In Situ and Ex Situ FTIR–ATR and Raman Microscopic Studies of Organosilane Hydrolysis and the Effect of Hydrolysis on Silane Diffusion Through a Polymeric Film

PETER EATON, PAUL HOLMES, JACK YARWOOD

1 School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michaels Building, White Swan Road, Portsmouth, PO1 2DT, United Kingdom

2 Pilkington plc, Group Research, Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, L40 5UF, United Kingdom

3 Materials Research Institute, Sheffield Hallam University, Pond Street, Sheffield, S1 1WB, United Kingdom

Received 31 July 2000; accepted 19 February 2001

ABSTRACT: We report combined FTIR–ATR and Raman microscopic studies of the distribution and redistribution of three different silane adhesion promoters in thin (10–20 μm) PVC films deposited on a Si/SiO₂/SiOH substrate (a "model" glass surface). It has been shown that the different functionalized silanes diffuse at different rates through the polymer (at 70°C) and therefore have different distributions at the polymer/glass interface. The differences in behavior have been rationalized in terms of their respective abilities to hydrolyze and condense, under the different humidity and temperature conditions used. As the level of humidity rises there is evidence that the diffusion rate (measured using a dual-mode sorption model) decreases as a result of hydrolysis and condensation in the polymer films. The data are of importance as a direct measure of the relation between humidity levels and the adhesive action of a silane promoter at polymer/glass interfaces. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2016–2026, 2001

Key words: organosilanes; diffusion; polymeric film; hydrolysis; condensation; dual-mode sorption

INTRODUCTION

Organosilanes are a class of materials with a wide range of industrial applications. Most of these applications make use of the ability of silanes to form a covalent bond to inorganic materials. Examples include the functionalization of silica for use as a chromatographic material, as chemical reagents, and as an adhesion promoter in polymer composites and laminates. In all these applications, silane must be hydrolyzed for condensation to take place. The reaction scheme (Scheme 1) shown emphasizes that silanes hydrolyze in the presence of water to form a hydroxysilane, which is more reactive than the corresponding alkoxysilane. The hydroxysilanes may then undergo a condensation reaction at a mineral surface (i.e., the surface to be functionalized).

In reality, however, the reaction can be much more complicated than that shown because of competing reactions. For example, two hydroxysilanes may condense to form a dimer. Indeed, the most common silanes have three alkoxy groups,
so each silane may be hydrolyzed to form a mono-, di-, or trihydroxyl form. Therefore it is entirely feasible for silanes to form polymeric chains (referred to as condensation). The overall reaction that will occur is highly dependent on variables such as the availability of water, the nature of the surface to be grafted, the chemical functionality of the silane, and the pH of the original solution. Because of the usefulness of the products of hydrolysis of organosilanes in both the scientific and commercial worlds, the reaction has been very widely studied, and a full survey of the available literature is beyond the scope of this study. However, the study of the hydrolysis of silanes in this context has mainly been ex situ (i.e., in solution), although the use of silanes in commercial applications is not usually from solution. Hydrolysis is performed in situ, using water in the ambient atmosphere.

The object of the work described in this study was to combine the use of confocal Raman microscopy and FTIR–ATR spectroscopy to study the effects, both in situ and ex situ, of the hydrolysis of organosilanes on the way in which they are able to diffuse and redistribute themselves within a polymeric/glass laminate. We attempted to use the techniques to monitor the effect of hydrolysis on the rate of diffusion within a PVC film cast onto a silicon ATR crystal (which comprises silicon/silicon oxide) at the polymer/substrate interface. Measurements were performed as a function of the humidity conditions to which the polymer film is exposed and depending on whether the silane was prehydrolyzed.

Both infrared and Raman spectroscopy were previously used to study the hydrolysis of silanes. For example, Raman techniques were used to study the hydrolysis of silanes in aqueous solution. The technique is highly suitable for such studies because it has the same ability to distinguish chemicals by their groups as constituent infrared spectroscopy, but can be applied more easily to aqueous solutions. The changes in Raman band intensity of vinylsilane and methacryl silane were used to follow the hydrolysis of such materials in aqueous solutions including the condensation to siloxane oligomers. However, such studies depend on the rate of hydrolysis, as indicated in a study of aminosilanes for which the process proceeded so quickly to condensation that the hydrolysis reaction could not be followed. The catalytic effect of the amine group in this context was also described elsewhere. Raman spectroscopy was also previously used by Bertelsen and Boerio to study the rate of \( \gamma \)-glycidoxypropyltrimethoxy-silane (GPS), which was strongly dependent on the water concentration in solution. After 2 h in aqueous solution, the species present (confirmed using \(^{29}\)Si–NMR) was the condensate. The correlation of the concentration of oligomers with durability tests on the specimens showed that a high concentration of silane oligomers was detrimental to sample durability. It was found that Raman spectroscopy could not be used to study condensation directly but that a measure of condensation was possible by measuring the decrease in the concentration of the Si–O–Si groups.

Other techniques were also used to follow siloxane hydrolysis, including FTIR spectroscopy and the measurement of isotherms on the Langmuir trough. Several silanes showed infrared bands near 1030 cm\(^{-1}\) that were assigned to the Si–O–Si stretching bands of oligomerized silanes. However, the infrared hydrolysis studies with which we are familiar were carried out on thin films of silanes on mineral surfaces rather than in situ in a polymer/glass laminate.

In situ studies investigations of silane hydrolysis in composite systems are even more limited. However, a laminate system used in the manufacture of circuit boards was examined using neutron reflection depth profiling. The silane layer (~ 80 Å thick) was sandwiched between a silicon wafer and an epoxy polymeric layer (~ 2 μm thick). It was found that, after humidity condi-
tioning, the thin interfacial layer of water was present at the silicon/silane interface. In laminates without silane this layer was found to be absent. This was a surprising result, given that it has been found\textsuperscript{19} that such silanes increase the laminate resistance to weakening by water. It is clear that a water-based reaction was occurring at the interface and the authors assumed that this reaction was hydrolysis. However, because the adhesive bond between the epoxy and silicon was not degraded by this process, it is clear that, if hydrolysis occurred, it was not complete. Some water was also found throughout the epoxy polymer layer but at a low concentration. The technique allowed depth profiling to be performed and it was found that there appeared to be a high level of penetration of epoxy into the silane layer. Conversely, no evidence of diffusion of silane into the epoxy layer was found.

However, in contrast to this work a system consisting of glass fibers treated with an aminosilane, mounted in an epoxy resin, was analyzed by FTIR microscopy. In this case the intensity of the OH band of water appeared to show the lowest intensity at the fiber surface. The apparent contradiction between the neutron and FTIR results, as far as we know, has not yet been explained. However, some evidence of \textit{in situ} hydrolysis was also seen by Dibenedetto and Scola.\textsuperscript{20} In a glass/silane/epoxy system the silane and epoxy were cast in the same solution to form a mixed layer. Using SIMS spectroscopy they discovered that, upon curing, the polymer appeared to form three distinct layers: a polymerized siloxane at the air/epoxy surface, oligomers at the center of the film, and again a polymeric siloxane structure at the glass epoxy interface. This is thought to be attributed to hydrolysis and condensation with the available water at the air/glass interface but little or no condensation was observed in the center of the laminate.

**EXPERIMENTAL**

The silanes studied were $[3$-(phenylamino)-propyl]trimethoxysilane, known as Y9669 ($>95\%$); $[3$-(amino)propyl]trimethoxysilane, known as A1110 ($97\%$); and $[3$-(mercapto)propyl]triethoxysilane, known as A1891 ($>80\%$), all obtained from Fluka Chemicals (Buchs, Switzerland). The structures are shown below.

Y9669: $\text{C}_6\text{H}_5\text{NH}($CH$_2)_3\text{Si(OMe)}_3$
A1110: $\text{H}_2\text{N}($CH$_2)_3\text{Si(OMe)}_3$
A1891: $\text{HS}($CH$_2)_3\text{Si(OEt)}_3$

The silanes were handled only in a dry nitrogen environment to prevent hydrolysis prior to the start of the experiments. In the case of experiments using prehydrolyzed silanes, the silanes were removed from their containers and exposed to the atmosphere for 24 h prior to use.

The polymer used was poly(vinyl chloride) (PVC), secondary standard, molecular weight 80,000, from the Aldrich Chemical Company (Milwaukee, WI). In plasticized films, the plasticizer was dihexyl adipate (DHA) provided by Pilkington plc (Ormskirk, UK). The plasticized films were produced by mixing 15\% w/w of DHA with PVC before casting from dimethylformamide. The substrates for film casting were polished silicon wafers. These wafers also functioned as micro-ATR crystals for FTIR–ATR experiments. These micro-ATR crystals produced approximately 40 reflections in the ATR experiment, and were therefore considerably more sensitive than standard ATR crystals.\textsuperscript{21} The crystals were also found to be suitable for use as substrates in Raman microscopy because of the lack of fluorescence, commonly seen with glass microscope slides. For infrared experiments, PVC films were cast from N,N-dimethylformamide to produce films of 10 $\mu$m thickness. To study diffusion, a large amount of silane was bushed onto the outside of the PVC film. For Raman microscopy experiments, similar laminates were constructed, but with 20 $\mu$m PVC films. In the Raman experiments, the silane was covered with a very thin (20 $\mu$m) coverslip to protect the microscope objective from silane adsorption. Because of the low signal-to-noise ratio and background absorption in some of the Raman experiments, the Raman data were analyzed by curve-fitting a Gaussian function to the peak of interest, and a second-order curve to the background. The area of the Gaussian function was used to estimate the integrated intensity of the Raman band. This was found to give more reliable results than those by simple integration, and also removed the possibility of interference from adjoining peaks.

Infrared measurements were made using a Mattson Polaris FTIR spectrometer, with 4 cm$^{-1}$ resolution. Spectra were collected by coadding 120 to 520 scans. Reference spectra were obtained in transmission on a KBr disc and diffusion measurements were made using micro-ATR accesso-
Raman measurements were made using a Renishaw Ramanscope 2000 fitted with a helium neon laser (633 nm) and a CCD detector. The spatial resolution in the z direction, achieved in confocal mode, was found to be approximately 1.8 μm. The measurement of this figure was previously described and involves measuring the full width at half height FWHH of the response of the microscope at the surface of a silicon reference sample.

RESULTS AND DISCUSSION

To follow diffusion of silanes into PVC films, FTIR–ATR spectroscopy was previously used. If the silane diffuses through the PVC film, the spectrum of the silane is measured in the FTIR–ATR experiment, and grows in intensity as the silane approaches the ATR crystal, until an equilibrium is reached. First, reference spectra of the three silanes were measured in transmission (Fig. 1).

**Ex Situ Hydrolysis**

To determine the kinetics of hydrolysis under ambient conditions, silanes were exposed to air by spraying neat silane onto potassium bromide plates. Changes in the infrared spectra of the silanes were then monitored over approximately 1 week. The spectra obtained for Y9669 are shown in Figure 2. In the case of Y9669, a band at 992 cm\(^{-1}\) decreased in intensity with time, whereas a shoulder on the band at 1080 cm\(^{-1}\) (at about 1020 cm\(^{-1}\)) increased in intensity. The band at 992 cm\(^{-1}\), which was assigned to the Si—O—Et stretching mode for an ethoxy silane,\(^{2,23}\) was therefore assigned to the Si—O—Me stretching mode in this case. The loss of this band confirms hydrolysis of the methoxy silane. A similar silane showed a shoulder at 1038 cm\(^{-1}\) upon condensation, and therefore we assigned the increase in the shoulder at 1020 cm\(^{-1}\) in the spectra of Y9669 to condensation of the silane to siloxane oligomers (see Scheme 1). The rate of hydrolysis of the silane may thus be followed by monitoring the intensity of the 992 cm\(^{-1}\) peak. It was found that the other silanes, A1110 and A1891, had similar bands that also showed very similar sensitivity to hydrolysis (not shown). In the case of A1110, the band was at 930 cm\(^{-1}\), and in A1891 it was at 958 cm\(^{-1}\).

The intensities of the bands used were plotted against time to determine the rate of hydrolysis of each of the silanes (see Fig. 3). It may be seen that Y9669 underwent rapid hydrolysis over the first 24 h in air, followed by much more gradual hydrolysis over the next week. A1110 also underwent immediate hydrolysis, but seemed to continue significantly to hydrolyze over the next week. On the other hand, A1891 initially underwent little change, even after 2 days. However, after 5 days there was a decrease in intensity, showing that hydrolysis had begun, and the reaction appeared to be still under way after 9 days. The relatively rapid hydrolysis of A1110 and Y9669 (i.e., the aminosilanes) may have been be-
cause the amino silanes were able to autocatalyze their hydrolysis.

**Diffusion with Prehydrolyzed Silanes**

Using the reference infrared spectra, one non-overlapping peak was selected for each silane to use as a marker for diffusion. The intensity of this peak was used to show how far towards the crystal the silane had diffused. It should be noted, however, that the relationship between FTIR–ATR band intensity and diffusion distance is nonlinear. The bands used to show diffusion are summarized in Table I. Diffusion of these silanes through plasticized PVC films was previously observed; however, this was for plasticized PVC films. It was found that in unplasticized (pure) PVC films, diffusion did not occur unless the films were heated to near the $T_g$ of the PVC (i.e., 70°C). Raising the temperature to the $T_g$ and plasticizing the polymer both induce enhanced flexibility of the polymer chains, thus presumably facilitating the diffusion of the silanes. To observe the rates of diffusion of the silanes, the films were periodically heated to 70°C and cooled before a measurement was made. Silanes were used as received and were exposed to atmospheric humidity for 24 h. From the previous section, it can be seen that, after 24 h of such exposure Y9669 underwent considerable hydrolysis, A1110 showed some change, and A1891 showed very little reaction. The results are shown for both unhydrolyzed and prehydrolyzed silanes in Figures 4 and 5 for Y9669 and A1891, respectively. The times shown in the figures refer to the treatment times at 70°C (followed by cooling). No diffusion was observed in the case of A1110. Figure 4 shows that hydrolyzed Y9669 took considerably longer to diffuse through the PVC film. Figure 5, on the other hand, shows very little change between the hydrolyzed and unhydrolyzed A1891.

The previous results (Fig. 3) showed that, whereas Y9669 underwent considerable hydrolysis after 24 h, A1891 did not. It was concluded that silanes that have undergone hydrolysis (and probably subsequent condensation) tend to diffuse more slowly through PVC films at 70°C. The reason that no diffusion was detected in the case of A1110 is not known. It seems possible that exposure to the atmospheric humidity caused such rapid hydrolysis that no diffusion could occur in that experiment. Another possibility is that an amine bicarbonate may be formed upon heating in the presence of CO$_2$. The product of this reaction would be evident in the FTIR spectra. However, because no diffusion occurred, no spectra were observed. There was no indication of bicarbonate formation in the spectra of the other

![Figure 2](image_url)  
**Figure 2** The Si—O stretching region of spectra obtained in transmission of Y9669 undergoing hydrolysis with atmospheric water.
aminosilane, Y9669, after heating. It is worth noting, however, that diffusion of A1110 through plasticized PVC was previously observed.\textsuperscript{22}

**In Situ Hydrolysis Under Controlled Conditions**

The work described in the previous section appeared to show that humidity could slow the diffusion of the silane Y9669, probably by hydrolysis and/or condensation of the silane. However, the use of atmospheric humidity to affect hydrolysis has the disadvantage of an uncontrolled level of water. It was decided, therefore, to treat the silanes at a known level of humidity, to assess how differing the amount of moisture would affect diffusion.

![Figure 3](image-url)  
**Figure 3** Intensities of peaks assigned to Si—O—C stretching versus time exposed to atmospheric humidity for each silane.

<table>
<thead>
<tr>
<th>Silane</th>
<th>Frequency (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y9669</td>
<td>1602</td>
<td>C—C ring stretch and N—H bend</td>
</tr>
<tr>
<td>Y9669</td>
<td>3408</td>
<td>N—H stretch</td>
</tr>
<tr>
<td>A1110</td>
<td>1600</td>
<td>N—H bend</td>
</tr>
<tr>
<td>A1891</td>
<td>2565</td>
<td>S—H stretch</td>
</tr>
</tbody>
</table>

![Figure 4](image-url)  
**Figure 4** The integrated intensity of the 1602 cm\(^{-1}\) band of hydrolyzed (□) and unhydrolyzed (△) Y9669 versus time, during diffusion in PVC at 70°C.

**In Situ Hydrolysis Under Controlled Conditions**

The work described in the previous section appeared to show that humidity could slow the diffusion of the silane Y9669, probably by hydrolysis and/or condensation of the silane. However, the use of atmospheric humidity to affect hydrolysis has the disadvantage of an uncontrolled level of water. It was decided, therefore, to treat the silanes at a known level of humidity, to assess how differing the amount of moisture would affect diffusion.

![Figure 5](image-url)  
**Figure 5** The integrated intensity of the \(\nu(SH)\) stretching band of hydrolyzed (□) and unhydrolyzed (△) A1891 versus time, during diffusion in unplasticized PVC at 70°C.
the diffusion. At the same time Raman microscopy was used to determine whether hydrolysis could be affected by moisture in the PVC/silicon laminate. It was thought that this might be an important effect because direct incorporation of the silane into the polymer laminate, without pre-hydrolysis, is sufficient to induce adhesion in the industrial lamination process. Given that some hydrolysis is thought to be necessary for adhesion to occur, it seems reasonable to assume that hydrolysis would occur inside a polymer laminate.

Figure 6 shows the results of an experiment used to explore the diffusion of Y9669 in a PVC film that had no prior special treatment (i.e., it had been exposed to atmospheric humidity). In an experiment similar to the infrared experiments described earlier, the intensity of the $1600 \text{ cm}^{-1}$ Raman band of the silane was measured near the polymer/silicon interface after the silane had been applied to the top of the laminate. If the silane diffused through the PVC film, one would expect to see an increase in the intensity of the Raman band over time. However, as discussed below, the spatial sensitivity of the two experiments (FTIR–ATR and Raman) was different, so direct comparison of the results is difficult. The microscope was focused, in confocal mode, a distance of 6 $\mu$m from the PVC/silicon interface of a laminate. The focal point was therefore 18 $\mu$m from the application point of the silane. In each experiment, the intensity was then monitored over a number of hours.

The results (Fig. 6) show that the silane Y9669 did indeed diffuse through the PVC film. The Raman intensity of the silane did not reach an equilibrium value during the experiment, indicating that diffusion was ongoing after 8 h. However, the diffusion did appear to have been slowing down by the end of the experiment. A Raman depth profile of the laminate was obtained afterward, which is shown in Figure 7. This shows that the silane had diffused throughout the PVC film. As was noted previously,22 a depth-profile distribution such as that in Figure 7 is thought to be indicative of an even distribution of the silane, with a small excess of silane remaining at the
air/PVC interface. The reduction in intensity throughout the depth of the PVC film is attributed to scattering of the laser light by the polymer film. An ATR infrared diffusion experiment was also performed on this sample (exposed to atmospheric humidity), the results of which are shown in Figure 8, along with the fitting to a dual-sorption model, obtained as previously described. It can clearly be seen that the diffusion appeared to occur much more rapidly in the infrared experiment than in the Raman diffusion experiment (Fig. 6). This was because of the thinner film used in the infrared experiments.

With the results (Figs. 6–8) of hydrolysis and diffusion in mind we then proceeded to explore what happened for a PVC film prepared in the same way but then exposed to a relative humidity of 44% for 48 h. This level of humidity was obtained by allowing the air to come into equilibrium with a saturated solution of K₂CO₃ (aq) (and checked with a hygrometer). The results of the Raman experiment are shown in Figure 9. Even though the experiment was performed for a longer time than that described earlier, the diffusion did not seem to have reached the inflection point at which it started to slow, and diffusion appeared to be slower than that seen in the previous experiment (Fig. 6). In fact, some laser-induced degradation led to an increase in background fluorescence. This meant that a depth profile in the same spot afterward was not possible. However, an infrared diffusion experiment was performed with a film treated in the same way. The results are shown in Figure 10, along with a fitting to the dual-sorption model. A comparison of Figure 10 with Figure 8 shows that two infrared diffusion experiments led to similar overall diffusion rates, although to different proportions (and hence different shapes) of the overall diffusion rates of mobile and partially mobile solute species (and hence different shapes).

Figure 8  The integrated intensity of the 1602 cm⁻¹ infrared band of Y9669 versus time, during diffusion. The laminate was exposed to atmospheric conditions.

Figure 9  The integrated intensity of the 1602 cm⁻¹ Raman band of Y9669 versus time, during diffusion. The laminate was exposed to K₂CO₃ (relative humidity 50%).
The third set of conditions used involved exposure of the film to a humidity of 90% for 48 h using a saturated solution of NH$_4$Cl(aq). For this experiment, the laser intensity was reduced and longer acquisition times were used, in an attempt to avoid thermal degradation of the PVC. The results of the Raman diffusion experiment are shown in Figure 11, from which we may deduce that the diffusion was considerably slower after the film had been treated at 90% humidity than at lower humidities. The depth profile shown in Figure 12 has a very similar profile to that in Figure 7, indicating complete diffusion through the film, with a small excess at the surface of the film. The results of an infrared diffusion experiment on a film treated with 90% humidity are shown in Figure 13. Comparison of Figure 13 with Figures 8 and 10 clearly shows that the diffusion rate was considerably slower than the diffusion in films with lower water levels. Table II confirms this trend and demonstrates that at the highest humidities there is a movement toward a single

![Figure 10](image10.png)  
**Figure 10** The integrated intensity of the 1602 cm$^{-1}$ infrared band of Y9669 versus time, during diffusion. The laminate was exposed to K$_2$CO$_3$(aq) (relative humidity 50%).

![Figure 11](image11.png)  
**Figure 11** The integrated intensity of the 1602 cm$^{-1}$ Raman band of Y9669 versus time, during diffusion. The laminate was exposed to NH$_4$Cl(aq) (relative humidity 90%).

![Figure 12](image12.png)  
**Figure 12** The integrated intensity of the 1602 cm$^{-1}$ band of Y9669 versus distance after diffusion into a laminate exposed to NH$_4$Cl(aq) vapor (relative humidity 90%).
Fickian diffusion process. It is thought that this trend is the result of hydrolysis and subsequent condensation, slowing the diffusion of the silanes, ascribed to steric effects. This is therefore indirect evidence of in situ hydrolysis of the silanes inside the PVC films.

The Raman data were analyzed by measuring how much the intensity of the Raman band increased over its initial value during a set period of 9 h. The results are shown in Table III. It can be seen that by this measurement, the Raman results show that there was a clear trend toward slower diffusion, from atmospheric conditions, through 44% humidity, to 90% humidity. This slower diffusion process with increased film humidity is thought to result from in situ hydrolysis and condensation of the silane.

Although the results from the two techniques should not be directly compared, one would expect the overall trend to be the same. The fact that the

<table>
<thead>
<tr>
<th>Condition</th>
<th>1602 cm(^{-1}) Band Area After 9 h/Initial Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric conditions</td>
<td>10.6</td>
</tr>
<tr>
<td>K(_2)CO(_3) (aq)</td>
<td>5.4</td>
</tr>
<tr>
<td>NH(_4)Cl (aq)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Raman experiments showed a larger decrease in diffusion rates with humidity level may be because of the way that the experiments were performed. In the Raman experiments, the laminate was covered with a glass coverslip after the silane was applied and taped in place on the sample holder. This may have prevented the PVC film from losing its internal humidity and coming into equilibrium with the atmosphere, whereas the infrared samples were exposed to the atmosphere during the course of the experiment, so one might expect humidity levels to decrease gradually to those in the atmosphere.

CONCLUSIONS

It was shown that all three silanes may be hydrolyzed by exposure to atmospheric conditions. In the case of Y9669, such hydrolysis leads to significantly slower diffusion through unplasticized PVC. Because of a lower propensity to hydrolysis, A1891 did not show slower diffusion after a 24-h exposure. Hydrolysis may also occur inside a polymer laminate. The level of humidity in a PVC film affects not only the distribution of a silane in a polymer laminate but also the extent of hydrolysis and condensation in that laminate. This in turn results in both a diffusion rate change to the interface and in the mechanism of diffusion (the relevant curves becoming more single Fickian as the level of humidity in the film increases). Our data confirm that the use of silane promoters to induce adhesion at polymer/glass laminate interfaces must take account of the water content of the polymer component and water levels in the substrate surface.

REFERENCES