ELSEVIER

Polymer 40 (1999) 1629–1636

polymer

Role of an active environment of use in an environmental stress crack resistance (ESCR) test in stretched polyethylene: A vibrational spectroscopy and a SEM study

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Received 3 February 1998; accepted 1 May 1998

Abstract

Characterisation of the role of an active environment of use in an industrial Environmental Stress Crack Resistance (ESCR) test has been carried out during the tensile deformation of polyethylene samples. We intended to map the presence of the active environment within the material using Raman and infrared spectroscopy. We found Raman not suitable for the detection of this environment inside the sample while by IR the environment seemed to be predominantly present within the transition fronts of the material. A stress-induced environment diffusion mechanism is suggested. By scanning electron microscopy (SEM) differences in the deformation process between drawing in air or in detergent became apparent. These results suggest that the environment penetrates into the sample during the necking process, stabilising crazing. At the molecular level it is likely that chain slip and unravelling of molecular disentanglements are facilitated. All these observations may also be operative during the ESC phenomenon as samples are subjected to stress, resulting in crazing. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Active Environment; Environmental Stress Crack Resistance (ESCR) tests; IR microscopy; SEM

1. Introduction

The term Environmental Stress Cracking (ESC) relates to the premature failure of polymeric materials in real life services under both small loads and the presence of active environments such as detergent solutions at about room temperature. In particular, ESC limits the lifetime of polyethylenes used in critical applications such as pipes, containers, linings under landfills, geomembranes, etc. The failure is associated with long-term low-level loading conditions and it is considered to develop more rapidly in the presence of certain chemical environments. This mode of failure is characterised by the presence of macroscopic 'cracks' in the material with a microscopic fibrous nature at the fracture surface. It is generally accepted that these cracks arise from the previous existence of a 'craze' ahead of the crack, i.e. at a point of stress concentration, which develops further with time. The precise molecular mechanisms leading to this mode of failure remain a matter of discussion [1–6].

Several rapid laboratory scale methods, including the Environmental Stress Crack Resistance (ESCR) test, have been developed to quickly predict real life ESC behaviour. The proposed molecular mechanisms of failure are principally based on the results of these methods. Actually, the industrial purpose of these methods, faster simulating ESC, is the ranking of the different grades of material as a function of their ESC resistances in a relatively short time. Methodologies involving previous cracks, notches, special sample shapes, low stress applying devices, aggressive liquid environments, medium–high temperatures, etc., have been put forward in order to quickly anticipate failure of materials under ESC conditions. The role of the environment in the overall ESC and in the ESCR tests and its interaction with the polymer have not been satisfactorily described. The role of the active environment in the ESC phenomenon is observed to be the acceleration of sample failure. This is believed to occur by absorption of the active environment by the polymer and subsequent 'lubrication' of polymer chains, resulting in earlier failure under Slow Crack Growth (SCG) conditions. This effect is supported by the reduction of the activation energy seen in various papers. Various authors [1–4] believe that this absorption

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PII: S0032-3861(98)00406-6

occurs in the amorphous phase. However, Ward et al. [7] suggested that the active environment (Igepal: $C_{19}H_{19}$–C_6H_4–O–$(CH_2CH_2O)_8$–CH_2CH_2OH; nonyl phenol ether glycol) could also diffuse inside the crystals. Nevertheless, no physical evidence of the detergent inside the polymer was unambiguously shown. This study aims at finding and locating the environment inside the polymer by using vibrational spectroscopic techniques and observing the physical effects that uniaxial deformation in the presence of the detergent produces compared with uniaxial deformation in air, using SEM. Samples were subjected to stress levels as normally used in ESC tests. A previous study showed a larger mass uptake of surfactant in films subjected to stress [8].

Although the effect of the environment is usually considered a unique effect, in practice some environments have produced a large effect and others have produced no effect at all on the ECS characteristics. For instance, water seems not to have a marked effect on the polymer properties regarding the ESC [1]. Short chain length alcohols seem to swell the polymer by diffusing inside [9], [10]. Wetting the polymer is another effect that certain environments produce [11]. The latter effect leads to a reduction of the free surface energy and reduces the local yield stress at the surface. This might initiate a craze at the surface. Because most of the industrial ESCR tests use commercial detergents as the active environment, we carried out this study with a commercial detergent (Rodhacal) which is the active environment used in an industrial Environmental Stress Crack Resistance (ESCR) test.

2. Experimental

2.1. Active environment

The commercial detergent Rodhacal-DS 10 was utilised as the active environment in this study. Rodhacal is an anionic alkylbenzenesulphonate detergent ($C_{18}H_{29}SO_3Na$). A saturated solution in water of this detergent was used in the current experiments in order to both increase the magnitude of the effect and to obtain a good detergent signal in the vibrational spectra. The usual concentration of this detergent used in the ESCR Notch test is 5 g/l. During drawing of the material at room temperature (cold-drawing), a saturated water solution of Rodhacal was held in contact with the polymer by placing several drops on the polymer surface.

2.2. Materials

2.2.1. Samples for spectroscopic studies

Two dumb-bell specimens (1) and (2) of sample CP1, an ethene–butene copolymer (see Table 1 for sample characteristics), were used in both Raman and infrared experiments. These specimens were stretched in a stretching device with the detergent solution on top of the polymer surface until necking was evident in part of the gauge-length of the samples. For obtaining Raman spectra, sample 1 was stretched in a house-made stretching device attached to the Raman microscope and was deformed slowly by hand until the gauge-length was partially necked. Micro-Raman spectra were recorded in depth on the sample, while the sample was still clamped and the detergent solution was over the polymer surface. For obtaining IR spectra, sample 2 was stretched in a Minimat polymer rig (Polymer Laboratories) at a speed of 0.5 mm/min up to a draw ratio (λ) of 3. Subsequently, the sample was removed from the clamps, carefully dried with a tissue to remove the detergent solution from the polymer surface, and measured using an IR spectrometer. Sample thicknesses before stretching were about 200 μm for sample (1) and about 30 μm for sample (2).

2.2.2. Samples for SEM study

Two dumb-bell specimens (3) and (4) of sample CP2 (see Table 1) were stretched to $\lambda = 3$, i.e. half of the natural draw ratio, in both air and in the presence of a saturated solution of the detergent Rodhacal, respectively. Sample (4) strained in detergent was held for 1 h in the detergent solution prior to stretching. Both samples were studied by SEM. Sample thickness was 200 μm for both samples. After having been drawn in the detergent, sample (4) was washed thoroughly with water and dried carefully with a tissue before the SEM study was carried out.

2.3. Micro-Raman confocal

The micro-Raman experiments were performed using a confocal microscope attached to a Jobin-Yvon U1000 Raman spectrometer. Further details of the setup can be found in Refs. [12, 13]. Both × 50 and × 100 times long working distance microscope objectives, with 514 nm excitation (20 mW on the sample) and a 300 μm pinhole were used. Spectra were recorded with 600 grooves/mm gratings, resulting in a spectral resolution of 6 cm^{-1}.

Table 1
Some sample characteristics

Sample	Density (kg/m^3)	(SCB) /1000	M_n ($\times 10^3$)	M_w ($\times 10^3$)
CP1	953	0.2 (E)	13	240
CP2	938	4.9 (E)	17	180

SCB, Short Chain Branching; E, ethyl branches.

2.4. IR microscope

IR spectra were recorded using an infrared microscope connected to the IFS85 FT-IR spectrometer (both from Bruker). Spectra were collected using 100 scans at a resolution of 4 cm^{-1}.

2.5. Internal reflection spectroscopy (attenuated total reflection (ATR))

A Split Pea accessory from Harrick was used. A silicium ATR crystal was used. Using a contact angle of 45°, this so-called single bounce accessory was placed in the FT-IR Perkin Elmer System 2000 spectrometer. Using this ATR setup, information from the top few micrometres of the sample under study were collected.

2.6. SEM

A Jeol-820 scanning electron microscope was used. Samples were gold coated prior to SEM observations.

3. Results and discussion

3.1. Testing IR and Raman for suitability of measuring penetration of environment in PE

Raman spectra were taken both from the detergent (solid state) and from the polyethylene sample (1), in order to search for a spectral range in which detergent and polymer could be simultaneously identified by means of non-overlapping bands. The spectral range chosen was 650–1200 cm^{-1} (see Fig. 1). In this range a broad band can be seen around 760 cm^{-1} (likely ring stretching in phase) arising from the detergent. Polyethylene shows the C–C stretching bands at 1060 cm^{-1} and 1130 cm^{-1} in the range recorded.

Fig. 2 shows a depth profile study of sample (1) after having been stretched with the detergent on top of the polymer surface. Spectra were taken while the sample was still clamped, focusing at 1, 6 and 8 μm above the polymer surface, at the polymer surface (0 μm), and at 2 and 4 μm below the polymer surface. The spectra were taken with a × 100 objective and 300 μm pinhole in a spot of the sample (not larger than 1 μm in the lateral dimension and with a depth resolution not larger than 2 μm) within the undeformed part close to the transition front. The thickness of the detergent layer at this point was about 10 μm. It can be observed from Fig. 2 that the detergent was no longer present after penetrating 4 μm inside the polymer surface.

A second experiment to search for detergent was carried out in another spot of the stretched sample away from the neck (see Fig. 3). In this spot only a thin layer of 2 μm of detergent could be seen on the polymer surface. Focusing 6 μm inside the polymer, a weak detergent band at 760 cm^{-1} could still be observed. However, the depth resolution is now about 6 μm (× 50 objective). Further movement of the focus inside the polymer sample results in the disappearance of the detergent band.

Mid-infrared experiments were carried out on sample (2). The IR spectrum of the detergent is shown in Fig. 4 together with the IR spectrum of the polyethylene. The very intense IR band of the detergent centred at 1200 cm^{-1} will be used for the characterisation of the detergent inside the polyethylene. This band is likely assigned to the strong S=O stretching of the sulphonate group. The presence of this detergent band could be found in the transmission IR spectrum of

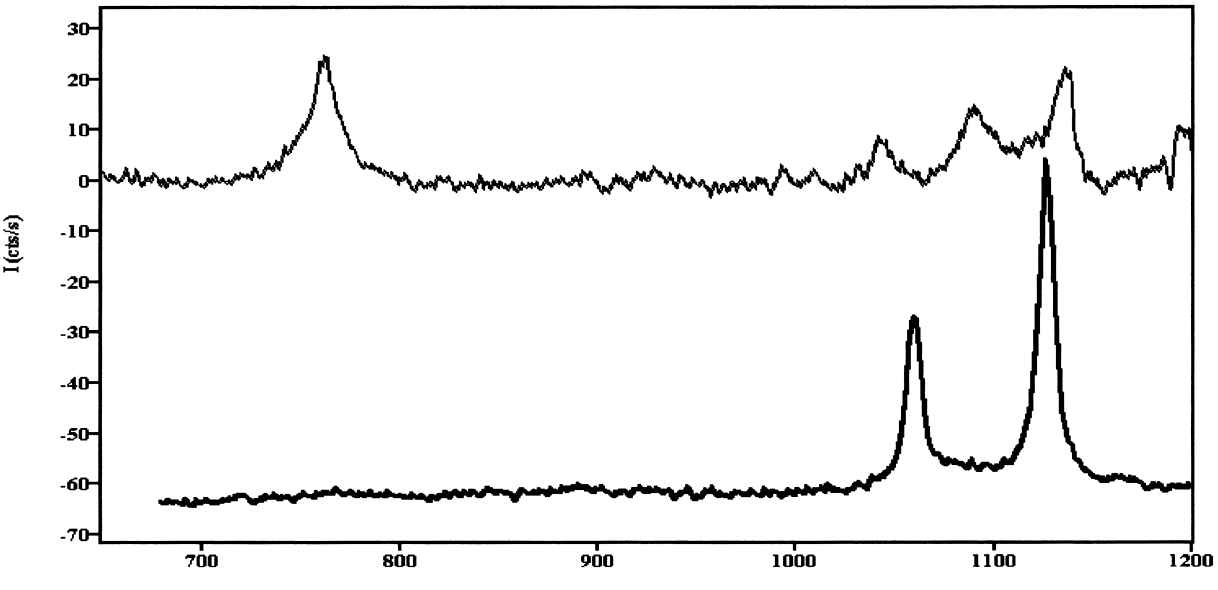

Fig. 1. Raman spectra of both the detergent Rodhacal (top) and polyethylene sample CP1 (bottom).

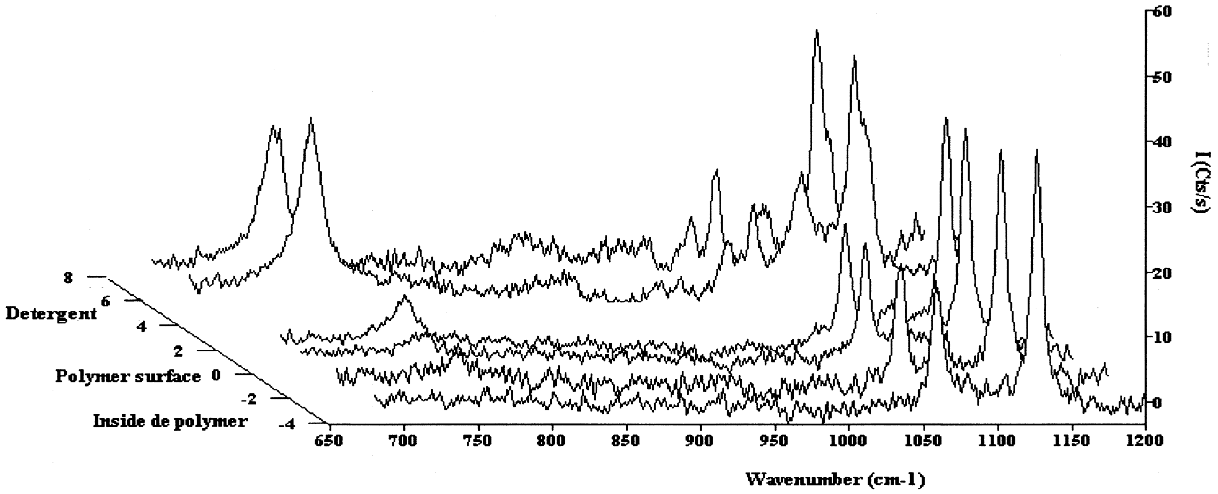

Fig. 2. Raman spectra plotted versus depth of focus (μm) taken in sample (1) with a × 100 objective and 300 μm pinhole. At 0 μm the microscope is focused at the polymer surface. Positive values (μm) mean that the focus spot is positioned above the polymer surface (detergent side) and negative values mean that the focus spot is positioned below the polymer surface (inside the polymer).

sample (2) at the various locations probed (see for instance Fig. 5).

We conclude from the previous experiments that Raman spectroscopy does not seem to be suitable for this study. Apart from the surface, where a top layer of detergent is present, the band of the detergent was not detected in spectra recorded with the laser spot focused inside the polymer. Consequently, a concentration profile in depth cannot be measured using confocal Raman spectroscopy. IR does, however, show the presence of detergent inside the polymer after cleaning the surface. We therefore conclude that IR is more sensitive to the presence of detergent than Raman spectroscopy and therefore it seems to be a more suitable technique for this particular study.

3.2. Further IR study

Fig. 5 shows the infrared transmission spectra taken at the various points indicated in the schematic of sample (2) (also shown in Fig. 5). The spatial resolution of the IR measurement in the lateral direction (axial resolution) is about 20 μm. The band of the detergent (around 1200 cm^{-1}) can be seen in most of the spectra. However, the concentration does not seem to be homogeneous, being clearly larger at points 4, 5, 6 and 10. Points 4, 6 and 10 were taken in the transition front areas (where the material is actually necking), and here the structure is already oriented. It is well known that infrared absorption can be directly related to concentration by the Lambert–Beer equation. However, in

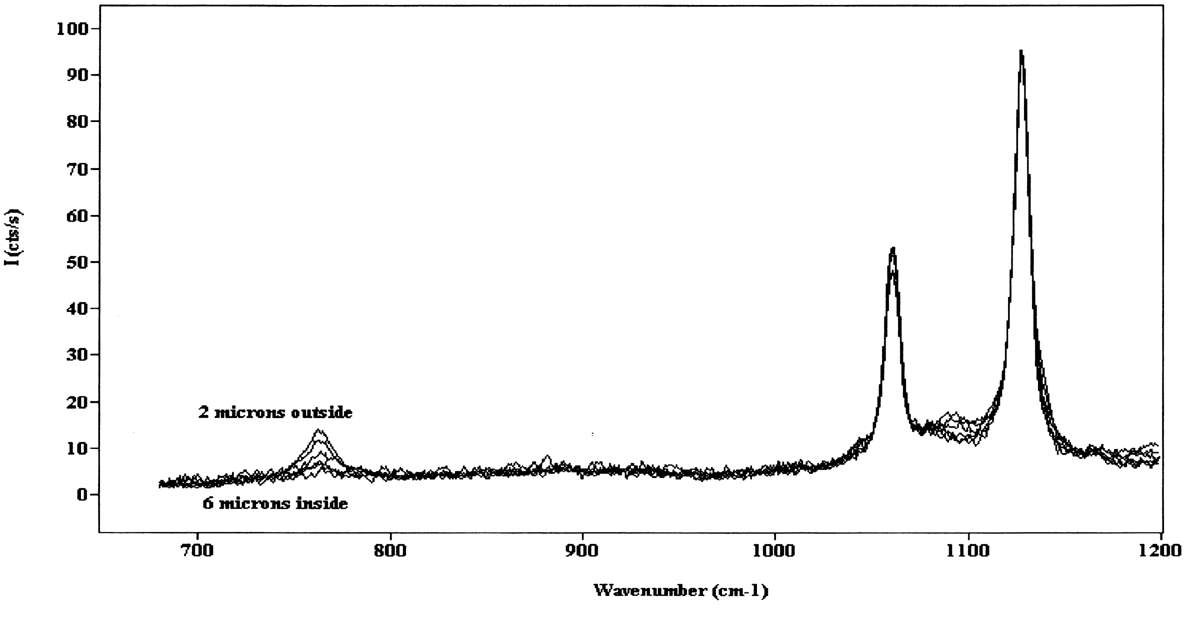

Fig. 3. Raman spectra taken with a × 50 objective and 300 μm pinhole at different depths of focus in sample (1). The spectra are normalised to the 1130 cm^{-1} polyethylene band intensity. Each spectrum was taken by progressively (from top to bottom spectra) deepening the focus spot 2 μm inside the polymer sample, beginning 2 μm outside the polymer and finishing 6 μm inside.

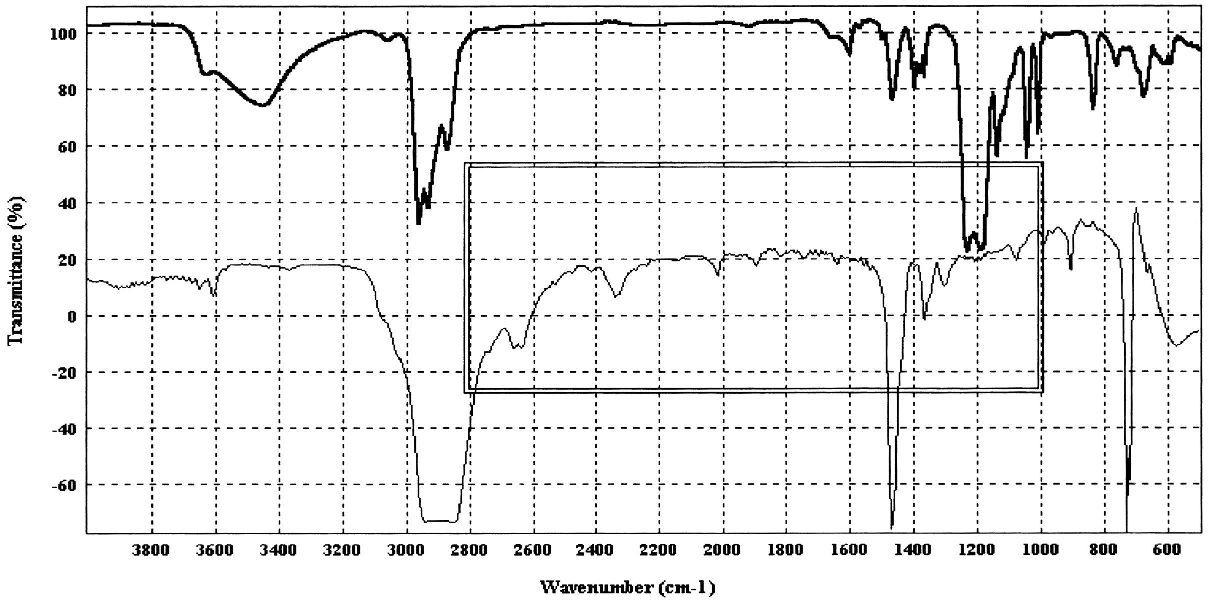

Fig. 4. Transmission infrared spectra of both the detergent (top) and polyethylene sample (2) (bottom). The rectangular inset indicates the range of interest.

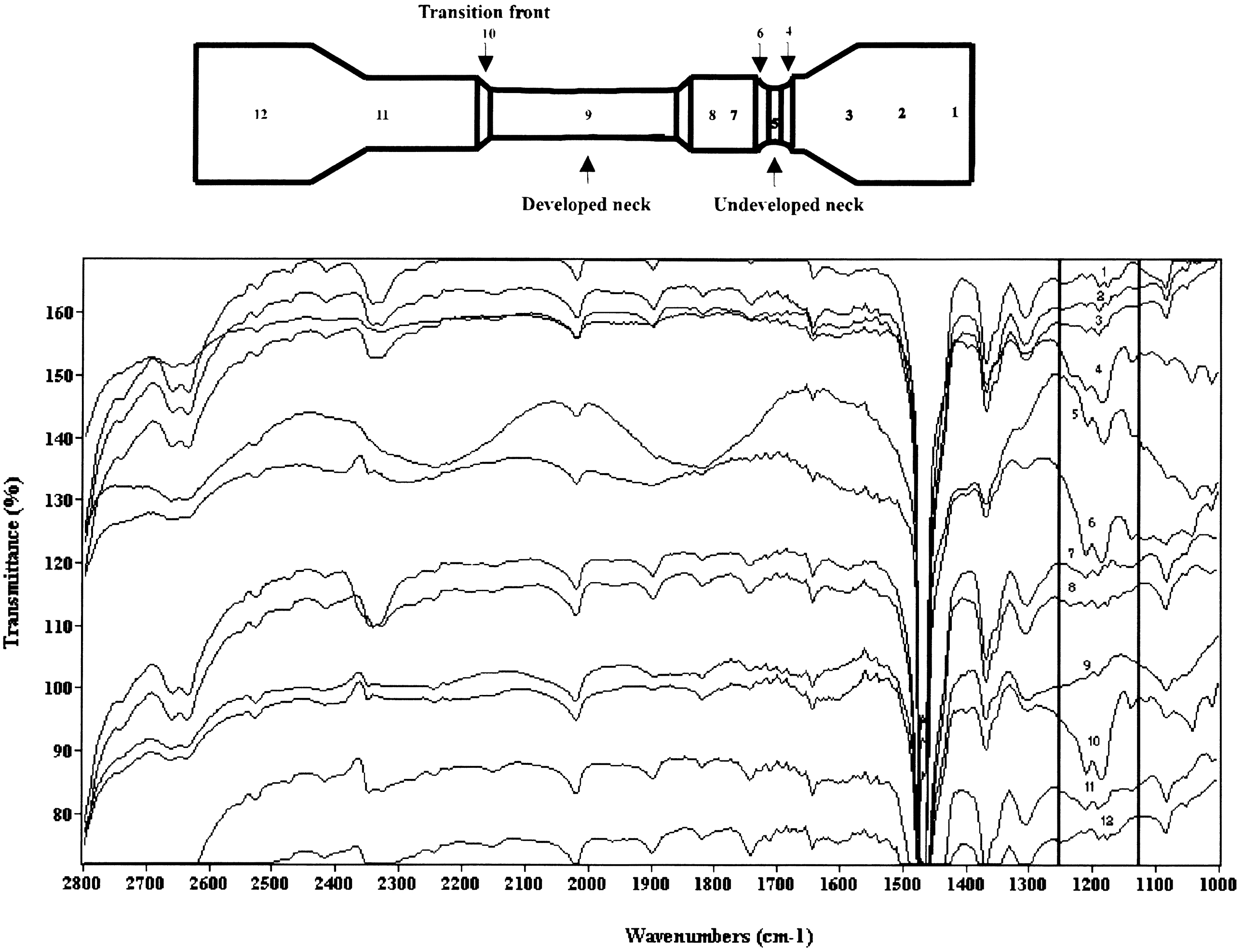

Fig. 5. Transmission infrared spectra taken at the various points indicated in the schematic of sample (2). All spectra were first normalised to the intensity of the 1460 cm^{-1} band and subsequently shifted in the y-axis direction for clarity purposes. Points 1, 2, 3, 7, 8, 11 and 12 were taken in undeformed parts of the sample, points 5 and 9 within the two necked parts of the sample and points 4, 6 and 10 were taken in the transition fronts of the sample.

order to compare two samples, differences in thickness have to be taken into account. Point 5 was taken in the middle of the so-called ‘undeveloped neck’. At point 9 (middle of the so-called ‘developed neck’) the concentration of detergent seems to be low. The spectra taken in the undeformed material (points 1, 2, 3, 7, 8, 11 and 12) also show a low concentration of detergent. Although differences in thickness are expected between the drawn and undrawn areas, we expect to compensate this effect by normalising all the spectra to the intensity of the bending band (1460 cm^{-1}). The above observations suggest that at the transition fronts the concentration of the detergent is higher. It is at these points (4, 6 and 10) that the stress is felt most strongly by the material and therefore where the molecular structure is changing most.

ATR measurements (surface measurements) were taken in both necked and undeformed regions of sample (2) (the positions of points 9 and 11 in Fig. 5, respectively). These ATR measurements are shown in Fig. 6 together with the transmission spectra taken at points 9, 10 and 11 of Fig. 5. As can be seen from this figure, the concentration of detergent at the surface is low compared with the concentration seen in the transmission spectrum of, for instance, point 10 and high/equal compared the transmission spectra of points 9 and 11. We have to remark at this point that the sample surface was cleaned prior to IR measurement. Consequently, the ATR results suggest that it is unlikely that a detergent signal such as that found in transmission at point 10, can be said to arise from only the surface. Thus, it seems that the concentration of detergent inside the transition front areas is higher than at the surface, whereas the concentration of detergent inside the undeformed and necked areas is lower/similar to that measured at the surface.

The IR results suggest that the detergent goes inside the polyethylene sample. However, the concentration of detergent is observed to be inhomogeneous throughout the sample. The results point to a larger uptake of detergent at the transition fronts; this further suggests a stress-induced detergent diffusion mechanism. In these areas (transition fronts), major changes occur in the sample, e.g. stress whitening related to voiding, crazing, etc., which might facilitate the diffusion of detergent molecules into the material.

Within the undeformed parts the concentration of detergent (uptake) seems to be very low. This is also the case for the necked material. A feasible explanation for the low concentration of detergent at the well-necked areas could be that in this highly oriented material the detergent has been squeezed out.

3.3. SEM study

To observe the visual physical effects that drawing in the presence of detergent produces on the polyethylene structure, a SEM study was carried out on two identical samples, (3) and (4), that were stretched to the same extent ($\lambda = 3$) in the presence of air and detergent (saturated solution of soap Rodhacal), respectively. The first macroscopic observation was that necking proceeded differently in air than in detergent. The neck length was 1.2 times higher for the sample drawn in air than for the sample drawn in detergent. Furthermore, the macroscopic appearance of the transition fronts were sharper for the sample drawn in air than for the sample drawn in detergent.

A SEM study of the samples led us to the following microscopic observations (see Fig. 7).

- The various parts of Fig. 7 suggest a different morphology for the two stretched samples. The differences are seen at any position within the deformed part.
- Fig. 7(a) and (b) indicate that these differences are

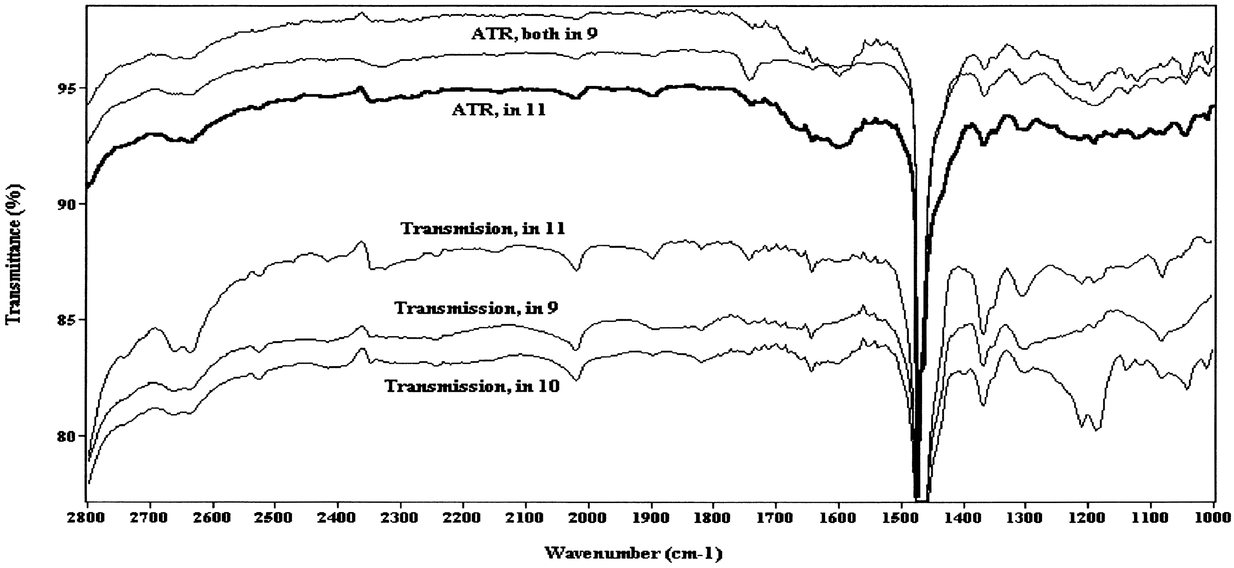

Fig. 6. ATR measurements (top three) at points 9 and 11 of sample (2) (seen in Fig. 5) and transmission IR measurements (bottom three) taken at points 9, 10 and 11 of sample (2) (also seen in Fig. 5). All the spectra were normalised to the 1460 cm^{-1} band and shifted in the *y*-axis direction for comparison purposes.

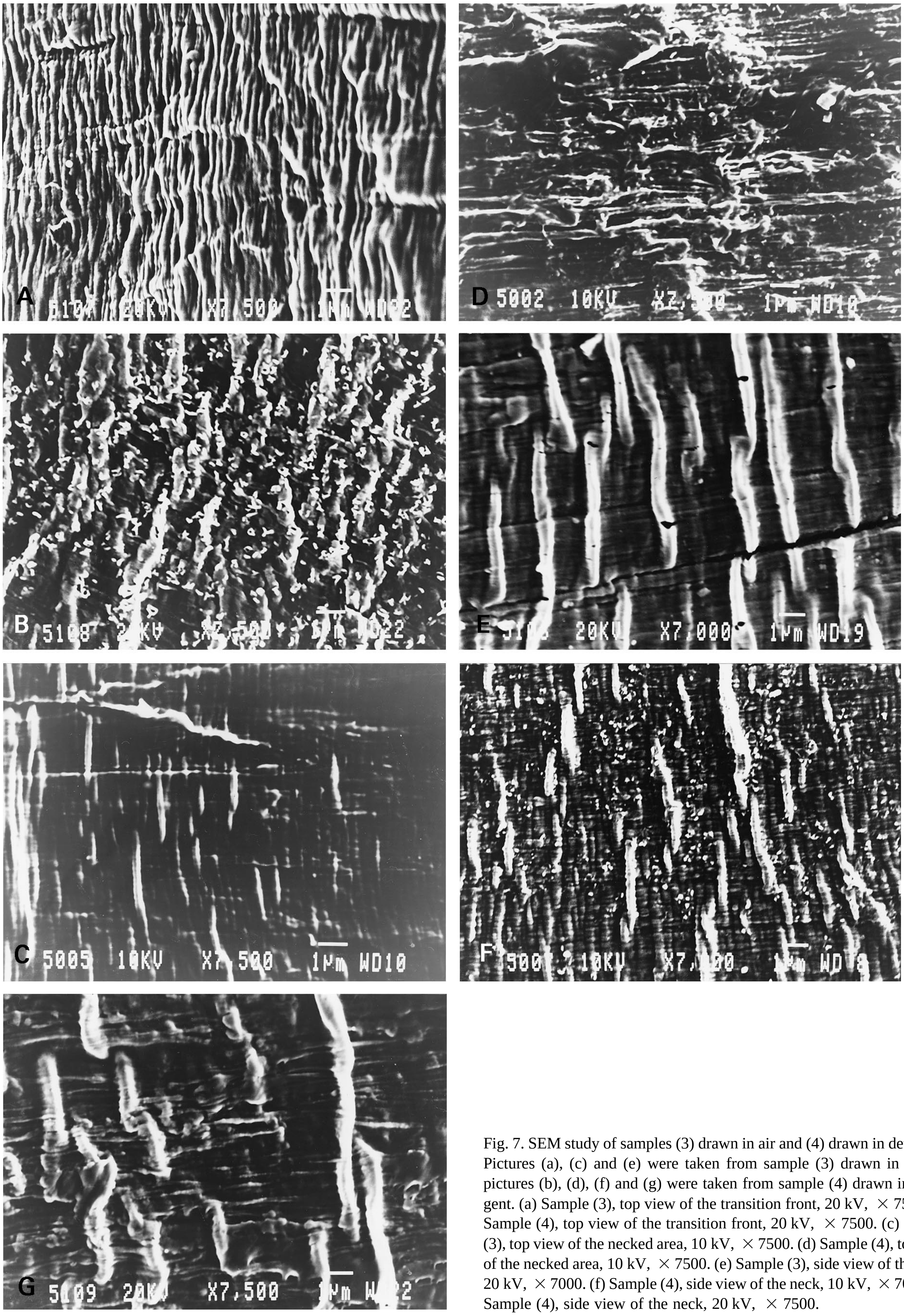

Fig. 7. SEM study of samples (3) drawn in air and (4) drawn in detergent. Pictures (a), (c) and (e) were taken from sample (3) drawn in air and pictures (b), (d), (f) and (g) were taken from sample (4) drawn in detergent. (a) Sample (3), top view of the transition front, 20 kV, × 7500. (b) Sample (4), top view of the transition front, 20 kV, × 7500. (c) Sample (3), top view of the necked area, 10 kV, × 7500. (d) Sample (4), top view of the necked area, 10 kV, × 7500. (e) Sample (3), side view of the neck, 20 kV, × 7000. (f) Sample (4), side view of the neck, 10 kV, × 7000. (g) Sample (4), side view of the neck, 20 kV, × 7500.

already apparent at the transition fronts (where the material is actually necking). At this position, drawing in air shows a well-ordered crazing process perpendicular to the drawing direction whereas drawing in detergent seems to show a non-regular crazing process, interrupted along the drawing direction, and with apparent wide open crazes.

- Fig. 7(c) and (d) give a top view of both materials within the necked area. The sample drawn in air (c) presents a compact fibrillar structure in the drawing direction, whereas the sample drawn in air shows areas with pulled out fibrils and voided crazes.
- Fig. 7(e) and (f) show a side view of the neck. The material drawn in air presents a dense and regular fibrillar structure, whereas the material drawn in detergent does not show this structure. Slight magnification of (f) results in (g). In (g) voided regions (crazes) and pull out fibrils are evident, suggesting a lack of compactness between fibrils along the neck.

To produce all the macroscopic and microscopic effects seen in the sample drawn in detergent, molecules of detergent must diffuse inside the polymer and reduce the cohesion between fibrils formed at yield regions. The detergent seems to stabilise the crazing process, avoiding, in a sense, regular packing of the fibrils into a dense structure. Stabilisation of the crazes is a well described process, the degree and type of which depend on the nature of the material and on the solvent [11]. J.J. Lear et al. [14] described the effect of Igepal (a non-ionic soap) thus: ‘‘When crack growth is attempted in the presence of the ESC agent, Igepal CO-630, the material within the crazes is less coherent with voids and large broken fiber ends visible. This is in contrast to the same experiments conducted in air where neither voids nor large broken fibrils were seen’’.

4. Discussion and conclusions

This study aimed to identify the role of an ESCR detergent (active environment) during tensile deformation of polyethylene samples. We first tried to map the presence of the detergent in the sample using IR. The detergent seemed to be predominantly present within the transition fronts of the material, where the effective stress and subsequent material changes (yielding process) are known to be greatest. As a consequence, a stress-induced detergent diffusion mechanism is suggested. However, the diffusion of detergent inside the sample was definitely suggested by a SEM study in which differences in the deformation process between drawing in air or in detergent became apparent. This can be understood by the detergent playing an active role throughout the material during the necking process. Voids and pulled-out fibrils were seen in the drawn material in the presence of detergent. This points to a stabilisation of the crazes and therefore to a weakening of the drawn material cohesion. This material behaviour has already been observed in the presence of other active environments like Igepal.

Diffusion of detergent molecules into the polymer due to stress might result in increased chain mobility and therefore in a reduction of the activation energy (plasticising effect) of the deformation process. Craze stabilisation can also be regarded as the reduction of the free surface energy of the fibrils by the detergent, impeding a regular packing of the fibrils. The latter effect would delay the overall necking (fibrils coagulation into a neck) process. At the molecular level it can be envisioned that chain slip and unravelling of molecular disentanglements are facilitated by the presence of a solvent (detergent). All these observations may also be operative during the ESC phenomenon as samples are subjected to stress, resulting in crazing. Nevertheless, further studies need to be carried out in order to identify the precise mechanism of interaction between the environment and the molecular structure of solid state of the polyethylene.

Acknowledgements

We would like to thank S. Bremmers (DSM Research) and B. Calvo (University of Valladolid) for experimental support. The management of DSM Research is acknowledged for permission to publish this work.

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