The Effect of Gamma Irradiation on Space Charge Behaviour and Dielectric Spectroscopy of Low-density Polyethylene

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Abstract: The influence of gamma irradiation on low-density polyethylene (LDPE) has been studied through space charge measurement and dielectric spectroscopy. Commercial LDPE film with a thickness of 100μm was irradiated with γ-rays at a dose rate of approximately 10kGy/h to different doses up to 100kGy in an atmosphere of air, vacuum and nitrogen respectively. Space charge profiles vary depending on irradiation environments and radiation dose. The space charge profile of a sample after irradiation at 100kGy in air is more complicated than those irradiated in vacuum and nitrogen at same dose. More importantly, the space charge decay rate for the irradiated samples is slower than that of the virgin sample, indicating that the irradiation had changed the material by the generation of deep traps for space charge. Irradiation in air also produced changes in the dielectric spectrum in the frequency range between 10^{-3}Hz and 10^{6}Hz where the imaginary part of the permittivity was found to be about one order of magnitude higher than that of the virgin sample (~10^{-4}). This was attributed to oxidation as samples with the same (or lower) radiation dose in vacuum or nitrogen showed no pronounced difference to that of virgin samples.

INTRODUCTION

It is believed that ionising radiation could alter molecular structure, cause chain degradation and therefore change the macroscopic properties of polymeric materials through the mechanisms of chain scission, branching and oxidation [1-4]. The effect of irradiation in polymer insulator has been studied for many years through thermally simulated discharge current (TSDC), electrical conduction and most recently space charge trapping [5, 6]. The increase in the presence of trapped charge and trapping characteristics after ionising radiation is generally attributed to different structural defects [1, 5]. In partially crystallised polymers such as low density polyethylene (LDPE), these traps are thought to be "cavity" defect traps in the amorphous region and defects at the crystalline surfaces.

Previous work using TSDC [1, 5] revealed that a radiation atmosphere could influence charge trapping features, and more charge was found within the sample irradiated in air compared to those irradiated in nitrogen or vacuum. However, the understanding of charge trap generation and its effect on charging behaviour after ionising radiation is limited. This paper reports research on the effect of gamma radiation on LDPE under different environments, through space charge behaviour and dielectric spectroscopy. The microstructure (i.e. crystalline and cross-linking) changes and generation of free radials due to irradiation is discussed in terms of its relationship to the dielectric spectra and space charge accumulation.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Additive-free LDPE film, ~100μm in thickness, was used in the present research to minimise the morphological difference and possible charge trapping due to additives or impurities. LDPE samples were cut from the film and cleared with alcohol, and then irradiated at room temperature with γ-rays at various doses from 10kGy to 100kGy in air, vacuum and nitrogen.

The dynamics of space charge (SC) accumulation and decay were measured by the pulsed electro-acoustic (PEA) technique. The specimens were stressed under a dc field of 50kV/mm and the space charge distribution was measured at different times within 60 minutes. The voltage was then removed and the SC-decay studied.

The irradiated specimens were also characterised by dielectric spectroscopy at various temperatures, to study the formation of free radicals (polar groups) by the gamma irradiation. The presence of polar groups (carbonyl) was checked by infra-red spectroscopy (FTIR).

RESULTS AND DISCUSSION

Dielectric spectroscopy

All samples irradiated under varied dose and atmosphere have been characterised by dielectric spectroscopy (DS). The dielectric loss factor (ε") of the control LDPE sample, see Figure 1, is ~ ~10^{-4} over all the measurement range as would be expected for a polymer such as polyethylene without any very polar groups. A similar value is found for the samples irradiated in vacuum or in a nitrogen atmosphere. However those samples irradiated in air have values of 10^{-3}~10^{-2} at frequencies above ~ 3Hz, and a strong increase with reducing frequency at lower frequency

that is usually associated with a Maxwell-Wagner response. It therefore appears that the radiation has both increased the amount of polar groups available for relaxation and the conductance of local polymer regions, probably through the generation of small radical groups.

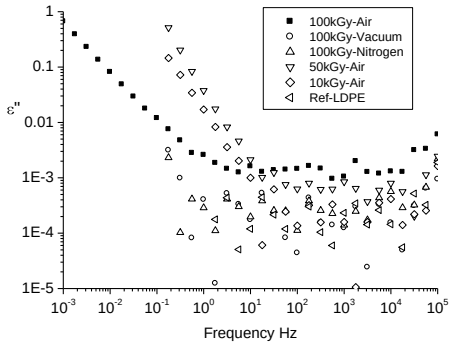

Figure 1. Dielectric loss factors of all samples at room temperature

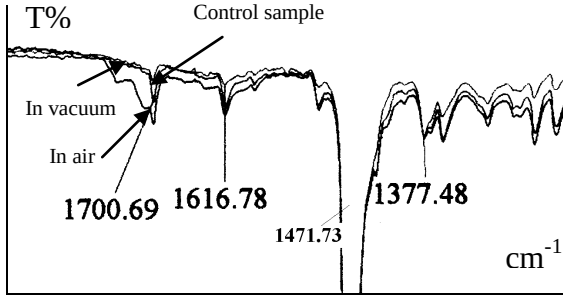

Figure 2. FTIR spectra of LDPE irradiated in different atmospheres

The increase of ε'' in air-irradiated samples could be related to oxidation that formed polar groups. The presence of such groups in these samples is revealed in their FTIR spectrum see Figure 2, which shows absorption peaks at 1616cm^{-1} and 1700 cm^{-1}. These peaks have been associated with oxidation in the form of hydroperoxy, hydroxyl and carboxyl groups in addition to carbonyl groups [7].

The dielectric spectrum of the irradiated samples has also been measured at temperatures of 30, 40, 50 and 60^{o}C. The results are shown in Figure 3 (a), (b) and (c).

In the samples irradiated in vacuum and nitrogen, ε'' shows a slight increase at temperature 60^{o}C when the frequency is below 10^{-2} Hz, see Figures 3 (a) and (b). In contrast, no relaxation at this frequency range was observed in the results of the control sample at the same elevated temperature. This is the region of the Maxwell-Wagner relaxation, a form of dielectric polarization that is typically observed when local regions of conduction are in series with blocking capacitive interfaces [8]. In this case the peak in ε" lies to lower frequencies than the measurement and only the effect of the series conductance is observed. The data indicates that irradiation without oxygen present results in some direct damage that aids the associated transport process to a small extent. This may be attributed to the microstructure change (crystalline and cross-linking) in the amorphous phase and the phase boundaries [1]. The dielectric spectrum of the samples irradiated in air exhibited a fully resolved Debye-shaped loss peak at T $\geq$ 50 °C, such as expected of a Maxwell Wagner process, with the peak shifting to higher frequency as the temperature was increased. The implication is that such irradiation has either increased substantially the concentration of charge carriers or their mobility or both, compared to the control and irradiation in a non-oxidising atmosphere. This conclusion is also supported by their space charge behaviour.

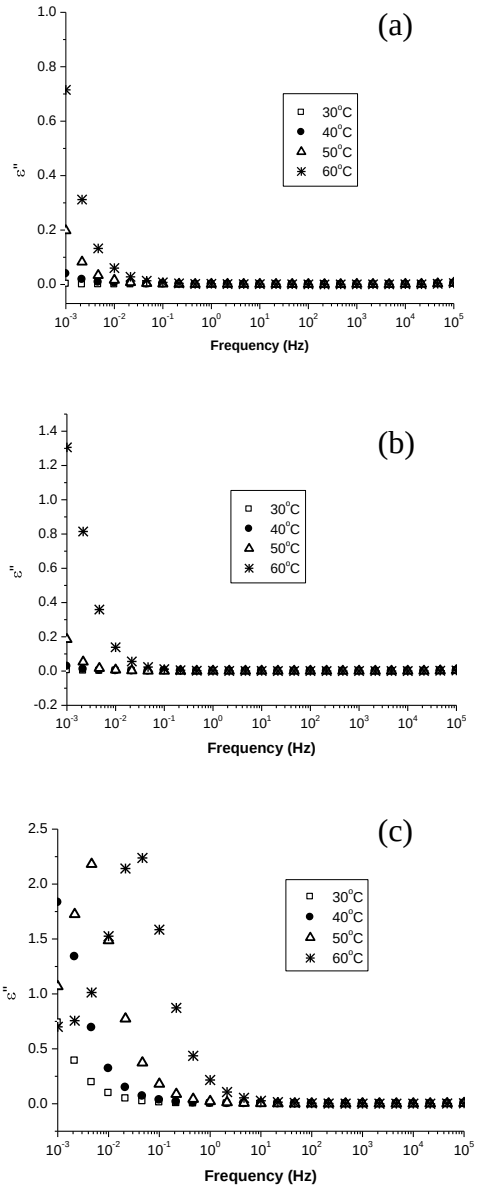

Figure 3. Spectra of dielectric loss factor of samples irradiated with 100kGy in (a) nitrogen (b) vacuum and (c) air, for a range of temperatures.

Space charge behaviour

Space charge measurements were made on the control sample and samples irradiated with a 100kGY dose of gamma rays. Accumulation was followed using an electric field of 50kV/mm applied for 60 minutes. The subsequent space charge decay was followed after the voltage had been removed from the samples. The space charge profiles at the end of the accumulation period and their subsequent decay are displayed in Figure 4. The sample irradiated in air exhibits a much more complicated space charge distribution than other two irradiated samples at same dose.

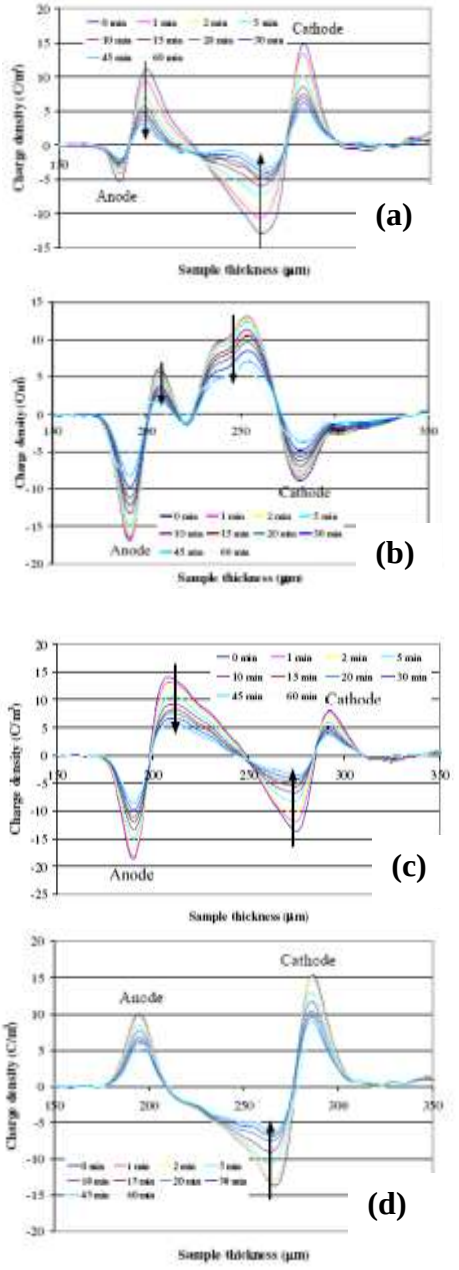

Figure 4. Space charge distribution accumulated after 60 minutes field stressing and its decay upon the removal of the external field, (a) control sample, (b) irradiated in air, (c) irradiated in vacuum, (d) irradiated in nitrogen

The space charge distributions in the control sample and that irradiated in vacuum have almost same pattern with homocharge injection at both electrodes, Figure 4(a) and (c). The charge decay rate of the sample irradiated in vacuum is also similar to that of the control sample, though a bit smaller. A completely different space charge profile was found in the sample exposed to the 100kGy gamma-ray dose in nitrogen, shown in Figure 4 (d). Negative charge accumulated near the cathode and extended into the bulk of sample, but no positive charge injection was observed. It would seem that electron injection still took place from the cathode but the irradiation treatment has significantly increased the electron mobility in the sample allowing the negative charge to be more easily conducted away from the cathode to the anode. Possibly the transported negative charge has neutralised holes from the anode, though an inhibition of hole injection cannot be ruled out. This behaviour therefore suggests that shallow traps have been induced by irradiation thereby facilitating change mobility.

The space charge in the sample irradiated in air is noticeably different from the other cases, both in terms of distribution and manner of decay, Figure 4 (b). Although interfacial injection occurred initially, the eventual charge distribution is governed by two positive peaks in the bulk of the material. One possible explanation for this is that irradiation in air has produced species that release electrons. These are swept to the anode where they reduce the quantity of injected holes. The positive ions are left behind in the bulk of the materials. It is not clear however, whether or not cathode injection takes place as seen in all the other samples.

Charge de-trapping analysis based on space charge decay

The space charge decay yields a way to investigate the change introduced by irradiation by supplying a means to evaluate trap depths and trap densities [9, 10]. The total charge in the bulk of the sample, during the decay period, has been calculated from equation (1) and its value plotted against the logarithm of the decay time, as shown in figure 5.

$$Q(t) = S\int_0^d |\rho(x)|\,dx \qquad (1)$$

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

As the space charge profile retains its shape during decay, it is reasonable to believe that the detrapping process controls the dynamics of charge decay [9-11]. It is also assumed [8] that the charge is trapped in states whose density has a top-hat energy distribution. In this case the decay follows equation (2) [8],

$$Q(t) \approx eNkT\left(C - \ln(t)\right) \qquad (2)$$

over a decay time, t, in the range defined by

$$\exp\left(\frac{\Delta_{\min}}{kT}\right) < \nu t < \exp\left(\frac{\Delta_{\max}}{kT}\right) \qquad (3)$$

N is the density of trap states per unit energy interval, and Δ_{min} and Δ_{max} the minimum and maximum trap depths, which can be obtained from the times at which the plot deviates from a straight line, as long as the detrapping attempt frequency can be estimated. Here $\nu = kT/h$ is used for the estimation as this frequency is related to incoherent thermal vibrations of the trap state [10].

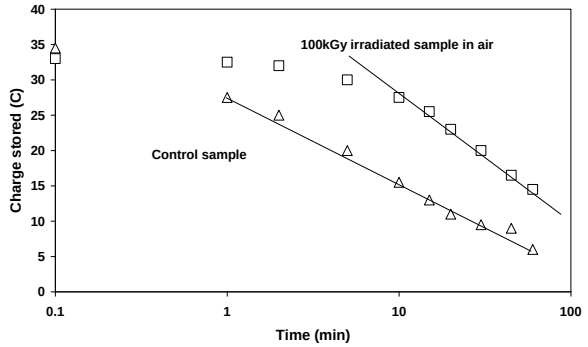

Figure 5. Space charge decay of control and gamma ray irradiated sample in air

Figure 5 shows that the decay of space charge in the control and gamma ray irradiated samples obeys equation (2) over a range of time. Using equation (3), the minimum depth of filled traps can be estimated for both samples, and are 0.89eV and 0.95eV for the control and irradiated sample respectively. The activation energy of the dielectric loss peak of the irradiated sample was found to be 0.88eV, which is close to these values as would be expected if the charge mobility were controlled by hopping between traps. The measurement time was not long enough to allow Δ_{max} to be directly evaluated, but extrapolation indicates that the appropriate times are ~100 and ~500 minutes for control and irradiated sample respectively and yields equivalent values of 1.01eV and 1.05eV for Δ_{max}. Since the gradient of the linear part of the plots in Figure 5 is bigger for the irradiated sample than the control the value of N for this sample must be bigger. This means that irradiation has increased the density of traps per unit energy interval. The control has a smaller value of Δ_{min} because the total amount of space charge generated in the experiment is essentially the same for both samples, see the values in Figure 5 at t = 0.1min.

CONCLUSIONS

Gamma ray irradiation of LDPE in different atmospheres brings about different material changes. Irradiation in air enhances oxidation resulting in an increase in the density of carbonyl, hydroperoxy, and hydroxyl groups. It also increases the low-field conductivity and is associated with the high-field generation of positive space charge in contrast to irradiation in non-oxidising conditions. The density of the charge trap centres is increased in comparison to the non-irradiated material indicating a relationship with the oxidised sites. Irradiation in vacuum and nitrogen only introduced a small enhancement of the low-field conductivity, but it was found that irradiation in nitrogen resulted in a shorter high-field transport time for negative carriers, sufficient to neutralise positive charge injection at the anode.

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