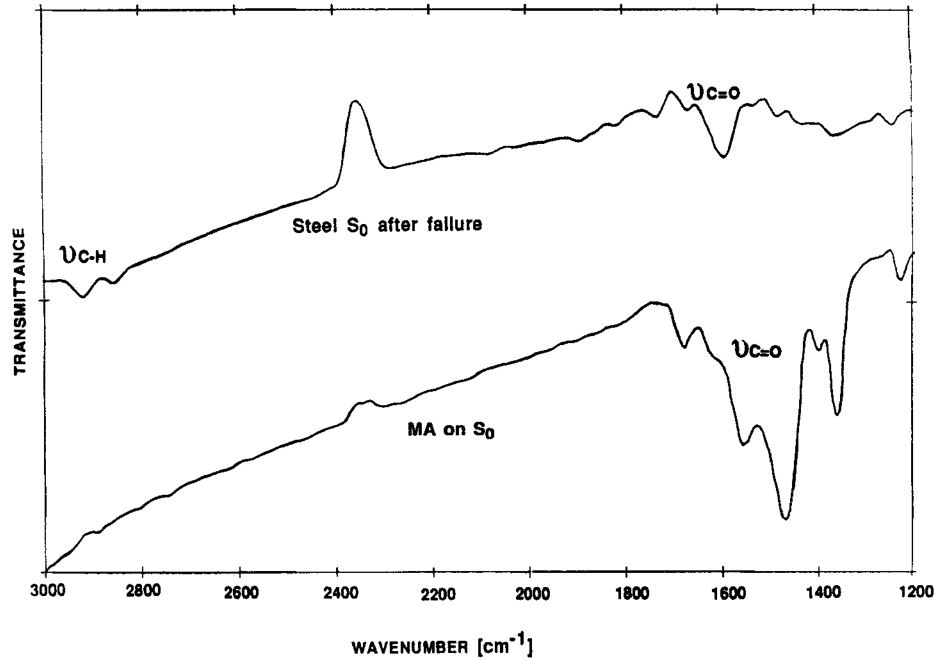

FIGURE 5 FTIR spectra of steel substrates S_0 after failure and after reaction with maleic anhydride.

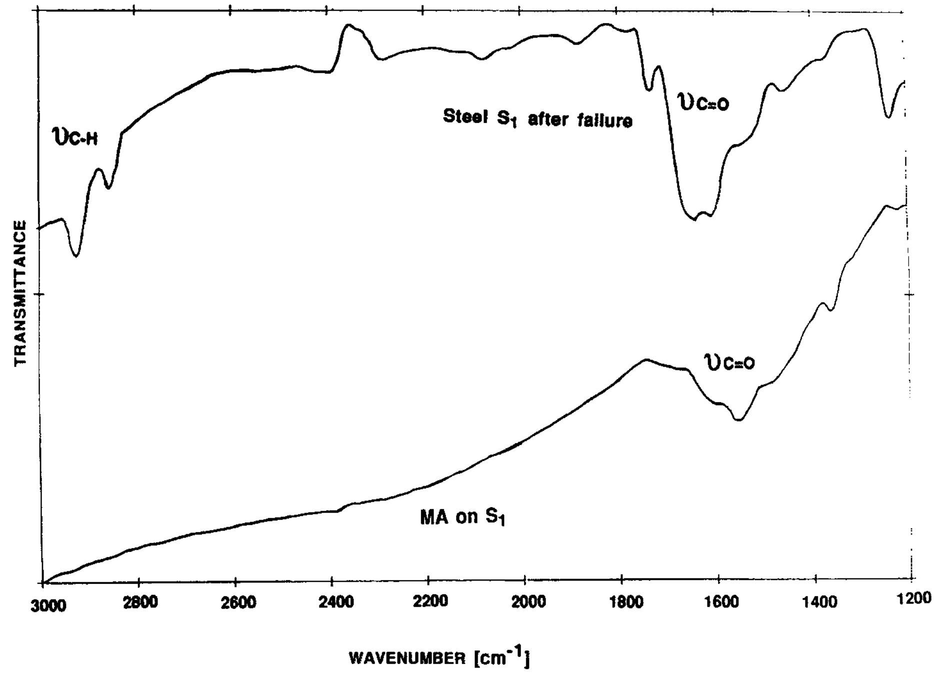

FIGURE 6 FTIR spectra of steel substrates S_1 after failure and after reaction with maleic anhydride.

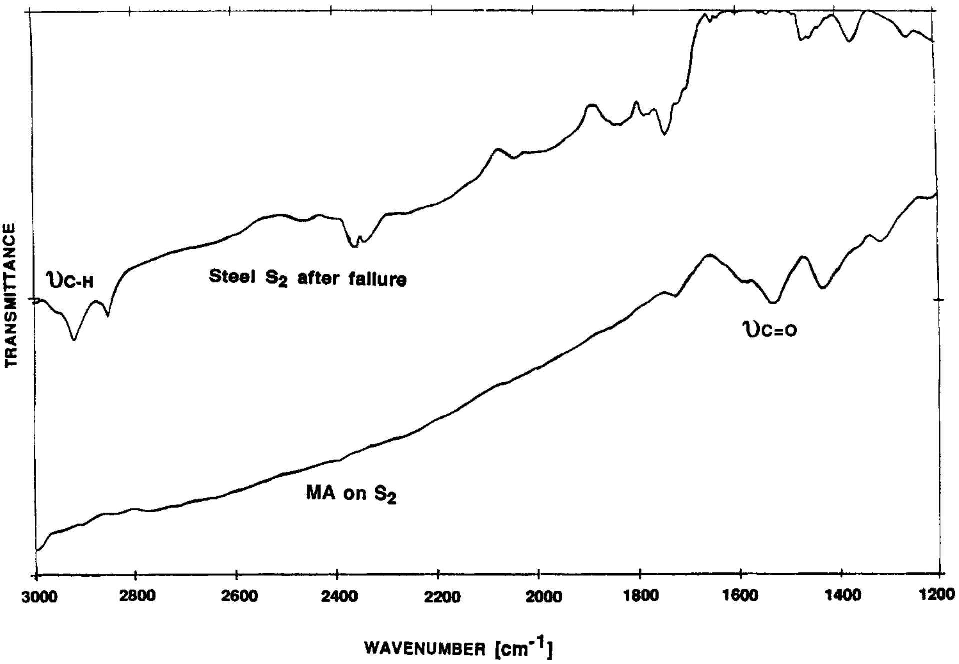

FIGURE 7 FTIR spectra of steel substrates S_2 after failure and after reaction with maleic anhydride.

CONCLUSION

The study of the adhesive behavior of polymer/steel sandwiches by the wedge test leads us to conclude that maleic-anhydride-grafted EVA reacts with the steel substrate and leads to interfacial strong bonding through carboxylates. These bonds have been evidenced by infra-red spectroscopy and are dependent on the surface treatment of the steel substrate; however, it has not been possible to define the element(s) (oxides or metals) which are participating in the bonding, due to the chemical complexity of the steel surface. This interface is of high strength whatever the surface composition of the metal as shown by the behavior in the wedge test. However, it is clear that the interfacial links between the polymer and the anti-corrosion-treated metal lead to stronger interfaces in a water environment than the ones obtained with bare steel, for which cathodic delamination seems to be the relevant mechanism.

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