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To cite this article: Somyot Tantipattarakul *et al* 2019 *J. Phys. D: Appl. Phys.* **52** 395302

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On the influence of morphology and chemical defects on charge transport dynamics in polyethylene: thermal ageing and concentration gradient

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Received 12 March 2019, revised 11 June 2019

Accepted for publication 4 July 2019

Published 24 July 2019

Abstract

A blend composed of a high-density polyethylene and a low-density polyethylene was subjected to thermo-oxidative ageing at 160 °C, under conditions where oxygen diffusion effects lead to a non-uniform distribution of chemical defects throughout the specimens. The existence of highly and lightly oxidised regions was demonstrated by Fourier transform infrared spectroscopy and confocal Raman microprobe spectroscopy and the effect of these on the dielectric behaviour of the system was investigated. Dielectric spectroscopy revealed a broad loss peak at frequencies above 1 Hz that increases in strength with increasing ageing time, which we associate with the motion of polar chain segments within the polymer. For ageing times below 3 h, samples exhibited reduced conductivity under a constant electric field compared with the initial unaged system; above 3 h, the conductivity was found to increase monotonically with ageing time and corresponded to the appearance of an additional low frequency (<1 Hz) dielectric loss process and marked migration of space charge into the bulk away from the relevant physical electrode. This change in behaviour was found to occur abruptly and the final distribution of space charge was found to correlate well with the distribution of ageing inducing chemical defects within the system. From these observations, the effects of chemical defects on charge transport dynamics are discussed.

Keywords: non-uniform ageing, polyethylene blend, thermal ageing, charge transport

(Some figures may appear in colour only in the online journal)

1. Introduction

Polyethylene is a versatile material that has found uses in areas ranging from cheap commodity items to numerous high performance applications [1, 2]. Soon after the first industrially viable synthesis of this polymer in 1933 [3], the importance of polyethylene as an electrical insulation material was realized and this position remains to this day. Indeed, the general acceptance of the impact of fossil fuels on the planet's atmosphere has led to significant investments in renewable generation technologies which, in turn, have required the

development of new generations of cable technologies. In 2014, for example, ABB reported on a 525 kV high voltage direct current (HVDC) extruded cable system [4], which was subsequently refined by NKT in 2017 to increase the operating voltage to 640 kV [5]. These advances were fundamentally built upon materials refinements and, in particular, novel strategies to reduce contamination levels within the cross-linked polyethylene (XLPE) insulation [6].

While impurities may be introduced during manufacture, the processes of ageing and degradation during use will also change the structure, chemistry and resultant properties of

polymers, which are closely related to their macromolecular architecture and chemical make-up. Consequently, any chemical reaction or physical process that affects these factors leads to changes in macroscopic characteristics. Exposure to elevated temperatures results in initial chain scission, which leads to the formation of free radicals, polymer fragmentation, the generation of low molecular weight products, crosslinking and chemical ageing by-products. In the presence of oxygen, the reaction of radicals formed in the initial chain scission step with available oxygen leads to the formation of hydroperoxides, which may subsequently decompose to form yet more radicals through chain branching reactions [7, 8]. In the case of polyethylene, early studies of such reactions [9, 10] reported, primarily, the formation of ketones, esters, carboxylic acids and aldehydes [11]. As such, an important factor relates to the diffusion of oxygen into the material, as described by Audouin *et al* [12]. Where ageing involves reactions with such molecules, the process becomes kinetically controlled by diffusion of the penetrant, such that the distribution of reaction products is determined by the diffusion of oxygen combined by its consumption and the relevant chemical reactions. This leads to the formation of a degraded surface layer of thickness $\sim D/k$, where D is the relevant diffusion coefficient and k the pseudo-first-order reaction rate constant for oxygen consumption.

The influence of ageing on the electrical performance of insulation systems has been considered by many workers and while the latter stages are reasonably well understood [13–16], appreciation of the initial phases remains poor. In general, initiation is believed to involve the chemical and physical modification of the pristine polymer through the formation of defective regions at the nano- and micro-scales [17]. Crine [18] suggested that the initial stage of degradation under a high electric field ($>20\text{ kV mm}^{-1}$) involves chain scission, the formation of free radicals and the generation of submicrocavities. Local accumulation of space charge (SC) then occurs, which increases the local electric field such that ageing is accelerated to failure. Laurent *et al* [19] have suggested that charge recombination leads to electroluminescence, which promotes ageing through photo-oxidation processes [7]. Tzimas *et al* [20] have suggested that charge trap generation may be attributed to changes in the physico-chemical structure of materials, albeit that these authors do not provide explicit evidence for the chemical changes initiating ageing. Elsewhere, Li *et al* [21] have suggested that the distribution of ageing-related changes through the bulk of XLPE insulation serves to affect electrical properties. Thus, while the published literature contains attempts to correlation global factors such as carbonyl index and crystallinity as indicators of ageing [21–23] with changes in electrical properties, relationships between the onset of electrically related ageing processes, physicochemical changes within the polymer and the key chemical reactions are not well understood.

In this paper we report on the first phase of a study of the impact of thermo-oxidative ageing on the electrical performance of polyethylene. Deliberately, the ageing conditions reported here were chosen not to be representative of those that would be experienced under service conditions but, rather, to exploit the finite rate of diffusion of oxygen into the

system, such that a non-uniform distribution of thermo-oxidatively generated ageing products could be produced. The aim of this was to consider the influence of these chemical species on interfacial charge injection processes and subsequent charge transport dynamics. Elsewhere [21], the effect of different distributions of the same chemical species throughout the bulk will be reported.

2. Sample preparation and experimental procedures

2.1. Sample preparation

The samples considered here were all composed of a polyethylene blend containing 20 wt.% high density polyethylene (HDPE: HD5813EA obtained from BP Chemicals) and 80 wt.% low density polyethylene (LDPE: LD100BW obtained from Exxon Mobil). The blend was prepared by mixing the two components in the melt (20 min at 160 °C), using a HAAKE PolyLab twin rotor R600 mixer. Thereafter, the blend was pressed into thin film specimens, $\sim 40\text{ mm}$ diameter and with a nominal thickness of 0.2 mm, between sheets of polyethylene terephthalate (PET) in an hydraulic press (Model MICRO-MOULD 10T) fitted with heated platens. For this, the polymer was melted at 160 °C under an applied load of 3 ton for 2 min, whereupon the pressure was briefly released to release any gases that may have become trapped in the blend during the melt mixing process. The pressure was subsequently reapplied and increased to 8 ton and held for 3 min. After this, the resulting film of polymer was quenched into distilled water, to give a specimen with a relatively simple morphology [24].

Blends of HDPE and LDPE have been widely studied in connection with many different issues [25, 26]. However, here, this choice was based on a simple rationale: such blends provide extensive scope to generate systems of constant molecular composition, but with different morphologies [24]. Specifically, in such systems, morphological evolution occurs through liquid/solid phase separation, based upon the principles of fractionation and segregation [27–29], whereby the spatial location of particular molecular fractions is governed, largely, by their defect content. In the work described here, quenching was employed to generate systems with as simple a lamellar texture as possible [24]. Elsewhere [30], we will subsequently report on the behaviour of material systems where specific crystallisation methodologies were deployed in order to exploit molecular self-assembly to distribute the same defects as considered here in controlled ways within different crystalline/amorphous phase structures.

2.2. Ageing procedure

Thermal ageing was performed in a fan oven (Heraeus, Kendro Laboratory Products UT6) at 160 °C for various times from 1 to 6 h. These conditions were determined from initial scoping experiments, in which treatment temperatures from 120 °C to 160 °C and times from 30 min to 24 h were explored. During the ageing process, each film was placed in contact with a PET

substrate, with the aim of producing specimens where the chemical composition varied through the thickness of the specimen. The upper surface, in contact with the air in the oven, would be expected to be more oxidised than the lower surface which, throughout, was in contact with the PET. For the sake of convenience, the upper, more affected surface/layer will subsequently be referred to as the oxidised surface/layer, while the lower less affected surface/layer is termed the non-oxidised surface/layer. After ageing, all samples were, again, quenched directly into distilled water at $\sim 20^\circ\text{C}$, for the reason given previously.

2.3. Chemical analysis

Fourier transform infrared (FTIR) spectroscopy in attenuated total reflection (ATR) mode was used to evaluate the effect of ageing on sample surface chemistry; a Thermo Scientific Nicolet iS5 FT-IR spectrometer with iD7 AR diamond crystal plates was used for this. All spectra were obtained over the wavenumber range $400\text{--}4000\text{ cm}^{-1}$ and, for each spectrum, 16 scans were averaged with 4 cm^{-1} resolution. To provide a quantitative measure of the degree of surface oxidation, the carbonyl index (CI) was calculated using:

$$CI = A_c/A_{ref} \quad (1)$$

where A_c is the area under the carbonyl peak located in the range of $1714\text{--}1726\text{ cm}^{-1}$ ($\text{C}=\text{O}$ stretch mode) and A_{ref} is the area of the chosen reference peaks at 2915 cm^{-1} (CH_2 and CH_3 symmetric and asymmetric stretch) [31].

The effect of ageing on sample chemistry was further considered using confocal microprobe Raman spectroscopy. Specifically, chemical variations as a function of cross-sectional position were investigated using a Renishaw RM1000 Raman system including a Renishaw NIR 780TF diode laser (wavelength 780 nm) with a maximum output power of 25 mW and a $\times 50$ objective lens. For these experiments, it was necessary initially to microtome cross-sections and, for this, the following procedure was adopted. Sheets of the styrene, ethylene/butylene, styrene linear triblock copolymer KRATON G1650 were first prepared and, then, softened through the application of drops of toluene. The sample of interest was then sandwiched between two sheets of the softened KRATON and the complete layered sample was left to harden through evaporation of the toluene, to give a composite block with sufficient mechanical integrity to undergo microtomy, which was performed at -40°C using an RMC MT7, CR-21 cryo-ultramicrotome. Raman spectra were finally obtained at equally spaced points ($10\text{ }\mu\text{m}$ separation) across the specimen, over the wavenumber range $500\text{--}3200\text{ cm}^{-1}$, using 10 consecutive 10 s extended scans and with the laser power set at 50%. The resulting raw spectra were then processed using Origin 2016 software to remove background scattering and were normalised with respect to the Raman peak at 1295 cm^{-1} ($\text{C}\text{--}\text{C}$ twisting mode) [32]. Carbonyl index values were again calculated for each acquisition point, where A_{ref} was taken as the area under the Raman peaks located around 2850 cm^{-1} (CH_2 and CH_3 symmetric and asymmetric stretch) and A_c the area under the carbonyl peak at $1720 \pm 5\text{ cm}^{-1}$ ($\text{C}=\text{O}$ stretch mode).

2.4. Electrical characterisation

Electrical properties of all specimens were investigated at room temperature (20°C) using the following three measurement techniques. Dielectric spectra were obtained using a Solartron 1296 dielectric interface together with a Schlumberger SI 1260 impedance/phase gain analyser. The sample was located in a Solartron 12962A parallel plate test cell with a guard ring electrode (the diameter of the measurement electrodes was 20 mm) and were tested according to ASTM standard D150-98 [33]. The derived data are presented as a complex relative permittivity over a frequency range from 0.1 Hz to 10 kHz with ten sampling points per decade and an overall accuracy of $\pm 5\%$. The effect of ageing on charge transport under a constant applied electric field was examined using samples with sputtered gold-coated 20 mm diameter electrodes, using a parallel plate test cell. Although these experiments adhered to the principles laid down in the ASTM D257 standard [34], often, the time required to reach steady state, corresponding to true DC conductivity, can be impracticably long. Since our intention here was merely to examine the *change* in charge transport behaviour resulting from ageing, rather than seeking to determine absolute DC conductivity values, current data were acquired at an applied field of $+40\text{ kV mm}^{-1}$ every 10 s over a period of 10000 s , using a Keithley 6487 picoammeter. Since all the aged samples were prepared in such a way as to be inhomogenous, with oxidised and non-oxidised layers, two data sets were obtained from each specimen. That is, one with the oxidised surface in contact with the anode and one with the oxidised surface in contact with the cathode. The effect of ageing on SC dynamics was investigated using the pulsed electro-acoustic (PEA) method [35]. Again, the applied field was chosen to be 40 kV mm^{-1} . For each sample, data were acquired for 3600 s with the field applied (voltage-on) and, subsequently, with the sample short-circuited (voltage-off). The anode and cathode materials were respectively a semi-conducting composite and aluminium; the aluminium cathode was at earth potential. As in the case of the conductivity measurements described above, separate experiments were performed using samples in which the oxidised surface was in contact with the anode and with the oxidised surface in contact with the cathode. Where required, the integrated SC (Q_{net}) in the bulk was calculated according to:

$$Q_{net} = \int_0^d |\rho(x)| \cdot S \cdot dx \quad (2)$$

where $\rho(x)$ is charge density, S is the electrode area and d is the thickness of the sample.

3. Results

3.1. The effect of ageing on chemical composition

3.1.1. Chemical modification of the surface. Figure 1 shows an infrared spectrum obtained from a reference sample, which contains the absorption bands that characterise the normal chemical structure of LDPE and HDPE. In this, the two absorption peaks at 717 cm^{-1} and 729 cm^{-1} are ascribed to the

Figure 1. The infrared spectrum of an unaged reference sample of the LDPE/HDPE blend.

rocking vibration of the methylene groups from LDPE and HDPE [31, 36], the peaks at 1377 cm^{-1} and 1471 cm^{-1} represent asymmetric and symmetric (umbrella mode) C–H bending vibrations of the methyl (CH_3) group, while the peaks at 2847 cm^{-1} and 2913 cm^{-1} correspond to the presence of symmetric and asymmetric-stretching of CH_2 methylene groups [36].

Figures 2(a) and (b) contain infrared data acquired after different ageing times at 160°C from the oxidised and non-oxidised surfaces respectively. From figure 2(a), it is evident that the chemistry of the oxidised surface was significantly changed for treatment times in excess of 2 h; in particular, increasing infrared absorbance within the ranges $800\text{--}1500\text{ cm}^{-1}$ (indicated as range A in figure 2) and $1600\text{--}1800\text{ cm}^{-1}$ (indicated as range B in figure 2) are seen. Within range A, the absorption bands are assigned to the vibrational modes of vinyl groups (vinylidene at 874 cm^{-1} , vinyl at 903 cm^{-1}), esters (at 1100 , 1170 , 1264 and 1289 cm^{-1}) and ethers (at 1112 and 1134 cm^{-1}) [32]. The absorption bands in range B are associated with ketones, located at 1716 cm^{-1} , esters and aldehyde at 1725 cm^{-1} , and γ -lactone at 1780 cm^{-1} . In contrast, from figure 2(b), the chemical changes that are seen in the non-oxidised surface are comparatively minor. In conclusion, the chemical modifications seen on ageing are consistent with the published literature [31, 37–39].

Figure 3 shows the variation in the carbonyl region in more detail for the oxidised surface, together with derived CI data for both surfaces. From the plots in figure 3(b), it is evident that the carbonyl concentration in both surfaces increases with ageing time. Initially (0–2 h), for the oxidised surface, the CI increases only slowly, before dramatically increasing for longer ageing times. For the non-oxidised surface, the initial low rate of increase in CI is maintained over the complete treatment time.

Published studies of thermal oxidation of polyethylene commonly consider this in terms of a number of processes [8, 40, 41], including: oxygen absorption; induction; autooxidation or autocatalytic reactions; termination. The time duration

Figure 2. Infrared spectra obtained from samples aged at 160°C for times ranging from 0 to 6 h: (a) data from the oxidised surface; (b) data from the non-oxidised surface.

and degree of oxidation for each stage has been associated with factors such as the C–H bond strength, the degree of crystallinity, the presence of substituents, impurities and antioxidants, etc. Furthermore, the rate of increase of CI will be affected by the local availability of antioxidant within the system; the increase in the rate of oxidation that occurs after 2 h for the oxidised surface may therefore be related to the local depletion of such species.

Figure 3(a) reveals the presence of a number of oxidation products in addition to carbonyl groups, including esters, aldehyde and γ -lactones, as presented above [37, 42]. Chabira *et al* [43], for example, ascribed the formation of such species to autooxidation processes associated with the proliferation of hydroperoxides and the reaction of consequent free radicals with existing ketones within oxidised polyethylene. The non-linear increase in CI with ageing time seen in figure 3(b) in the oxidised surface highlights the effect of the local availability of oxygen on the variation in CI at each surface, which is determined by the extent of oxygen consumption through reaction with the polymer during ageing. As such, a key factor in defining the rate of increase in CI is the local

Figure 3. Infrared spectral data relating to carbonyl groups, obtained from samples aged at 160 °C for times ranging from 0 to 6 h: (a) infrared spectra of the oxidised surface; (b) variation in carbonyl index with ageing times at both surfaces.

availability of antioxidant within the system. Consequently, whenever antioxidants are depleted due to their reaction with free radicals generated during induction, the oxidative rate will increase significantly as a result of the propagation of radicals through auto-oxidation [44]. The precise duration of the induction time has been shown to depend on a number of factors, including temperature, available oxygen, antioxidant content and antioxidant characteristic. Nevertheless, Chabira *et al* [39] reported qualitatively comparable behaviour to that seen in figure 3(b), with an induction of 4320h being seen when samples of LDPE were aged at 70 °C for periods of up to 15120h. They additionally showed that the measured CI tended to saturate at long ageing times, an effect they associated with the chemical reactions involved in termination. Anandakumaran and Stonkus [45] also reported comparable behavior, in the case of XLPE and ethylene/propylene rubber samples aged for periods of up to 24000h at temperatures ranging from 115 °C to 140 °C; this work reported that the induction time was reduced by approximately 50% on increasing the ageing temperature by 10 °C. Indeed, Huang

Figure 4. The infrared absorbance in the vinyl region obtained from the oxidised surface of samples aged at 160 °C for times ranging from 0 to 6 h.

et al [46] reported an induction time of just 2 h when a temperature of 160 °C was employed to age HDPE. As such, the effect of thermal ageing on carbonyl concentration seen at the oxidised surface in figure 3 is consistent with published data.

Figure 4 demonstrates the presence of vinyl groups in the oxidised surface, in addition to the oxygen-containing moieties discussed above; the concentration of these, similarly, increases markedly for ageing times in excess of 3 h. Such species have been associated with thermo-oxidative processes and a number of publications have suggested that the concentration of vinyl groups (vinyls, vinylidenes and t-vinyls) can be employed as a measure of ageing, being involving in chain scission and cross-linking processes [47, 48]. Chabira *et al* [39] reported that vinyl groups were formed in LDPE aged at just 70 °C and attributed their formation to mechanisms including the decomposition of ketones. Johnston *et al* [47] have described how the formation of vinyl groups facilitate crosslinking in polyethylene systems aged above the melting temperature, through their reaction with secondary alkyls.

As such, the fact that the time dependence of the concentration of vinylidene and vinyl groups in figure 4 broadly matches the data presented in figure 3 is consistent with published data. However, their relatively low concentration may be due to their consumption through crosslinking [43, 48].

3.1.2. Modification of bulk chemistry. Figure 5 shows Raman spectra obtained from the cross-section of a sample aged for 6 h. These data were acquired starting from ~10 μm beneath the oxidised surface (uppermost spectrum) and show the progressive variation in Raman scattering to a position on the cross-section corresponding to 190 μm below the oxidised surface (lowest spectrum). From this figure, it is evident that the intensity of Raman bands associated with primary alcohols (C–C–OH symmetric stretch; 871 cm⁻¹), double bonds (C=C stretch; 1618 cm⁻¹) and carbonyl groups (C=O stretch; 1720 cm⁻¹) are dependent upon the measurement position.

Figure 5. The Raman spectra obtained from different positions of the sample aged at 160 °C for 6 h.

However, to illustrate the variation in material chemistry with internal position, the same general procedure presented in figure 3(b) was again used and variations in CI with position are shown in figure 6, for samples aged for 3 h to 6 h.

From figure 6, it is evident that the CI values obtained from Raman spectroscopy are numerically less than those obtained from FTIR, because of the different physical mechanisms involved [32]. A consequence of this is that the low amounts of oxidation found by FTIR after ageing for 1 h and 2 h were not detectable by Raman spectroscopy. The data demonstrate that, for ageing times of 3 h and above, the CI drops monotonically from the oxidised surface (10 μm) into the bulk and that below a depth of $\sim 130 \mu\text{m}$ remains constant. We therefore define these two regions as the oxidised and non-oxidised layers respectively, as indicated in figure 6. Such heterogeneous composition profiles have been explained in terms of oxygen diffusion-limited effects by Audouin *et al* [12] and Clough and Gillen [49] and have been shown to be influenced by ageing-induced chemical and physical changes within the system. In addition, Gugumus [50] suggested that such diffusion-related effects are likely to be promoted at high rates of oxidation (e.g. at high temperature $\sim 150 \text{ }^\circ\text{C}$). Comparable heterogeneous sample oxidation has also been reported in connection with radiochemical and photochemical ageing [38, 51, 52].

While numerous mechanisms can be invoked to explain the precise form of the spatial variations in the chemical concentration described above, for the purposes of this study, it is clear that both the infrared and Raman data presented amply demonstrate that the chosen ageing treatment has been effective in producing specimens in which the chemical composition is non-uniform, as intended.

3.2. Dielectric response

Figure 7 shows the effect of ageing time on the dielectric response of the system. From figure 7(a), the real part of the relative permittivity can be seen to increase progressively with ageing time across the complete frequency range considered

Figure 6. Spatial variation in carbonyl index through the cross-section of samples aged at 160 °C for 3 h to 6 h, as determined by confocal microprobe Raman spectroscopy.

here. Carbonyl groups are polar moieties and, therefore, would be expected to respond to an applied electric field. As such, increases in the concentration of such species within a matrix made up of the non-polar hydrocarbon chains of pristine polyethylene [53–55] should lead to a general increase in the real part of the relative permittivity, as observed.

In discussing the imaginary permittivity (ϵ'') data presented in figure 7(b), initially consider the results obtained after ageing for 3 h. Mujal-Rosas *et al* [56] examined the dielectric response of an ethylene/vinyl acetate (VA) copolymer containing 18% VA, reporting a broad loss peak spanning the range 1 Hz to above 1 MHz that they associated with the motion of polar chain segments within the system.

Elsewhere, the effect of ageing on the dielectric response of polyethylene has been reported. Linde *et al* [23] and Kim *et al* [57] both showed that XLPE aged at 85 $^\circ\text{C}$ –150 $^\circ\text{C}$ exhibited a broad relaxation peak extending from $\sim 1 \text{ kHz}$ to 10 MHz. Comparable behaviour has also been reported for severely aged LDPE [58] and HDPE [59]. Elsewhere, Suljovrujic [60] suggested that such a dielectric response may be related to the mobility of polar chains segments or disordered chains located in amorphous regions (the dielectric β and γ -relaxation) and at the surface of crystalline regions (α and γ -relaxation) [59], such that the relaxation shifts to higher frequencies with increasing amorphous fraction (see aged LDPE and HDPE). In the case of the polyethylene blend system considered here, the broad dielectric relaxation peaks located at frequencies above 1 Hz in figure 7(b) are therefore in line with published data and readily explicable in terms of various moieties/defects (cleaved chains, crosslinks, $\text{C}=\text{O}$, $\text{O}-\text{H}$ and $\text{C}=\text{C}$) located at a range of different structural locations within the polymer morphology.

Consider now the data shown in figure 7(b) obtained from the sample aged for 4 h and above. Here, an additional process is evident at low frequency, which results in an increase in the imaginary permittivity with decreasing frequency below about 1 Hz. This phenomenon may be related to a number of processes, including Maxwell–Wagner–Sillars interfacial polarisation and charge transport [53, 61, 62].

Figure 7. The dielectric response of the reference and treated samples for 1 h to 6 h: (a) real and (b) imaginary permittivity.

While interfacial polarisation may occur at the electrodes, the heterogeneity of samples aged for 3 h and above provides another mechanism, which stems from spatial variations in physical properties as a consequence of the concentration profile of ageing-induced chemical species. Fu *et al* [63] considered the effect of γ -irradiation on the relaxation behaviour of LDPE. While ϵ'' was found to increase progressively with decreasing frequency to 10^{-3} Hz when data were acquired at room temperature, increasing the measurement temperature to above 50°C revealed a distinct low frequency loss peak. These workers related this to an increase in the number or the mobility of charge carriers within the aged regions of their specimens; as noted above, heterogeneous oxidation effects have been reported in connection with radiochemical and photochemical ageing [38, 51, 52]. As a consequence, in such non-uniform samples the flow of current will largely be restricted to the more conductive regions, leading to internal polarisation. Finally, for the data presented in figure 7(b), evaluation of the slope of log/log plots of ϵ'' against frequency reveals a power law behaviour with an exponent ranging from ~ -0.3 (sample aged for 4 h) to ~ -0.5 (sample aged for 6 h). Since these values fall above the value of -1 [64] expected for DC conduction, we suggest that the imaginary dielectric data obtained from samples aged for times greater than 3 h presented in figure 7(b) are best interpreted in terms of a combination of charge transport and polarisation phenomena.

Figure 8. The plot of time dependence conductivity of the samples aged for the variation times with the oxidised surface in contact with cathode, at 20°C .

3.3. DC conduction

Figure 8 shows exemplar time dependent DC conduction data, which were obtained from differently aged samples with the oxidised surface in contact with the cathode. Consider, first, the data obtained from the unaged reference sample, where the derived conductivity falls from initial values around $10^{-16}\text{ S cm}^{-1}$ over a period of $\sim 5000\text{ s}$ and, thereafter remains stable at $\sim 4 \times 10^{-17}\text{ S cm}^{-1}$. Comparable behaviour has been reported in numerous other studies [65, 66]. For example, Upadhyay and Reddy [65] measured the conduction current in LDPE for 10 h at electric fields ranging from 20 to 200 kV mm^{-1} . In this work, it was reported that, at 40 kV mm^{-1} , the current decreased from its initial value and remained steady after about $\sim 7000\text{ s}$, broadly in line with the results presented in figure 8.

Although the data obtained from the sample aged for 1 h is qualitatively comparable to the above, it is evident that the current that flows through this system is reduced. As a consequence, the scatter in the derived data is markedly increased as a result of the measurements approaching the sensitivity limit of our apparatus. Finally, the sample aged for 5 h is characterised by a marked increase in conductivity but, again, the time dependency corresponds to a decrease over the initial period of $\sim 5000\text{ s}$, followed by stability.

Presentation of all our data, including repeats, in the form shown in figure 8 would result in a loss of clarity, since many of the data sets overlap with one another. Consequently, we have chosen to represent, in figure 9, the effect of ageing time on charge transport in terms of two parameters. First, it is evident from figure 8 that the current flow is largely constant for poling times beyond 5000 s and, therefore, we have taken the average of the final ten data points (obtained from 9910 to 10000 s) as a measure of quasi-steady state current. In addition, a secondary quantity was also determined, namely the initial ‘transient’ current (average of the first ten data points, obtained from 10 to 100 s). Both of these measures are presented in the form of conductivity, to eliminate geometrical

Figure 9. Measures of the effect of ageing on charge transport, at 20 °C, for samples aged from 0 to 6 h with the oxidised surface in contact with: (a) the anode and (b) the cathode electrode.

factors and, by considering these two extreme metrics in concert, we provide a reasonable representation of the *changes* in conduction behaviour resulting from ageing.

In view of the asymmetry deliberately introduced into the aged samples, measurements were conducted with the oxidised surface in contact with both the anode and the cathode. However, since both experimental arrangements gave comparable forms of behaviour, the common features of figures 9(a) and (b) will, initially, be considered together. From figure 9, it is evident that the initial effect of aging is to reduce the overall conductivity of the system, such that both the initial and final conductivity values measured up to 3 h of ageing fall below those measured for the unaged reference samples. Further ageing beyond 3 h leads to a reversal in this trend, whereupon the conductivity values progressively increase, which correlates well with the onset of the low frequency dielectric loss process seen in figure 7(b). Thermo-oxidative ageing for different temperatures and times, previously reported in many studies, leads to increases in conductivity which have been associated with increases in carbonyl concentration [55,

67–69]. This correlation of increased carbonyl concentrations and conductivity is reasonable for our data for ageing times in excess of 3 h, while the observed *reduction* in conductivity (see figure 9) with *increased* carbonyl content (see figure 3(b)) at lower ageing times, indicates a more subtle causal link.

Recently, an ageing-induced initial reduction in conductivity followed by a progressive increase has previously been observed reported by Li *et al* [70], who reported reduced conductivity for thermally oxidised LDPE films, when ageing was conducted at 90 °C and 100 °C for less than 240 h and 120 h respectively. They interpreted this as arising from the presence of a low concentration of carbonyl groups within the system that act as deep traps. Initially, the resulting SC reduces the local electric field at the interfaces between the electrodes and the PE and serves to inhibit charge injection. Conversely, for ageing times in excess of those indicated above, they suggested that, then, the observed increase in conductivity arose through enhancement of charge injection by a high density of deep traps close to both surfaces coupled with tunnelling and hopping processes between such traps, which are increased in concentration and distributed further into the bulk. However, this interpretation is somewhat speculative in that only the integrated carbonyl concentration throughout the specimen volume was evaluated [68], without any direct measures of the spatial distribution of these chemical groups within the system, as considered in the work reported here.

Consider now the effect of experimental geometry on the measured conductivity. From both figure 9, a threshold time is apparent at which the conductivity begins to rise monotonically with further ageing. In the case of positive charge injection (figure 9(a)) this appears to occur slightly earlier than for negative charge injection (figure 9(b)), assuming that charge injection from the electrode adjacent to the oxidised surface is the dominant process. Nevertheless, on the basis of the above data alone, such differences are not statistically significant.

3.4. SC accumulation

3.4.1. Oxidised surface at the anode. Figure 10 show SC profiles obtained from differently aged samples, with the anode in contact with the oxidised surface. From figure 10(a), heterocharge is formed in the unaged reference sample, with a significant amount of charge being present particularly adjacent to the cathode. For ageing times less than 3 h, the relatively low degree of degradation results in a significant decrease in SC accumulation, as shown in figures 10(b)–(d); the heterocharge adjacent to the cathode being replaced by a small amount of negative homocharge. However, for longer ageing times, drastic changes in SC profile are evident, as shown in figures 10(e)–(g), where the increasingly oxidised region leads to the accumulation of a large amount of positive charge within the bulk. In particular, the charge progressively moves from the anode towards the cathode with increasing poling time; no induced charge is then evident on the physical anode. The presence of positive charge near to the cathode results in a dramatic increase in the local electric field, which

Figure 10. SC profiles for ageing times from (a)–(g) 0 h to 6 h, with the anode in contact with the oxidised surface.

would be expected to promote negative charge injection from the cathode into the bulk. This is not seen experimentally, presumably due to a combination of spatial resolution limitations and the fact that PEA is only capable of revealing the net local charge.

Due to the dramatic change in SC profile that occurs between 3 h and 4 h, further data were acquired within this ageing period to determine the threshold for such a marked change; results are shown in figures 11(a)–(d). Comparison of figures 11(a)–(d) reveals a distinct change in behaviour, in that while the former contains little positive SC, the latter shows positive anode charge abruptly becoming re-distributed into the bulk. Increasing ageing time from 3:15 h to 3:45 h (see figures 11(b)–(d)) leads to a progressive increase of the accumulated SC and its progressive distribution further into the bulk.

3.4.2. Oxidised surface at the cathode. Figures 12(a)–(f) show SC profiles obtained from samples aged for 1 h to 6 h, with the cathode in contact with the oxidised surface. Again, for ageing periods from 1 h to 3 h, the amount of accumulated charge is very low. However, a large amount of negative charge is evident in samples aged for 4 h and above, which moves into the bulk of the treated samples thereby, presumably, enhancing positive injection from the anode. These results parallel

those shown in figure 10 in that at low levels of oxidation (ageing periods from 1 h to 3 h) net SC is suppressed, while in the more severely oxidised specimens (figures 10(e)–(g)), extensive positive charge migration occurs into the bulk, with a consequent increase in the local electric field adjacent to the cathode. Comparing figures 10(g) and 12(f), for example, suggests that the density of accumulated SC in the latter case is somewhat higher, an assertion supported by numerical integration of the SC data according to equation (2). Indeed, such data processing suggests that the integrated charge present within the bulk is less for the data presented in figures 12(a)–(c) than for the equivalent results in figures 10(b)–(d), while at longer ageing times, a higher density of SC results when the oxidised surface is adjacent to the cathode (figures 12(d)–(f)).

Examination of samples aged for periods between 3:07 h and 3:45 h reveals behaviour that is broadly consistent with the trends shown in figure 11 and, therefore on grounds of brevity, these are not shown here. However, with the cathode in contact with the oxidised surface, the onset of appreciable SC accumulation is reproducibly displaced beyond 3:30 h, with little SC being seen up to this ageing time. As in the case of the conductivity data shown in figure 9, this suggests some asymmetry in the response of the system when comparing the cases of the oxidised surface being in contact with the anode and cathode.

Figure 11. SC profiles for the ageing times between 3 h and 4 h, with the anode in contact with the oxidised surface.

4. Discussion

The results presented above demonstrate that the chosen ageing regime has led to a range of non-uniform distributions of chemical defects, notably carbonyl groups, within the system and that these are concentrated in what we have termed the oxidised layer. This is consistent with the work of Audouin *et al* [12], who explained the processes theoretically by kinetic reaction and oxygen diffusion rate modelling [71]. Li *et al* [21] also reported that accelerated ageing of an XLPE cable (at 100 °C for 8760 h) led to a non-uniform distribution of chemical and physical defects across the thickness of insulation, which they associated with the difference in temperature between the inner and outer regions of the insulation. However, this work did not investigate the dependence of ageing and physico-chemical and electrical changes as function of times, while in our work the ageing effects on chemical and electrical properties of PE were analysed based on the increase in ageing time.

Our results also show that while such ageing effects influence the electrical properties of the material, this neither occurs progressively nor monotonically with increasing ageing time. This discontinuity in behaviour is counter to the changes in chemical compositions seen by both FTIR and Raman spectroscopy (see in figures 3(b) and 6), where the concentration of ageing-related chemical defects increases monotonically. Nevertheless, the changes in both trends is relevant, since physical and chemical defects, respectively considered as shallow and deep trapping sites for charge carriers [72, 73], affects SC accumulation and conduction mechanism in polymers leading to changes in electrical performance [74].

In addition to different trap depth energies, Meunier *et al* [72] have demonstrated that charge carriers reside in deep traps, associated with carbonyl groups and conjugated double bonds, for much greater times than in shallow traps. The density of trapping sites would rationally be anticipated to increase with the severity of ageing [20, 75, 76] such that, here, the spatial variation in the carbonyl concentration (see in figure 6) can be taken as a proxy for the spatial distribution of the density of deep trap (with trap depth energy in range of ~0.9–2.0 eV [72, 77]) through the thickness of the various aged samples.

The effects of ageing on SC and charge transport dynamics have been considered in a number of studies in connection with trapping processes and the characteristics of the charge carriers involved [76, 78, 79]. Commonly, ageing is reported to lead to the presence of shallow and deep traps, which increase the accumulation of both negative and positive charge carriers. Tzimas *et al* [20] fitted a mathematical model to experimental SC results obtained from samples of XLPE aged at 90 °C under an applied alternating current (AC) field of 19 kV mm⁻¹ for 10000 h. The results were interpreted in terms of a greater increase in the concentration of deep traps (depth > 1 eV) than shallow traps. These conclusions aligned well with previous results obtained using the thermal-stimulated current (TSC) technique [80]. The presence of deep traps was found to lead to an increase in the amount of accumulated positive charge within the system which, in turn, reduced the life of the insulation. These workers tentatively suggested that such traps could be related to chemical species, such as carbonyl groups, generated during ageing. Ouyang *et al* [78] used an isothermal surface potential decay

Figure 12. SC profiles with the ageing times for (a)–(f) 1 h to 6 h, with the cathode in contact with the oxidised surface.

(ISPD) approach to compare the effect of ageing on the electrical behaviour of XLPE aged at temperatures below (100 °C) and above (160 °C) the melting temperature of this polymer. Through a combination of experiment and modelling, these workers showed that in relatively lightly aged samples, the different ageing conditions used (100 °C for 1440 h and 160 °C, 96 h) equivalently affected the accumulation of SC. It was suggested that homocharge trapped in deep traps (again, associated with carbonyl groups) modified the local electric field near the electrodes, thereby inhibiting further charge injection. However, at higher carbonyl contents (ageing at 160 °C for 192 h), SC accumulation increased dramatically and, based on their ISPD model, these workers estimated the trap depth and trap density. From this, it was suggested that the observed increase in accumulated charges resulted from enhanced charge injection. Specifically, they suggested that in these more highly aged samples, a significant relative increase in the concentration of shallow traps led to a higher detrapping rate, which weakened the inhibiting effect of the homocharge that dominated in less heavily aged samples. However, the FTIR results presented in this paper demonstrate that the concentration of carbonyl groups present in the system did not decrease on prolonged ageing, indicating that SC dynamics is dependent upon the precise *distribution* of trap energies present in the system. Elsewhere, Li *et al* [70] have proposed that when deep traps are present in sufficient concentration, tunnelling from one to another may provide an additional mechanism for charge transport.

For ageing times up to 3 h, the results presented above in figures 10–12 are consistent with lightly oxidised regions containing a relative low density of deep traps; these acts to promote homocharge near the sample/electrode interface and as such, reduces the local electric field and, thereby, hinder further charge injection. Also, the presence of deep traps can

lead to a reduction in the effective number of charge carriers by a factor θ , which defines the ratio of free charge carriers to the summation of free charge and trapped charge carriers. Conventionally, in space charge limited conduction (SCLC), this is represented in terms of an effective mobility, $\mu_{eff} = \theta\mu$, which leads to a reduction in the current density, J :

$$J = \left[\left(n_0 e \mu_{eff} \frac{V}{d} \right) + \left(\frac{9}{8} \varepsilon_0 \varepsilon_r \mu_{eff} \frac{V^2}{d^3} \right) \right] \quad (3)$$

where μ is the mobility of free carriers, n_0 is the concentration of electrons injected over the electrode-insulator barriers, e is a magnitude of the electronic charge, V is the applied voltage, d is the thickness of the dielectric film, ε_0 and ε_r are the permittivity of free space and the relative permittivity of the material respectively. We therefore interpret the reduction in conductivity seen in samples aged for up to 3 h in terms of a combination of inhibited charge injection and SCLC. Indeed, similar processes have been postulated to explain charge transport dynamics in nanocomposites, where the source of the deep traps is the added nanoparticles [81, 82].

If, according to SCLC theory, charge trapping acts to reduce charge carrier mobility, then the SC distributions and increased overall conductivity seen in samples aged for more than 3 h appear anomalous. However, Huzayyin *et al* [83] used density functional theory (DFT) computationally to investigate the effects of the distance, $\Delta\lambda_D$, between neighbouring deep traps, simulated by carbonyl groups, on charge transport process in PE. Their simulations showed that when the separation between discrete traps is reduced to the effective distance ($\Delta\lambda_{D,eff}$), it increases interchain charge transfer, and thereby conduction, due to the consequent overlapping of the associated wavefunctions. They later extended the above to consider the effects of carbonyl groups and other chemical defects including iodine and vinyl groups on hole mobility

in PE [77]. The simulation results indicate that the increase in hole mobility would be greatest for iodine, followed by carbonyl and vinyl groups. Moreover, Boufayed *et al* [84] used a model based upon bipolar charge transport and hopping to demonstrate that an increase in effective mobility occurs at a critical charge density in PE. The experimental effects shown in figures 9–12 can therefore be explained in this way and indicate that the theoretical critical charge density or inter-trap separation corresponds to a carbonyl index value of ~ 0.24 .

Finally, the data presented above suggest that polarity reversal with respect to the oxidised surface affects the behaviour of the system. While it is reasonable to postulate the same chemical defects react to different charge carriers in different ways, the differences seen here are not great and rely critically on apparent differences in behaviour that occur only for oxidation times between 3 h and 4 h. As such, we feel that the effects seen require further investigation and that speculation on the apparent effects reported here are therefore not warranted at this time. This, and related phenomena, will be discussed further in subsequent publications, where the potential of HDPE/LDPE blends in conjunction with controlled crystallisation will be exploited in order to control the precise spatial distribution of molecular defects within the material.

5. Conclusion

The effects of ageing on the bulk electrical properties of PE insulation have been widely examined, both experimentally and by simulation, often, in connection with the role played by ageing-induced moieties, such as carbonyl groups. However, the spatial distribution of such species and their effect on local electrical properties are not well understood. In this paper, we have demonstrated the impact of thermal ageing and the resulting distribution of chemical species on SC and charge transport processes. By choosing the specific ageing conditions used here—160 °C in air for periods of up to 6 h—the finite rate of oxygen diffusion through the material has been used to generate a non-uniform distribution of ageing-related defects through the thickness of samples, which consequently contain highly and lightly oxidised regions. As expected, the oxidation degree indicated by the carbonyl index increased significantly with ageing times beyond 2 h. Also, since carbonyl groups are polar species, this increases the polarisability of the material and increases the dielectric losses in aged samples. In particular, we relate the observed increase in the imaginary permittivity at frequencies below 1 Hz to a combination of polarisation effects and charge transport processes. For ageing times up to 3 h, the relatively low level of induced chemical changes equates to a relatively low density of deep traps and leads to homocharge accumulation and an appreciable reduction in SC compared to the reference sample. We interpret this in terms of a combination of the homocharge suppressing charge injection and prolonged trapping serving to reduce the effective carrier mobility, in accordance with SCLC theory. Together, these two processes serve to reduce the

measured conductivity, despite the associated increase in the concentration of ageing-induced defects. However, the severe oxidation that results from ageing times beyond 3 h result in large amounts of SC accumulation and migration of charge carriers into the bulk. This abrupt change in behaviour suggest that a high density of traps, even deep traps, increases the possibility of injected charge carriers moving into the bulk. We associate this with the precise spatial distribution of traps that form and a reduced effective distance between neighbouring traps leading to an increase in the effective carrier mobility. Such effects become more pronounced once the CI reaches a threshold of ~ 0.24 .

In conclusion, the results presented above demonstrate that the defects formed by thermo-oxidative ageing markedly affect the SC and charge transport dynamics within polyethylene. While such an assertion is unsurprising, the non-monotonic effects seen coupled with the abrupt change in behaviour at a critical defect density are, we suggest, unexpected and may provide important clues concerning the processes that precede the ultimate electrical failure of this technologically important insulation material.

Acknowledgments

The authors acknowledge the Electricity Generating Authority of Thailand and the University of Southampton for financial sponsorship. All data supporting this study are openly available from the University of Southampton repository at <https://doi.org/10.5258/SOTON/D0821>.

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