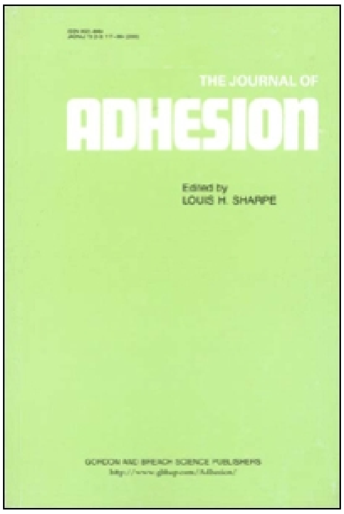

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SURFACE MODIFICATIONS ON EVA TREATED WITH SULPHURIC ACID

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In this study, treatment with sulphuric acid was used to increase the adhesion of an ethylene–vinyl acetate copolymer containing 20 wt% vinyl acetate (EVA20). The treatment with sulphuric acid improved the wettability of EVA20 due to the creation of different oxygen and sulphonic acid moieties on the surface. The treatment also created cracks and heterogeneities on the EVA20 surface, and enhanced T-peel strength values of EVA20/polychloroprene adhesive + 5 wt% isocyanate joints were obtained. The loci of failure of the joints were mixed, i.e., adhesional and cohesive in the adhesive. Peel strength values of both as-received and sulphuric acid-treated EVA20/polychloroprene adhesive joints increased after ageing at 50°C and 95 wt% relative humidity for 72 because the complete cure of the adhesive was thereby was produced. The durability of the EVA20 treated with sulphuric acid was monitored between 15 min and 5 years. High peel strength values were obtained for times up to 61 days; the joints produced with the treated EVA20 five years after treatment showed lower peel strength value due to the creation of a weak boundary layer produced by reaction of the residual sulphuric acid on the surface with EVA20. On the other hand, different experimental variables in the treatment of EVA20 with sulphuric acid were considered. The optimum treatment conditions for EVA20 were obtained by immersion in highly concentrated sulphuric acid (96 wt%) for one minute followed by neutralisation with ammonium hydroxide.

Keywords: EVA; Surface treatment; Sulphuric acid; Contact angle; ATR-IR spectroscopy; SEM; T-peel strength

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INTRODUCTION

Ethylene–vinyl acetate (EVA) copolymers are materials commonly used as sole material in the footwear industry and in the manufacture of toys and need to be joined with adhesives. In the footwear industry, EVA is used as shoe soling material, either in the form of cross-linked microcellular material or as a thermoplastic, and it is bonded using polyurethane or polychloroprene adhesives [1]. Because the vinyl acetate content in the EVA is, in general, low (*i.e.*, high polyethylene content), poor adhesion is generally obtained and thus a surface treatment is necessary [2].

The performance of an adhesive joint depends largely on the quality of the interface created between the adherend and the adhesive [4]. Improved adhesion to polymer surfaces can be achieved by using a variety of methods such as moulding [3], oxidation with acids [4], UV radiation [5], graft copolymerisation [6], and corona dicharge treatment [7] among other procedures. These surface treatments introduce a variety of functional groups onto the treated surface and cause specific interactions that make the surfaces more reactive, generally leading to increased adhesion properties. Hjertberg *et al.* [8] improved the adhesion of polyethylene-aluminium laminates by introducing polar moieties such as vinyl acetate groups. Novak *et al.* [9] used EVA as a modifier to improve the adhesion of polypropylene.

EVA materials are difficult to bond, and some surface preparation has been suggested for bonding with epoxy adhesive [10]. Furthermore, corona discharge treatment has been shown to be an adequate treatment for EVA materials [11] to improve their adhesion properties. However, in the footwear industry, joining of EVA is not feasible using epoxy adhesives, and the treatment with corona discharge is not sufficient to assure high adhesion. Therefore, an alternative and easy-to-apply chemical surface treatment would be of interest for EVA materials. In this study, EVA was treated with sulphuric acid, and the surface modifications responsible for its increased adhesion towards polychloroprene adhesive were studied.

The term "cyclisation" is often used for the treatment of polymers with sulphuric acid, because the reaction of natural rubber (polyisoprene) with sulphuric acid produces cyclic hydrocarbon structures. Cyclisation has often been used for bonding rubber to metal by means of epoxy or phenol formaldehyde adhesives [12], and it appears to be most successful when applied to unsaturated diene rubbers. The surfaces of vulcanised diene rubbers, such as natural rubber, nitrile-butyl rubber, and styrene-butadiene rubber, can be treated with concentrated sulphuric acid to yield a cyclized layer of rubber on the surface. This layer is quite brittle and when flexed develops microcracks, which are believed to help in subsequent bonding by acting as centres for the mechanical interlocking of the adhesive with the rubber surface. However, the residual acid left in the outermost treated surface may accelerate ageing or assist moisture attack at the bond line [12–14]. The thickness of this layer depends on the length of the treatment with sulphuric acid, and the cohesive strength of the surface layer has been shown to be a limiting factor in the adhesion properties.

The proposed mechanism for cyclisation of polymers is sulphonation, *i.e.*, the hydrogen of the C-H bond is removed and replaced by a SO_3^- moiety, which is then hydrogenated to form a sulphonic acid moiety at the site of attachment. This sulphonic acid can be neutralised with a base to create more stable species. Neutralisation with ammonium hydroxide extracts the hydrogen from the sulphonic acid, leaving a stabilised ion pair (SO_3^- NH_4^+). Neutralisation can also be performed using amines (methyl amine, isobutylamine, tetramethylene pentamine). Practically all engineering plastics (with the exception of fluorocarbons and some silicones) which contain tertiary C-H bonds are suitable for sulfonation [13, 14].

There are some previous studies [8–10, 13] dealing with the improved adhesion of several polymers treated with sulphuric acid, but, to our knowledge none of them have been devoted to EVA materials. In this work a study of the surface modifications produced by treatment of an EVA material with sulphuric acid has been carried out. In addition, considering that the effectiveness of the cyclisation is influenced by several different experimental variables, in this study the concentration of H_2SO_4 (25 to 96 wt%), the neutralisation with or without NH_4OH, and the durability of the treatment were considered.

EXPERIMENTAL

Materials

An EVA copolymer containing 20 wt% vinyl acetate (EVA20) supplied by REPSOL QUÍMICA (Santander, Spain) was used in this study. The melt flow index is 3 g/10 min, and the Shore A and D hardnesses are 91 and 39, respectively (data supplied by REPSOL QUÍMICA [9]). The polymer was received as pellets and was moulded in a Margarit JSW injection machine (JSW, Yokohama, Japan) to obtain test samples of 150 mm length, 60 mm width, and 2 mm thickness. The following injection conditions were used: Temperature = 170°C; injection time = 6 s; injection pressure = 60% of total pressure (1570 bar;

1 bar = 10^5Pa); mould temperature = 20°C. The injection-moulded pieces were cut into test samples of 20 × 30 × 2 mm size for characterisation and 150 × 30 × 2 mm for adhesion tests.

Adhesive joints of EVA20 were made using a commercial two-component solvent-based polychloroprene adhesive consisting of polychloroprene (Telcopren 3.003, supplied by Composan Adhesivos S.A., San Vicente del Raspeig, Spain) and 5 wt% isocyanate (Desmodur RF, supplied by Bayer AG, Leverkusen, Germany). The two components of the adhesive were mixed just before application. The adhesive contains 25 wt% solids and its Brookfield viscosity is 3.0 ± 0.2 Pa·s. The thickness of the adhesive layer applied on the EVA20 was 100 µm. The adhesion of EVA20 was evaluated from T-peel tests of EVA20/polychloroprene adhesive joints.

Treatment with Sulphuric Acid

The treatment of EVA20 with sulphuric acid was carried out using the following consecutive steps: (1) Immersion of the EVA20 in sulphuric acid for 1 min; (2) Removal of EVA20 from the sulphuric acid bath followed by neutralisation with hot distilled water for 5 min, immersion in ammonium hydroxide (15 wt%) for 1 s, and exhaustive washing at room temperature with distilled water, with the neutralisation carried out until neutral pH was obtained; (3) Drying off the treated EVA20 under infrared radiation at moderate temperature (lower than 60°C) for 8 min.

Experimental Techniques

Contact Angle Measurements

The surface-treated EVA20 was placed into the thermostated chamber of a Ramé Hart 100 goniometer (Ramé Hart, Mt. Lakes, NJ, USA). The chamber was previously saturated with the vapour of the test liquid (water) at 25°C for at least 10 min before placing a drop of water on the EVA20 surface. At least three replicates of the same treated EVA20 surface were analysed. The contact angles on the surface-treated EVA20 were measured 15 min after placing 4 µl drops of bidistilled deionised water on the surface. The experimental error was ± 2 degrees.

Attenuated Total Multiple Reflection-Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of treated samples were obtained using a Nicolet FTIR 505 spectrometer (Nicolet, Isenberg, Germany). To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed (ATR-IR spectroscopy) and a KRS-5 crystal was used. One hundred scans at a resolution of 4 cm^{-1} were obtained and averaged. Under these experimental conditions, the chemical modifications produced to a depth of about 5 μm of the treated EVA20 surface were analysed.

SEM

Scanning Electron Microscopy (SEM) allowed the morphological modifications on EVA20 to be analysed (a JEOL SEM JSM 840 apparatus was used; JEOL, Tokyo, Japan). The samples were secured on copper mounts using silver paint and coated with gold to obtain the SEM micrographs.

T-Peel Strength Measurements

T-peel strength measurements were carried out for adhesive joints produced with two similarly treated EVA20 test pieces. Before applying the adhesive, the treated EVA20 was flexed to develop cracks and facilitate the mechanical interlocking with the adhesive. The polychloroprene adhesive + 5 wt% isocyanate mixture solution was applied with a brush to the treated EVA20 surface, and the solvent was allowed to evaporate for 1 h. The dried adhesive film was heated to 100°C under infrared radiation (reactivation process) to impart hot tack and then to facilitate the interlocking of the adhesive films under pressure (0.8 MPa for 10 s). The adhesive joints were conditioned at 25°C and 50 wt% relative humidity before undergoing the T-peel test. The T-peel tests were obtained 72 h after joint formation using an Adamel L'Homargy DY-32 test instrument (Adamel, Paris, France) (peel rate = 0.1 m/min). The values obtained were the average of five replicates (standard deviation was less than 10%).

The durability of the adhesive joints was tested using accelerated ageing tests consisting of exposure of the joint for 3 days at 50°C and 95 wt% relative humidity, followed by one day at room temperature prior to conducting the T-peel tests. Three replicates were obtained for each experimental variable.

RESULTS AND DISCUSSION

This section is divided into four parts: (1) The effects produced by treatment of EVA20 with sulphuric acid; (2) the durability of the treatment of EVA20 with sulphuric acid; (3) the influence of the concentration of sulphuric acid on the effectiveness of the treatment of EVA20; and (4) the effect of the neutralisation of the treated EVA20 with ammonium hydroxide.

Surface Modifications Produced by Treatment of EVA20 With Sulphuric Acid

The treatment of EVA20 was carried out by immersion for 1 min in concentrated H_2SO_4 (96 wt%) followed by neutralisation with ammonium hydroxide. The wettability of the EVA20 surface was characterised by contact angle measurement. The as-received EVA20 shows a high water contact angle (78 degrees) because of the low polarity of this polymer. The treatment with H_2SO_4 produces a decrease in contact angle (to 63 degrees) due to improved wettability of the EVA20.

The increase in the wettability of EVA20 after treatment with H_2SO_4 can be ascribed to modifications in surface chemistry and morphology. The ATR-IR spectrum of the as-received EVA20 (Figure 1) shows the characteristic bands due to the acetate group ($\nu_{c=o}$ at 1737 cm^{-1},$\nu_{o\text{-}c=o}$ at 1242 cm^{-1}, and $\nu_{c\text{-}o\text{-}c=o}$ at 1025 cm^{-1}) and the characteristic bands of ethylene (ν_{sCH2} at 2848 cm^{-1}, ν_{asCH2} at 2919 cm^{-1}, ν_{CH2} at 722 cm^{-1}, and ν_{CH3} at 1462 cm^{-1}). The treatment with sulphuric acid creates sulphonic acid moieties (O=S=O stretching at 1167 cm^{-1} and 1050 cm^{-1}, S-O stretching at 870 cm^{-1}, and -S-OH stretching broad band at 3100–3400 cm^{-1}) on the EVA20 surface; also, C=C double bonds (=CH_2 in plane deformation at 1450 cm^{-1}, C=C stretching at 1650 cm^{-1}) produced by the cyclisation reaction are observed. Although the carbonyl bands of EVA20 seem to decrease after treatment with sulphuric acid, the intense

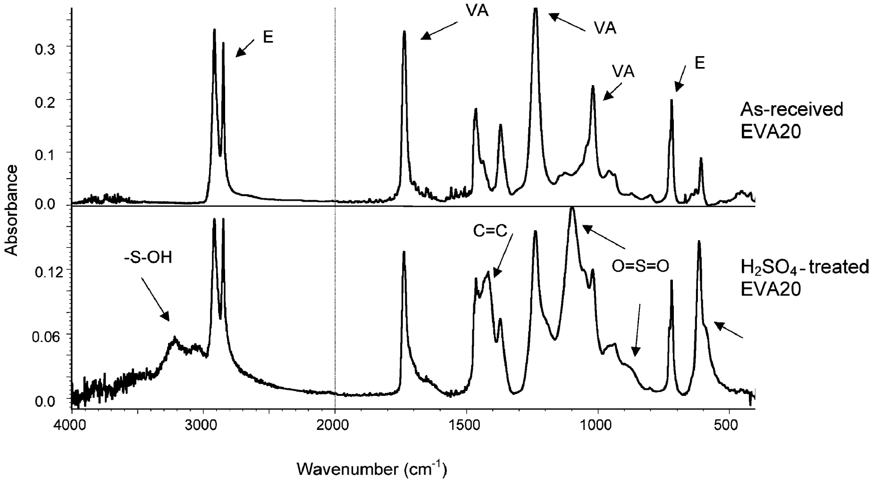

FIGURE 1 ATR-IR spectra of the as-received and H_2SO_4-treated EVA20. E = ethylene; VA = vinyl acetate.

bands originated by the sulphonic acid and C=C moieties cause changes in the relative intensity of the bands. Furthermore, the relative intensity of the bands obtained using the ATR-IR technique should be considered carefully (for example, the roughness created on EVA20 by treatment with sulphuric acid allows a poor contact with the KRS-5 crystal).

The morphology of the EVA20 surface is also modified by treatment with sulphuric acid. SEM micrographs (Figure 2) show the homogeneous surface of the as-received EVA20, which is modified by treatment with H_2SO_4. This treatment produces cracks and roughness, and some free rounded EVA20 particles can also be observed on the surface.

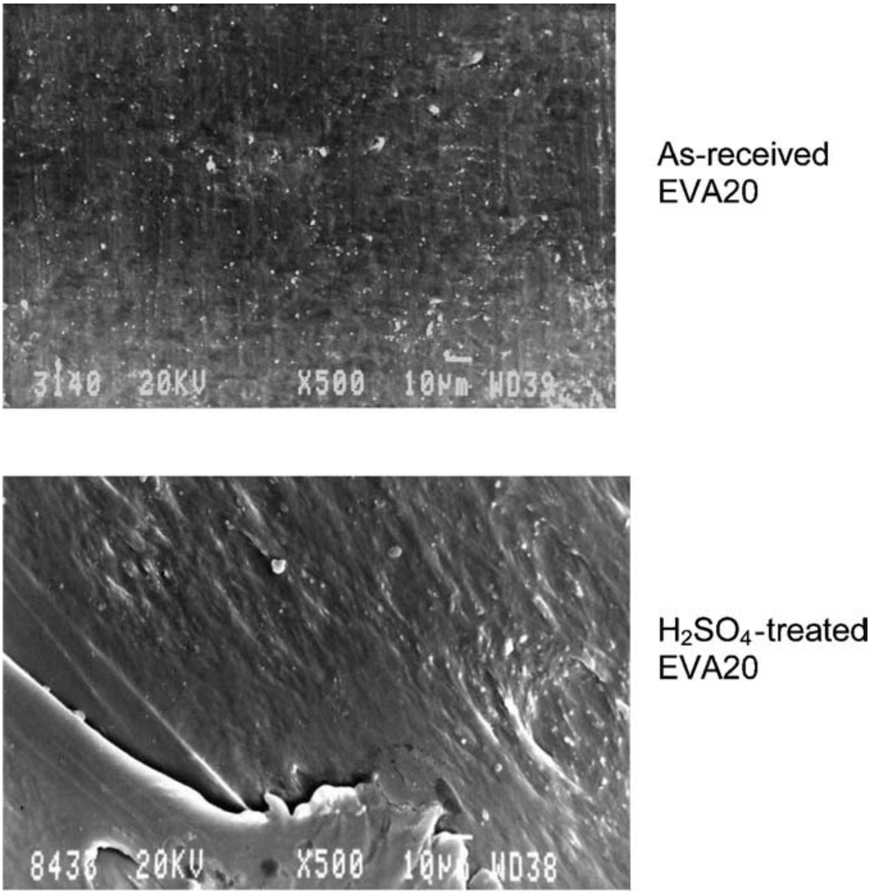

FIGURE 2 SEM micrographs of the as-received and H_2SO_4-treated EVA20.

Adhesion was obtained from T-peel tests of EVA20/polychloroprene adhesive + 5 wt% isocyanate joints. Whereas the joint produced with the as-received EVA20 shows a peel strength of only 1.1 kN/m, the treatment of EVA20 with H_2SO_4 increases the peel strength to 2.8 kN/m. This increase is due to improved wettability, creation of oxygen and sulfonic acid moieties, and surface roughness in EVA20 treated with sulphuric acid.

The loci of failure in the adhesive joints were assessed by analysis of the failed surfaces obtained after peel testing, using ATR-IR spectroscopy. The ATR-IR spectra of the as-received and H_2SO_4-treated EVA20, and the adhesive (before joint formation) are given in Figures 1 and 3, respectively. Some typical bands allow the differentiation of the adhesive and the EVA 20. In fact, the intense bands at 1739 and 1238 cm^{-1} in EVA20 are not detected in the ATR-IR spectrum of the adhesive, and the bands at 2268 cm^{-1} (N=C=O), 1521 cm^{-1} (C-N), 1184 cm^{-1} (C-O), 837 cm^{-1} (C-H), 799 cm^{-1} (C-H), and 699 cm^{-1} (C-O) are typical of the adhesive. The failed surface was referenced as the P surface (that one which visually corresponds to the adhesive) and the E surface (that one which visually corresponds to the EVA20).

In the joint produced with the as-received EVA20 (Figure 4a) an adhesional failure was obtained. In fact, the ATR-IR spectrum of the P surface is similar to that of the adhesive, and the ATR-IR spectrum of the E surface corresponds to that of the EVA20. However, the locus of failure of the joint produced with EVA20 treated with H_2SO_4 is different (Figure 4b). The ATR-IR spectrum of the P surface mainly corresponds to the adhesive, whereas the ATR-IR spectrum of the E surface shows the bands due to the sulphuric acid-treated EVA20 and

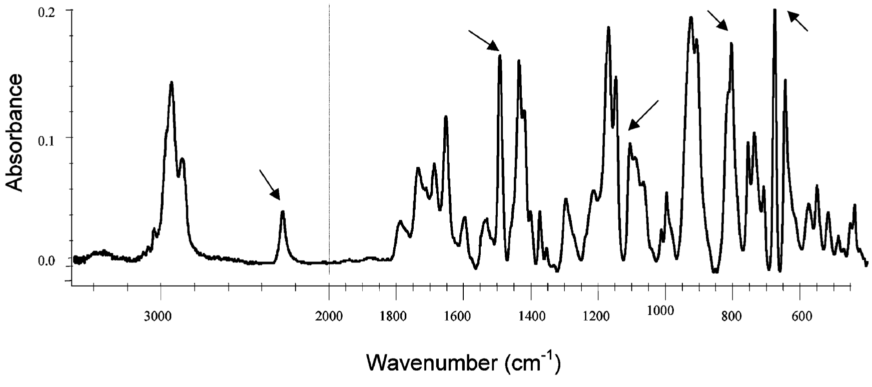

FIGURE 3 ATR-IR spectrum of the polychloroprene adhesive + 5 wt% isocyanate.

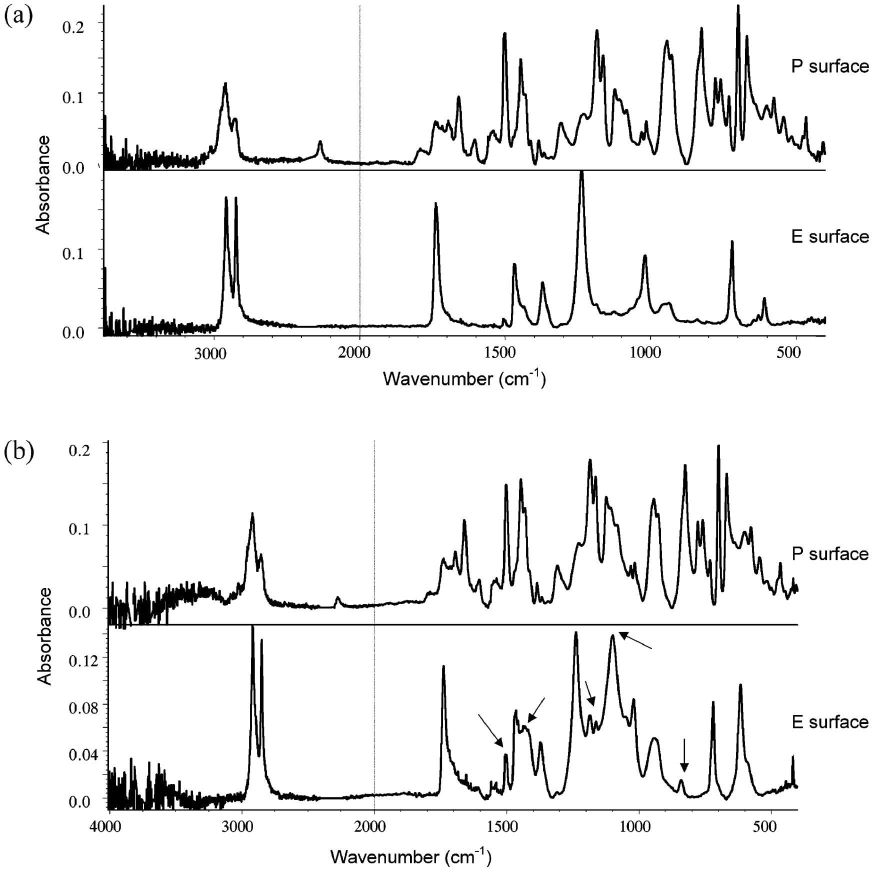

FIGURE 4 (a) ATR-IR spectra of the failed surfaces of as-received EVA20/polychloroprene adhesive + 5 wt% isocyanate joint. (b) ATR-IR spectra of the failed surfaces of sulphuric acid-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint.

several bands of the adhesive (1501, 1446, 1184, and 825 cm^{-1}). Therefore, during the peel test some adhesive is transferred to the treated EVA20 surface, giving a partial cohesive failure in the polychloroprene and, thus, a mixed failure is produced (adhesional + cohesive failure in the adhesive).

Durability of the adhesive joints was studied by means of accelerated ageing tests. Table 1 shows that the ageing at 50°C and 95 wt% relative humidity for 72 h produces an increase in peel strength values in adhesive joints produced with either as-received or sulphuric acid-treated EVA20. The loci of failure of the unaged and aged

TABLE 1 Peel Strength (kN/m) of As-received and Sulphuric Acid-treated EVA20/Polychloroprene Adhesive + 5 wt% Isocyanate Joints After Different Ageing Tests Were Carried Out

Adhesive joint	Ageing conditions	Peel strength (kN/m)
As-received EVA20/ adhesive	None	1.1 (A)
	50°C/95 wt% relative humidity/72 h	2.6 (A)
	50°C/72 h	1.3 (A + $C_{EVA)}$
	25°C/95 wt% relative humidity/72 h	1.0 (A)
Sulphuric acid-treated EVA20/adhesive	None	2.8 (A + $C_{ADHESIVE}$
	50°C/95 wt% relative humidity/72 h	3.5 (A + $C_{ADHESIVE}$)
	50°C/72 h	2.2 (C_{EVA})
	25°C/95 wt% relative humidity/72 h	1.0 (A + $C_{ADHESIVE}$)

Locus of failure: A = adhesional; C_{EVA} = cohesive failure in EVA20; $C_{ADHESIVE}$ = cohesive failure in the adhesive.

as-received EVA 20/polychloroprene adhesive joints are adhesional (Figure 5a), but higher peel strength is obtained after ageing. The ATR-IR spectrum of the P failed surface of the aged joint is similar to that of the unaged joint (Figure 4a), except for the absence of the

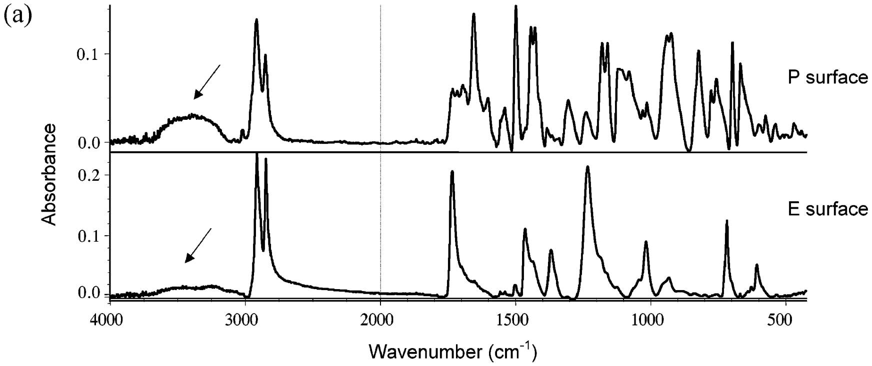

FIGURE 5 (a) ATR-IR spectra of the failed surfaces of as-received EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 50°C and 95% relative humidity for 72 h. (b) ATR-IR spectra of the failed surfaces of sulphuric acid-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 50°C and 95% relative humidity for 72 h. (Continued).

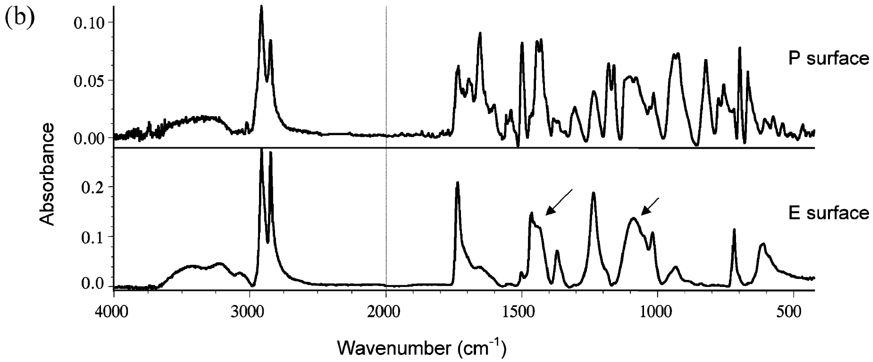

FIGURE 5 Continued.

isocyanate band at 2260 cm^{-1} and the appearance of OH moieties (broad band at 3400 cm^{-1}). This may likely indicate that the reaction of the polychloroprene with the isocyanate is completed during ageing, allowing an increase in cohesive strength of the adhesive and, thus, a greater peel strength value is obtained. Similarly, the loci of failure of the unaged and aged sulphuric acid-treated EVA20/polychloroprene adhesive joints are similar (adhesional + cohesive failure in the adhesive), but the failure is less cohesive in the adhesive after ageing (Figure 5b). In fact, the ATR-IR spectrum of the P surface corresponds to the polychloroprene adhesive, and the ATR-IR spectrum of the E surface shows bands of the EVA20 and the adhesive (Figure 5b).

The ATR-IR spectra of the failed surfaces do not show any chemical change in the EVA20, but changes in the adhesive are produced, likely due to the complete reaction of the isocyanate with the polychloroprene. As has been stated [17], the addition of isocyanates to polychloroprene adhesives provides good adhesive strength, improved water resistance, and facilitates low temperature curing. The mechanism of the curing reaction is not fully understood and was not considered in this study.

To confirm that the reaction of the polychloroprene and the isocyanate during ageing is responsible for the improved peel strength values (Table 1), two additional ageing tests were carried out: (1) Ageing with only temperature (50°C for 72 h) and (2) Ageing at room temperature under high relative humidity (95 wt% relative humidity for 72 h). The peel strength values obtained after these ageing tests are given in Table 1. Similar or lower peel strength values are obtained in the aged joints with respect to the unaged ones, and the loci of failure of the joints are different.

Ageing at 50°C for 72 h produces similar peel strength in the as-received EVA20/polychloroprene adhesive joint (Table 1), but the failure is more cohesive in the EVA20 with respect to the unaged and aged at 50°C, 95 wt% relative humidity joints (Figure 6a). In fact, the ATR-IR spectrum of the E failed surface corresponds to the EVA20, whereas the ATR-IR spectrum of the P surface exhibits bands of the adhesive and the EVA20. For the sulphuric acid-treated EVA20/polychloroprene adhesive joint, ageing at 50°C for 72 h decreases the peel strength but the

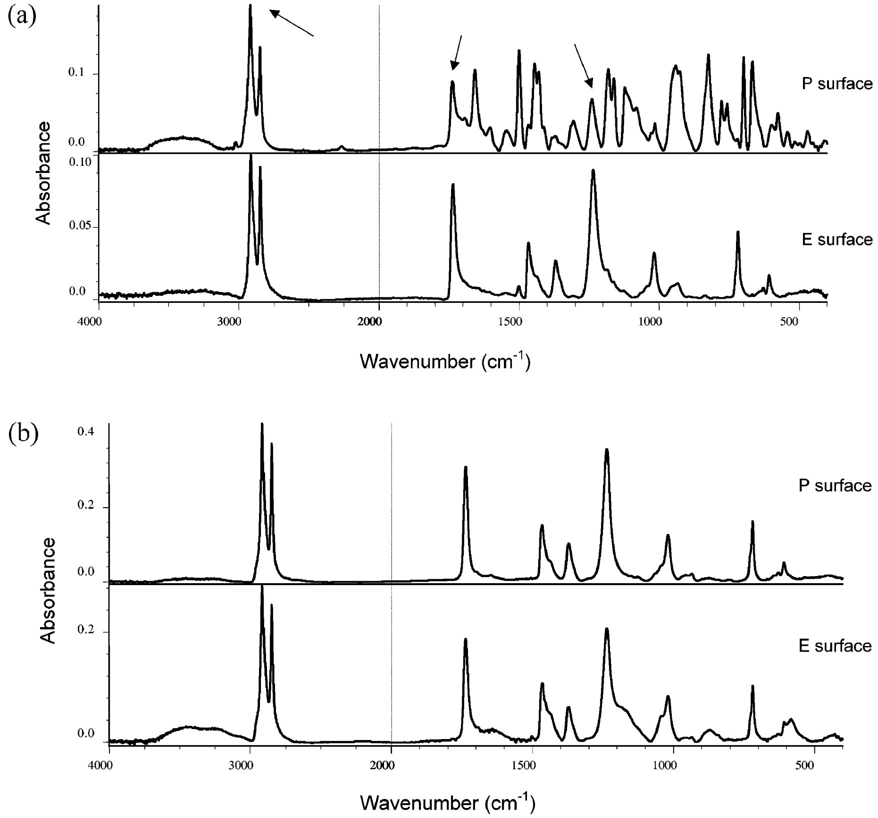

FIGURE 6 (a) ATR-IR spectra of the failed surfaces of as-received EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 50°C for 72 h. (b) ATR-IR spectra of the failed surfaces of sulphuric acid-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 50°C for 72 h.

failure is located in the EVA20, *i.e.*, a cohesive failure in the EVA20 is produced (according to Figure 6b, similar ATR-IR spectra are obtained for both the E and P failed surfaces, and both the ATR-IR spectra are similar to that of the EVA20). Therefore, the adhesion between the treated EVA20 and the adhesive is improved after ageing. Furthermore, Figures 6a and 6b do not show evidence of residual isocyanate band at 2268 cm^{-1}, indicating the complete cure of the adhesive.

Ageing at room temperature and 95 wt% relative humidity also decreases the peel strength of the joints (Table 1). The ATR-IR spectra of the P failed surfaces show the existence of unreacted isocyanate (band at 2268 cm^{-1}), and the loci of failure are similar to the corresponding unaged joints (Figures 7a and 7b). Therefore, the

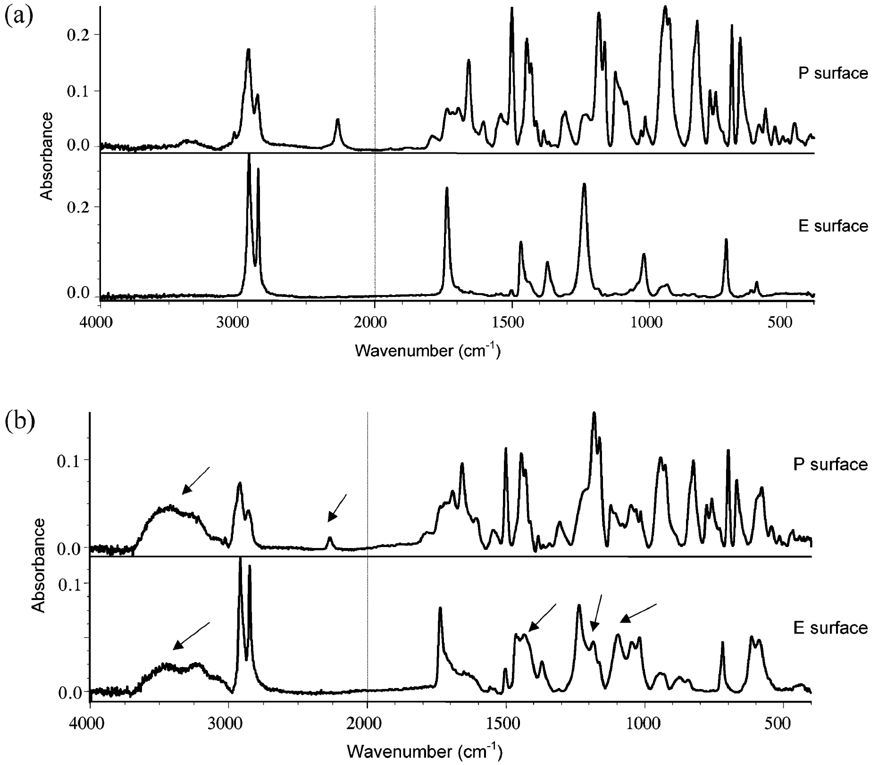

FIGURE 7 (a) ATR-IR spectra of the failed surfaces of as-received EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 25°C and 95% relative humidity for 72 h. (b) ATR-IR spectra of the failed surfaces of sulphuric acid-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint after ageing at 25°C and 95% relative humidity for 72 h.

cure of the adhesive is not complete, confirming that the improved adhesion in the joints aged at 50°C with or without humidity is due to the completion of the cure of the polychloroprene adhesive.

Durability of the Treatment of EVA 20 with Sulphuric Acid

As-received EVA 20 was immersed in 96 wt% sulphuric acid for 1 min, followed by neutralisation with ammonium hydroxide and drying under IR lamp at 60°C for 8 min. The durability of the treatment was monitored between 15 min and 5 years. The treated samples were stored in closed boxes at room temperature before characterisation and adhesive joint formation.

Contact angle values of treated EVA20 tend to decrease as time increases from 63 degrees (immediately after treatment) to 50 degrees (5 years after treatment). This indicates that the reaction of the sulphuric acid with EVA20 continues with time. ATR-IR spectra of sulphuric acid-treated EVA20 between 15 min and 61 days (Figure 8) do not show significant differences, although the bands due to O=S=O groups between 800 and 1150 cm^{-1} become more intense due to reaction of the residual sulphuric acid on the EVA20 surface. Five years after treatment, the ATR-IR spectrum of the sulphuric acid-treated

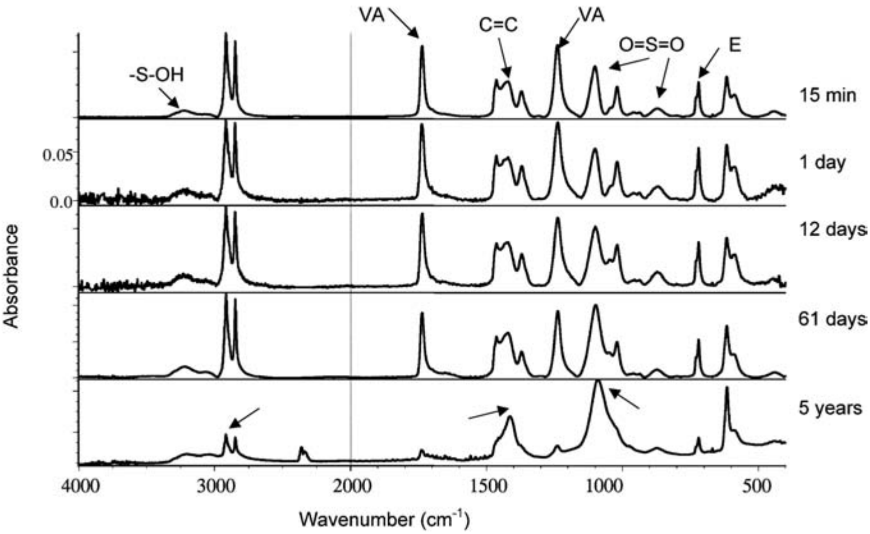

FIGURE 8 ATR-IR spectra of H_2SO_4-treated EVA20 as a function of the time after treatment. E = Ethylene, VA = Vinyl acetate.

EVA20 shows a greater degree of cyclisation evidenced by the more intense bands at 1167 (O=S=O moieties) and 1450 cm^{-1} (C=C moieties), and the removal of the typical bands due to EVA20 (2919, 2848, 1739, 1238, and 722 cm^{-1}), indicating that the reaction of EVA20 with sulphuric acid continues with time even after neutralisation with ammonium hydroxide is carried out. This is in agreement with the lower contact angle value (50°) obtained on the treated EVA20 surface 5 years after treatment. This sample has been designated EVA20 (5 years) in this article.

T-peel strength values of sulphuric acid-treated EVA20/poly chloroprene adhesive joints are given in Figure 9. The peel strength values increase after treatment of EVA20 with sulphuric acid, and the values are relatively similar to those found as the time after treatment increases up to 61 days, indicating the adequate durability of the treatment of EVA20 with sulphuric acid. However, the joint produced with the treated EVA20 (5 years) exhibits a noticeable decrease in peel strength, which can be ascribed to degradation of the outermost surface produced by a more extended reaction of EVA20 with sulphuric acid. In fact, whereas the loci of failure in the

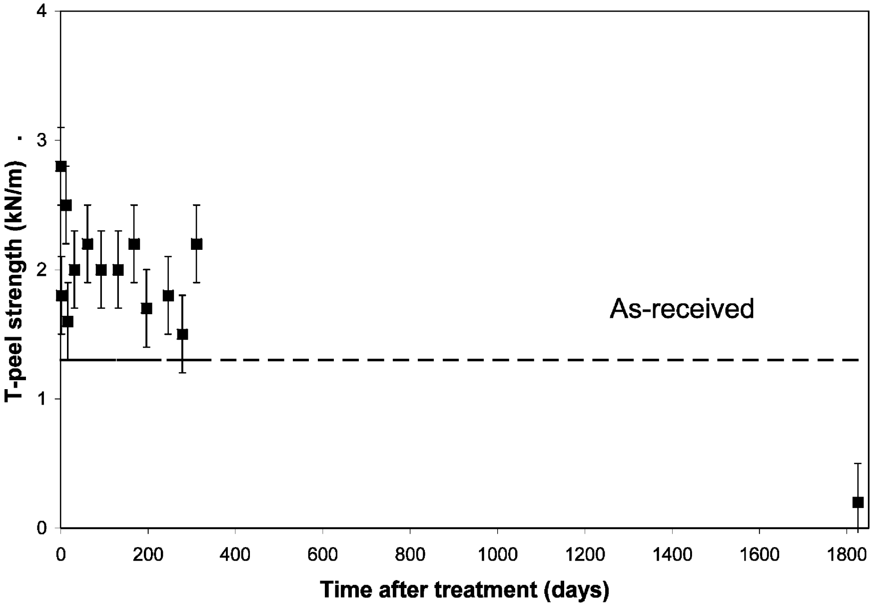

FIGURE 9 T-peel strength values of H_2SO_4-treated EVA 20/polychloroprene adhesive + 5 wt% isocyanate joints as a function of the time after treatment of EVA20.

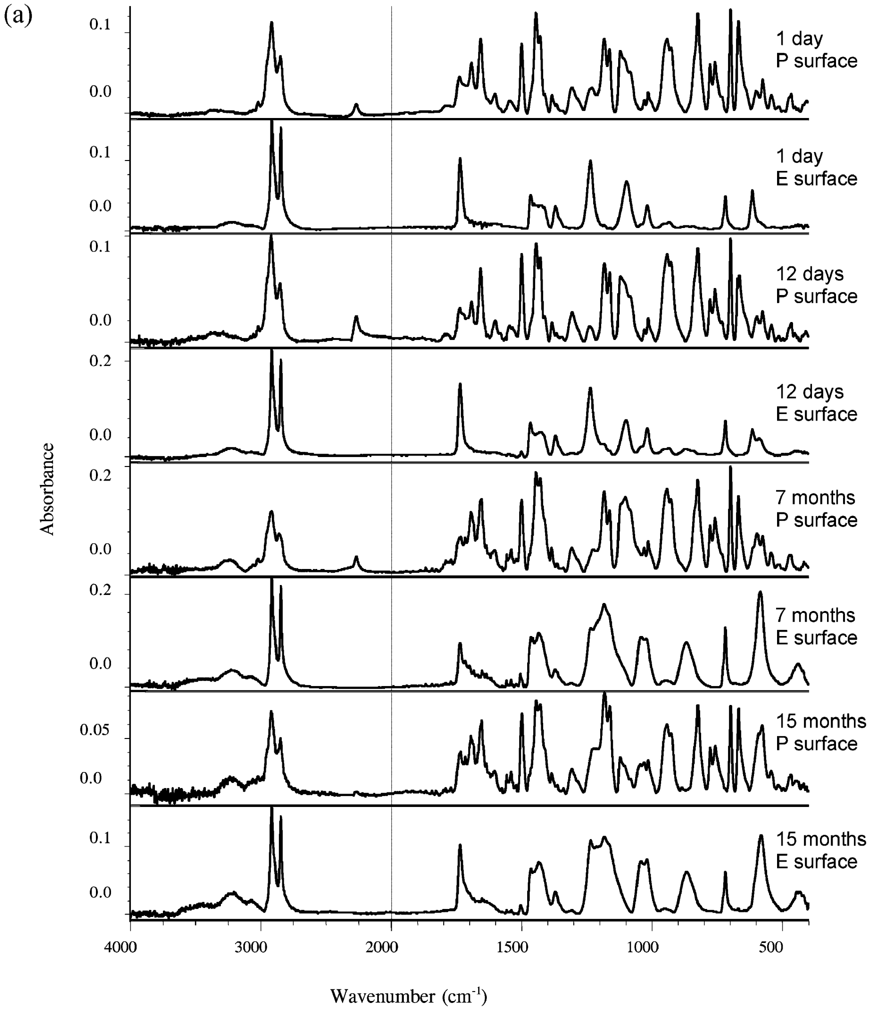

FIGURE 10 (a) ATR-IR spectra of the failed surfaces of H_2SO_4-treated EVA20 (joints produced at different times after treatment)/polychloroprene adhesive + 5 wt% isocyanate joint. (b) ATR-IR spectra of the failed surfaces of H_2SO_4-treated EVA20 (5 years after treatment)/polychloroprene adhesive + 5 wt% isocyanate joint. (Continued).

joints produced up to 15 months after treatment of EVA20 with sulphuric acid were always mixed (adhesional + cohesive failure in the adhesive), as shown in Figure 10a, the locus of failure for the joint produced with EVA20 (5 years after treatment) is different.

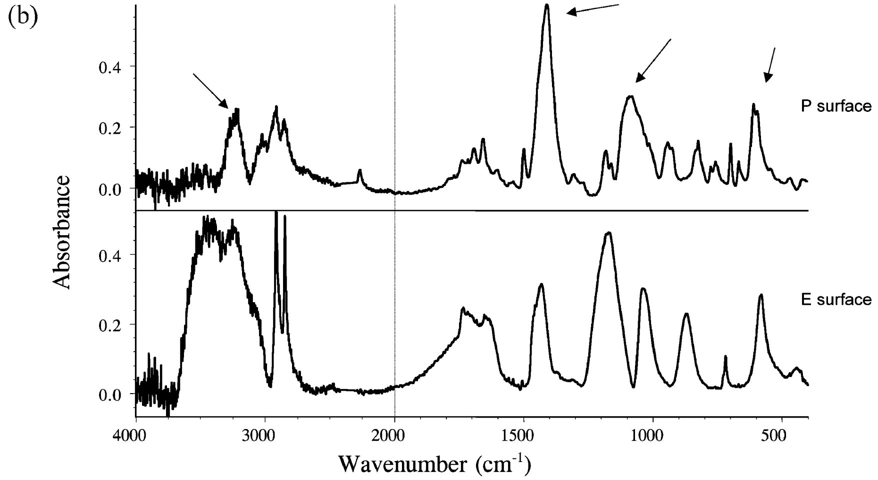

FIGURE 10 Continued.

Figure 10b shows the ATR-IR spectra of the failed surfaces of the joint produced with treated EVA20 (5 years) after peel test is carried out. The ATR-IR spectrum of the E failed surface shows the bands due to sulphonic acid moieties and cyclisation, and some bands of EVA20. By comparing with the ATR-IR spectrum of the EVA20 5 years after treatment but before joint formation, we see that the bands of EVA20 only appear when the joint is peeled. Because the ATR-IR spectrum of the P failed surface mainly shows the bands due to -S-OH, C=C, and O=S=O and some bands of the polychloroprene, it can be concluded that the failure is mixed and mainly produced in a weak boundary layer of degraded sulphuric acid-treated EVA20 surface. The existence of such a weak boundary layer can explain the decrease in peel strength obtained in the joint produced with treated EVA20 (5 years) (Figure 9).

Influence of the Concentration of the Sulphuric Acid in the Treatment of EVA20

The concentration of the H_2SO_4 used in the treatment of EVA20 may affect the performance of the treatment in adhesion. The concentration of H_2SO_4 was varied between 24 and 96 wt%. The treatment with H_2SO_4 does not decrease the contact angle of the as-received EVA20, except if a concentration of 96 wt% is used (Table 2). In fact, the ATR-IR spectra of the EVA20 treated with sulphuric acid of concentrations below 48 wt%

TABLE 2 Contact Angle Values (Water, 25°C) of As-received and Treated EVA20 with Different Concentrations of Sulphuric Acid

Treatment	Contact angle (degrees)
As received	78
24 wt% H_2SO_4	79
32 wt% H_2SO_4	82
48 wt% H_2SO_4	82
96 wt% H_2SO_4	63

show no changes from the surface spectrum of the as-received EVA20 (Figure 11), indicating a lack of chemical modifications when diluted H_2SO_4 is used. The relative intensities of the bands at 1450 cm^{-1} (typical of C=C moieties produced by treatment with sulphuric acid) and 722 cm^{-1} (typical of ethylene in EVA20, which remains unchanged after surface treatment with sulphuric acid) are given in Table 3. By increasing the sulphuric acid concentration to 96 wt% a larger relative intensity is obtained, indicating the greater effectiveness of the treatment of EVA20 with concentrated sulphuric acid.

The absence of chemical modifications and the lack of improved wettability obtained in EVA20 treated with sulphuric acid of concentrations below 48 wt% justify the poorest increases obtained in the peel strength of the adhesive joints (Figure 12). Although there are

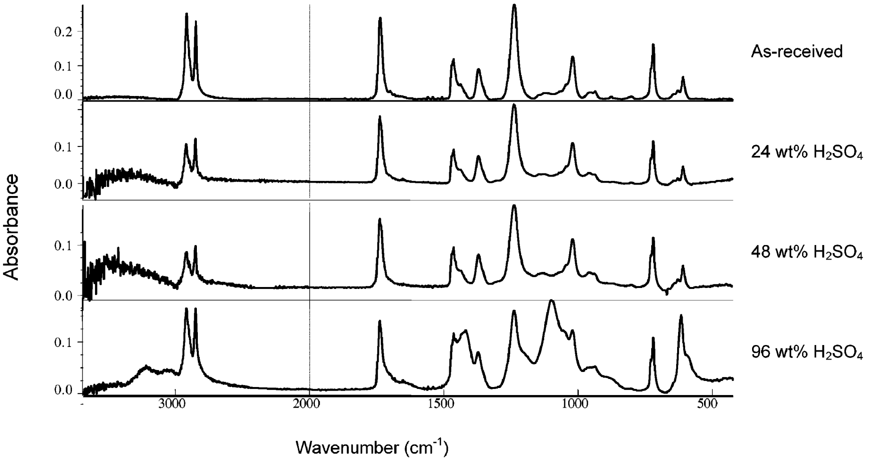

FIGURE 11 ATR-IR spectra of EVA20 treated with H_2SO_4 of different concentrations.

TABLE 3 Relative Intensities of the Bands at 1450 cm^{-1} (C=C Moieties Produced by Treatment of EVA20 with Sulphuric Acid) and 722 cm^{-1} (Methylene Group of Ethylene in EVA20) for the As-received and Treated EVA20 with Different Concentrations of Sulphuric Acid

Treatment	I_{1450}/I_{722}
As received	0.21
24 wt% H_2SO_4	0.30
32 wt% H_2SO_4	0.32
48 wt% H_2SO_4	0.31
96 wt% H_2SO_4	0.98

slight increases in peel strength upon increasing the concentration of sulphuric acid, only the treatment with 96 wt% sulphuric acid produces a noticeable adhesion improvement. Furthermore, the loci of failure in the joints produced with EVA20 treated with diluted sulphuric acid are adhesional (Figure 13 shows a typical representative example), because one of the failed surfaces corresponds to the adhesive (P surface) and the other to the as-received EVA20 (E surface)

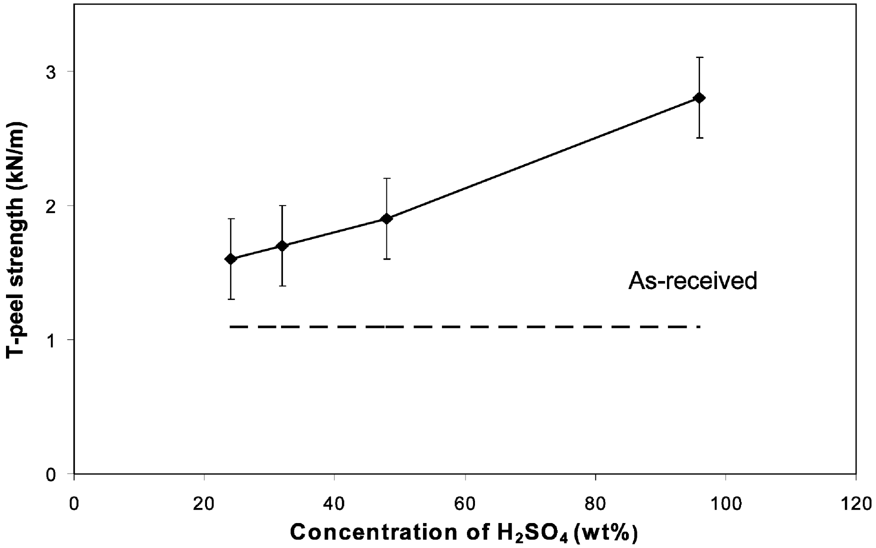

FIGURE 12 T-peel strength values of H_2SO_4-treated EVA 20/polychloroprene adhesive + 5 wt% isocyanate as a function of the concentration of the sulphuric acid.

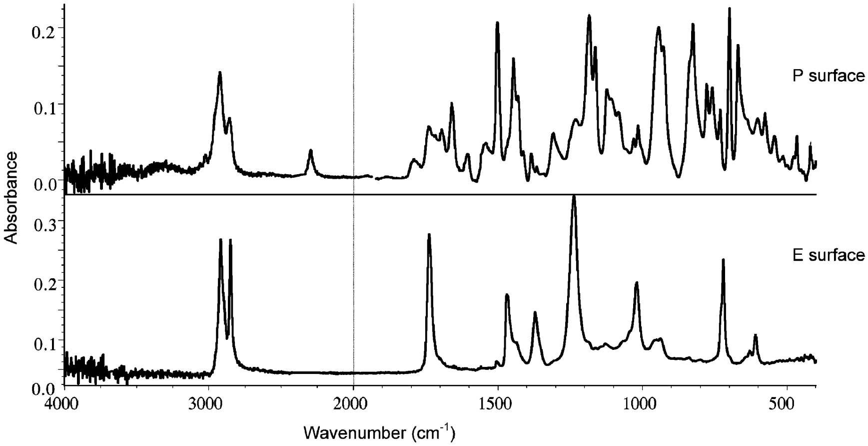

FIGURE 13 ATR-IR spectra of the failed surfaces of 24 wt% sulphuric acid-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint.

(Figure 13). Therefore, the treatment with concentrated H_2SO_4 is mandatory to produce improved adhesion and adequate surface modification of EVA20.

Neutralisation of Sulphuric Acid-Treated EVA20 With and Without Ammonium Hydroxide

It has been shown [13, 14, 16] that the neutralisation of sulphuric acid-treated polymers using a base is a key step in the effectiveness of the treatment. Therefore, in this study the neutralisation of the EVA20 treated with H_2SO_4 was carried out in two different ways: (1) Izmmersion in hot water followed by extensive washing with distilled water until neutral pH in the rubber surface was obtained and (2) immersion in hot water + neutralisation with a 15 wt% NH_4OH + extensive washing in distilled water. These two processes will be referred to as "without" and "with" NH_4OH, respectively.

Water contact angles on EVA20 neutralised with and without ammo nium hydroxide are 63 and 69 degrees, respectively; both values are lower than that of the as-received EVA20 (78 degrees), indicating that neutralisation with or without ammonium hydroxide does not provide significant differences in the wettability of EVA20 treated with sulphuric acid. The ATR-IR spectra of Figure 14, however, show more significant chemical modifications of EVA20 surface when the neutralisation is carried out with NH_4OH, confirming that more stable sulfonic acid and C=C species on the sulphuric acid-treated EVA20 are

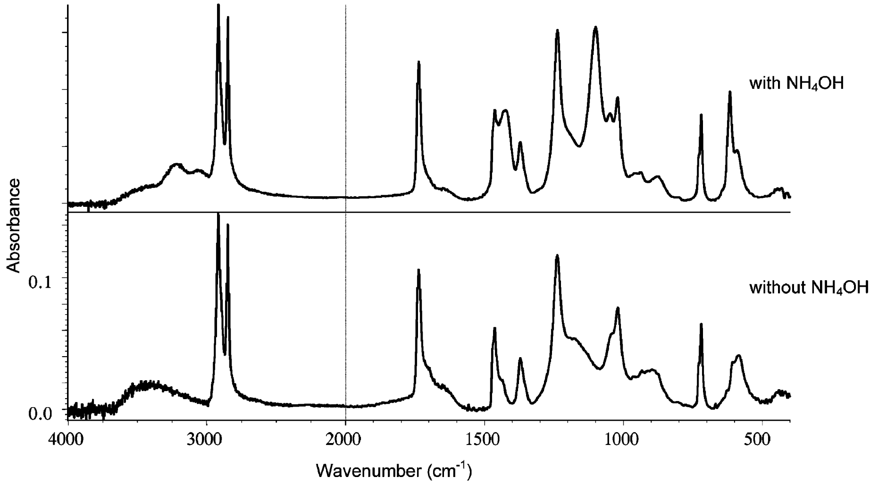

FIGURE 14 ATR-IR spectra of EVA20 treated with 96 wt% sulphuric acid and neutralised with and without NH_4OH.

produced, in agreement with previous results using different polymers [13, 14, 16].

The T-peel strength of the H_2SO_4-treated EVA20/polychloroprene adhesive + 5 wt% isocyanate joint produced with treated EVA20 neutralised without NH_4OH is much lower (0.1 kN/m) than for that neutralised using NH_4OH (2.8 kN/m). This decrease in peel strength can be ascribed to the lower degree of chemical surface modification on the treated EVA20 surface produced by neutralisation without NH_4OH, which may also favour the degradation of the adhesive by the remaining unstable acidic moieties on the treated EVA20 surface. In fact, the ATR-IR spectra of the failed surfaces corresponding to the joint produced with EVA20 treated with sulphuric acid followed by neutralisation without NH_4OH (Figure 15) show an intense band due to S-OH moieties (3200 cm^{-1}) in both failed surfaces, and a mixed failure (adhesional + cohesive failure in the adhesive) is also obtained.

Consequently, the removal of unstable acidic moieties on the treated EVA20 surface with ammonium hydroxide is important to produce optimum adhesion and performance of the sulfuric acid treatment of EVA20.

CONCLUSIONS

Treatment with sulphuric acid modifies the surface chemistry of EVA20 by creating C=C and sulphonic acid moieties. Furthermore,

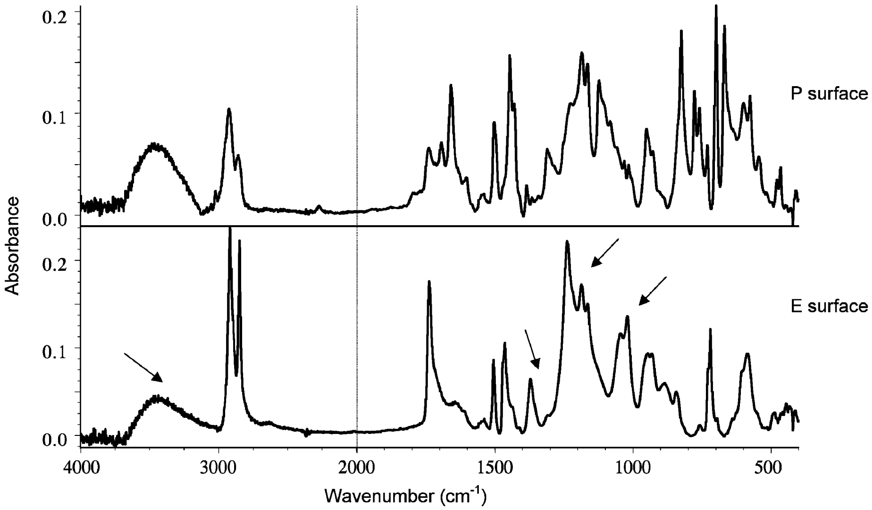

FIGURE 15 ATR-IR spectra of the failed surfaces obtained after peel testing of H_2SO_4-treated EVA20 neutralised without NH_4OH/polychloroprene adhesive + 5 wt% isocyanate joint.

improved wettability and some cracks are produced on the EVA20 surface as a consequence of the treatment. The treatment with sulphuric acid increases the peel strength of joints produced with polychloroprene adhesive + 5 wt% isocyanate, and a mixed failure (adhesional + cohesive failure in the adhesive) is obtained. The peel strength of the joints is improved after ageing due to complete curing of the adhesive. Furthermore, the modifications produced on the EVA20 surface after treatment remained for at least 61 days. Finally, the use of concentrated sulphuric acid (96 wt%) and neutralisation with ammonium hydroxide are essential to produce adequate performance of the treatment of EVA20.

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