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On the characterisation of electrically stressed polyethylene before and after chemical treatment

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Low-density polyethylene (LDPE) was characterised for its dielectric and electrical properties before and after chemical treatment. A reduction in the permittivity and dielectric loss was observed in the polymer after treatment with hexane. The intensity in the Raman Spectrum in the disordered longitudinal acoustic mode region (DLAM) also was reduced due to a hexane treatment. Using thermally stimulated discharge current (TSDC) and laser-intensity-modulated method (LIMM) techniques it was observed that charge injection can be enhanced in the polymer matrix in the empty sites, created by the removal of the low molecular weight impurities with chemical treatment.

1. Introduction

Low-density polyethylene (LDPE) has been widely used as electrical insulating material due to its properties such as low permittivity and tan δ [1–3]. Investigations of the ultraviolet absorption [4] and luminescent emission spectra [5] of polyethylene have shown that samples can contain a significant concentration of aromatic molecules. These impurities contribute to an increase in electrical conductivity [6] and can cause a change in dielectric properties of the polyethylene itself.

In untreated polyethylene samples the conductivity was found around $2 \times 10^{-19}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [7]. On immersing the polyethylene samples in hexane the conductivity can be reduced by two orders of magnitude, by removing some of low molecular weight hydrocarbon impurities. This result indicates that the conductivity of untreated polyethylene is purely extrinsic in nature, originating from some kind of impurity hopping process, dominating the conduction [7].

The present paper reports the results obtained in studying the effect of hexane treatment on dielectric properties of low-density polyethylene (LDPE) and the change observed in Raman spectra due to this treatment. Furthermore the spatial distribution of polarisation was obtained in this work by using the Laser-Intensity-Modulated Method (LIMM) [8]. These measurements were carried out on both untreated and hexane treated LDPE samples.

2. Experimental

Commercially available low-density polyethylene films of average thickness of 50 μm were used. The samples were cleaned with ethyl alcohol and immersed in hexane (Aldrich) for 12 hours. Circular aluminium electrodes of area $4.91 \times 10^{-4}\ \mathrm{m}^2$ were deposited on both sides of the sample by vacuum evaporation.

The dielectric properties of untreated and hexane treated LDPE with and without ageing in AC and DC fields were obtained using dielectric spectroscopy in the frequency range of 10^{-5} to 10^5 Hz. In the frequency range of 20 Hz to 10^5 Hz a General Radio Bridge (model 1621) was used while an EG&G Lock-In Amplifier, model 7265 was used to cover the frequency range of 5×10^{-2} Hz to 10 Hz. In the low frequency range of 10^{-5} Hz to 3×10^{-2} Hz the time domain technique of the measurement of discharge current with subsequent Hamon [9] approximation method were used.

For discharge current measurement, the polyethylene film was placed in an evacuated chamber and a Fluke high voltage power supply, (model 410 B), was used to charge the sample at a field of 10^5 V/m for a period of 27 hours. The discharge current was measured for 3 hours. The Raman spectra were obtained in the two main spectral regions of interest in the study of the polyethylene, i.e., the internal mode region from 900–1500 cm^{-1} and the disordered longitudinal acoustic mode (DLAM) around 200 cm^{-1}. For poling the samples, at high fields, a Trek power supply was used

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for both DC and AC poling. In both cases the samples were poled with 10^7 V/m for 1 hour in a silicon oil bath at 70°C.

For the LIMM measurement the sample with aluminium electrodes on both surfaces, was put in the evacuated chamber with optical window. Each surface of the film was exposed to a sinusoidal modulated thermal energy of He-Ne laser beam (1×10^{-3} W, $\lambda = 0.63 \times 10^{-9}$ m). The frequency range of modulation was from 20 Hz to 3 kHz and it was controlled by an electromechanical chopper.

The non-uniform thermal force, which propagates into the sample, interacts with the spatially distributed polarisation and space charge to produce a complex pyroelectric current, which is a unique function of the modulation frequency and spatially distributed polarisation and space charge. The real and imaginary parts of this current are measured with a lock-in amplifier (EG&G Model 5206), whose reference phase is provided by the same frequency generator which drives the electromechanical chopper. The experimental pyroelectric current data are transformed into the desired spatial distribution by using a numerical analysis [9].

3. Results and discussion

Fig. 1 shows the behaviour of the permittivity (ε') and the dielectric loss (ε'') for the (○) untreated LDPE, (Δ) hexane treated LDPE and hexane treated LDPE electrically stressed with AC (□) and DC (•) field of 10^7 V/m.

The low-frequency data of ε'' were calculated from discharge current measurement by using the well known equation [9],

$$\varepsilon'' = \frac{I}{2\pi f C_o V} \tag{1}$$

where I is the discharge current, $f = 0.1/t$ is the Hamon frequency, C_o is the capacitance of the measuring electrodes without the sample and V is the charging voltage.

It can be observed from Fig. 1 that there is a reduction of dielectric loss in the hexane treated LDPE in comparison with the result obtained for the untreated sample. Also immersing the sample in hexane reduces the value of permittivity at 1 kHz from 2.32 to 2.27. This reduction in the dielectric constant can be attributed to the removal of some impurities such as anthracene and benzoic acid [7] when hexane penetrates the polyethylene lattice.

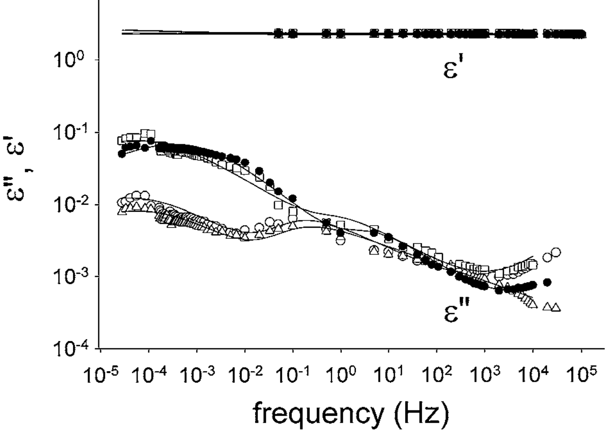

Figure 1 Complex permittivity of LDPE with (Δ) and without (○) chemical treatment and with AC (□) and DC (•) ageing after treatment.

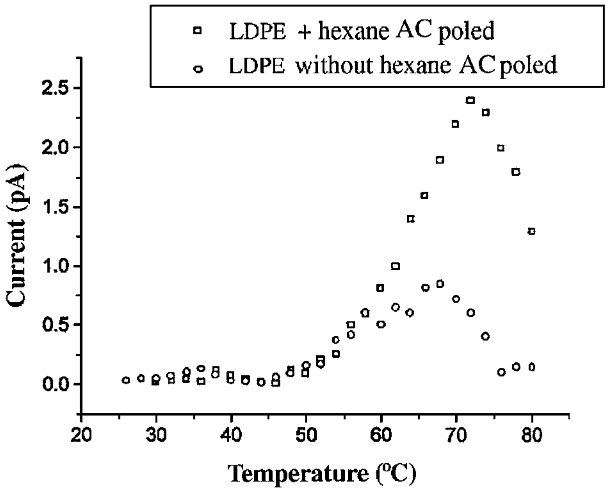

Figure 2 TSDC for untreated (○) and hexane treated (□) LDPE electrically stressed with AC field of 10^7 V/m. Heating rate of 2.0 degree/min. Samples poled at 70°C.

The broad peak around 1 Hz may be attributed to impurities that could not be removed by hexane treatment. This peak was also observed in crosslinked polyethylene (XLPE) and was attributed to the presence of antioxidants or other polar additives [11]. This peak becomes broader with the electrical stress, which may be due to an ageing process. The peak around 10^{-4} Hz is related to space charge and it can be seen also in the thermally stimulated discharge current (TSDC) measurement (see Fig. 2). As expected, the contribution of space charge is significantly high in electrically stressed samples.

The dielectric losses in the range of 10^{-5} to 10^5 Hz were combined and fitted using the "universal" relaxation law [12]. The low frequency permittivity $\varepsilon'(\omega)$ values were calculated using the Kramers-Kronig relation [13],

$$\varepsilon'(\omega) = \varepsilon_\infty + P \int_{-\infty}^{\infty} \frac{\varepsilon''(\omega)}{\omega - x}\, dx \tag{2}$$

where ε_∞ is the value of permittivity at the highest value of frequency and P is the Cauchy principal value of the integral.

Similarly with hexane treated LDPE, electrically stressed with DC field, it can be observed that there is an increase of space charge contribution in the peak around 10^{-4} Hz in comparison with that for the electrically unstressed sample. In the frequency range of 5×10^{-2} Hz to 10 Hz the values of ε' and ε'' were calculated using the relations [14],

$$\varepsilon' = \frac{dI_y}{\omega \varepsilon_o S V} \tag{3}$$

$$\varepsilon'' = \frac{dI_x}{\omega \varepsilon_o S V} \tag{4}$$

where d is the sample thickness, I_y and I_x are the in phase and quadrature current, respectively, $\varepsilon_o = 8.85 \times$

10^{-12} F/m is the vacuum permittivity, S the electrode area.

Fig. 2 shows the thermally stimulated discharge current obtained for both, untreated and hexane treated LDPE samples after AC poling with 10^7 V/m for 1 hour at 70°C. The short-circuited current was measured using an electrometer Keithley, model 617 while the sample was heated at a linear rate of 2.0 degree/minute. The peaks observed around 70°C in TSDC measurement correspond to dielectric loss peaks, observed at 10^{-4} Hz (see Fig. 1). The correspondence between these peaks was confirmed using the relation [15],

$$\omega = \frac{A}{hkT^2} \tag{5}$$

where A is the activation energy, h is the reciprocal of heating rate, k is the Boltzmann constant, T is the temperature of maximum current in the TSDC and ω is the angular frequency. Using $k = 1.38 \times 10^{-23}$ J/K, $A = 1.5$ eV [6], $h = (2\,\text{K/min})^{-1}$, the values of 7.93×10^{-4} Hz and 7.75×10^{-4} Hz were found for untreated and hexane treated samples, respectively. The peak around 70°C is a polarisation peak. It can be observed that the magnitude of the current released near the poling temperature for the hexane treated sample is high, indicating that more space charge was trapped in the empty sites, vacated by some impurities.

Fig. 3 shows the TSDC current for untreated and hexane treated LDPE DC poled at 70°C with 10^7 V/m for 1 hour. Again the peak around 70°C indicates that charge trapping can be enhanced in the hexane treated sample. In a single injection process less charge can be injected than in the case of a double injection. There is evidence of a small peak around 30°C as well in the AC poled sample (Fig. 2) and this peak may be due to a local motion of a segment of the main chain. In the dielectric spectroscopy there is evidence of this peak in the range of 10^{-4} Hz (see Fig. 1).

The structural information on the crystalline state of polyethylene can be obtained from three spectral regions in the Raman spectra [16]. The region of 900–1500 cm^{-1} provides quantitative information with respect to the elements of phase structure [17, 18]. Secondly the information on ordered sequence length distribution can be obtained in the longitudinal acoustic mode (LAM) in the wave number range of 5–50 cm^{-1} [19]. Finally the region around 200 cm^{-1} gives information on the long-range conformational disorder, i. e., the disordered LAM (DLAM) [20].

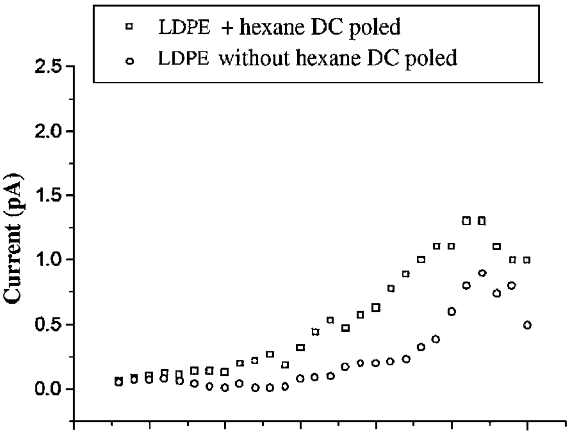

Figure 3 TSDC for untreated (○) and hexane treated (□) LDPE poled with DC field of 10^7 V/m. Heating rate of 2.0 degree/min. Samples poled at 70°C for 1 h.

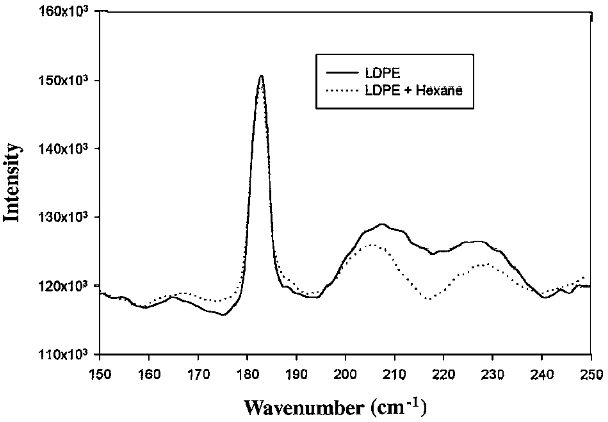

Figure 4 Raman spectra for LDPE and hexane treated LDPE.

Fig. 4 shows the Raman spectra for LDPE and hexane treated LDPE in the DLAM region. It can be observed that the effect of the solvent is a reduction of the conformational disorder in a long-chain molecule. This reduction can be related to the removal of the low molecular weight impurities from the polymer matrix. The observed relative difference in the spectral behaviour around 200 cm^{-1} is of course subject to base line corrections. Neither, AC nor DC electrical stress caused any variation in Raman spectra in both the internal and the LAM modes. Further work is in progress for the Raman study in the range of 200 cm^{-1} and 5–50 cm^{-1}.

These samples were also investigated by Fourier Transform Infrared spectroscopy (FTIR) in the range of 1000–2000 cm^{-1} and no significant variation in the oxidation level was found.

Figs 5–8 show a typical variation of the spatial distribution of polarisation from the mean value P_0 for the four different cases, i. e., DC and AC electrically stressed untreated and hexane treated LDPE. The nature of the internal field distribution also is shown.

The LDPE film of thickness L may contain a combination of a spatially distributed non-uniform polarisation distribution $P(x)$ and a non-uniform space charge $\rho(x)$. Using the appropriate relation [10] from the experimentally measured current as a function of frequency, the polarisation or space charge distributions can be obtained.

The fundamental LIMM equations are [10],

$$\begin{aligned}\frac{I_L}{I_0} &= 1 + C_1 \int_0^1 P(y)\left(\frac{v \cosh vy}{\sinh v}\right) dy \\ &\quad + C_2 \int_0^1 \rho(y)\left(\frac{\sinh vy}{\sinh v} - y\right) dy\end{aligned} \tag{5}$$

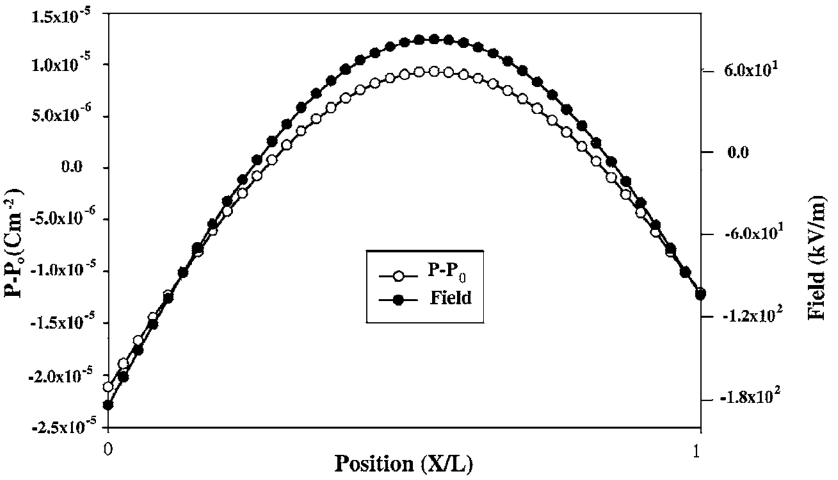

Figure 5 Variation of (○) spatial distribution of polarisation from the mean value and (•) the field distribution in low density polyethylene DC poled (10^7 V/m at 60°C for 1 h).

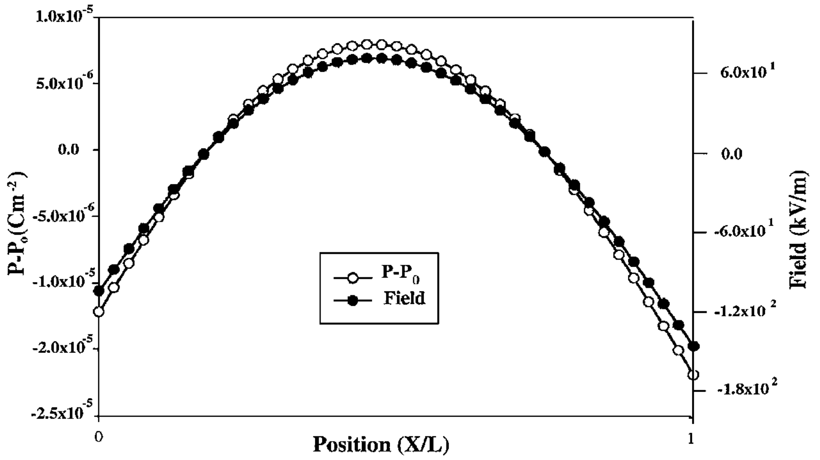

Figure 6 Variation of (○) spatial distribution of polarisation from the mean value and (•) the field distribution in hexane treated low density polyethylene DC poled (10^7 V/m at 60°C for 1 h).

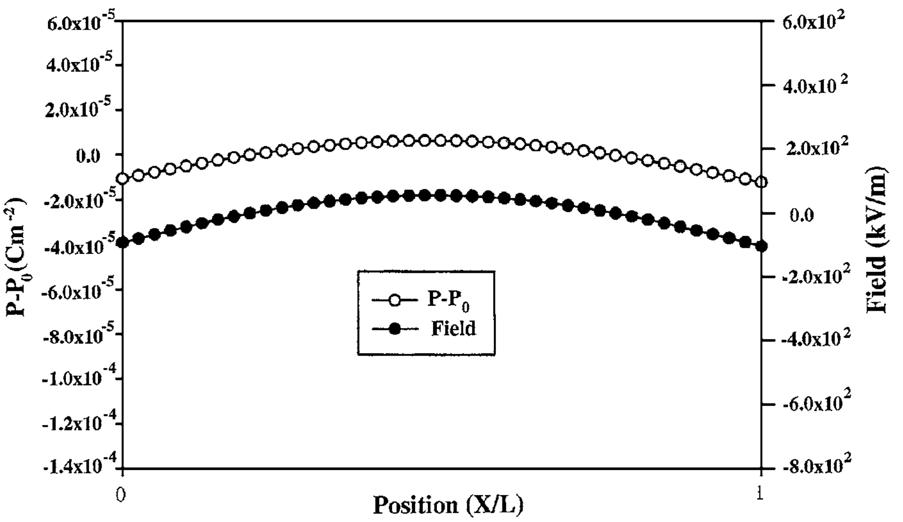

Figure 7 Variation of (○) spatial distribution of polarisation from the mean value and (•) the field distribution in low density polyethylene AC poled (10^7 V/m at 60°C for 1 h).

$$\frac{I_z}{I_0} = 1 + C_1\int_0^1 P(y)\left(\frac{v\cosh[v(1-y)]}{\sinh v}\right)dy - C_2\int_0^1 \rho(y)\left(\frac{\sinh[v(1-y)]}{\sinh v} - (1-y)\right)dy \qquad (6)$$

where

$$v = \left(\frac{\omega}{2k}\right)^{1/2} L(1+i)$$

$$C_1 = \frac{\alpha_p + \alpha_x + \alpha_\varepsilon}{p}$$

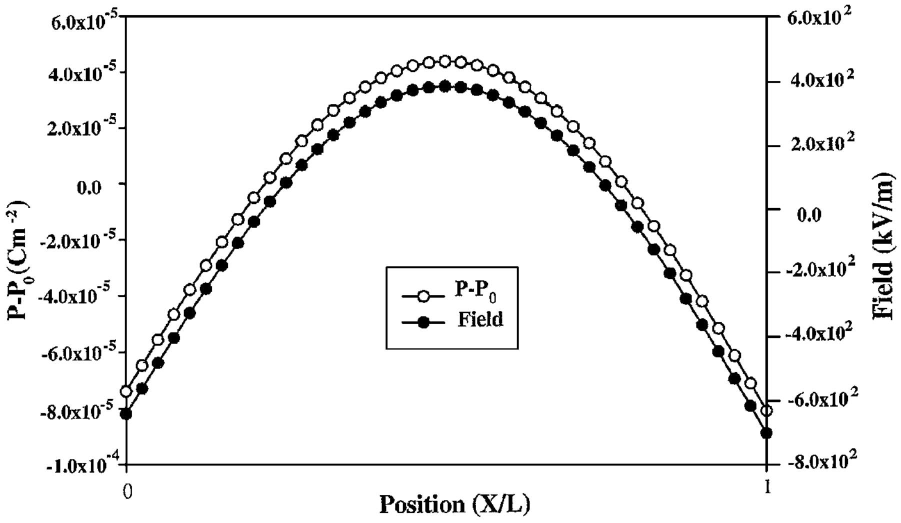

Figure 8 Variation of (○) spatial distribution of polarisation from the mean value and (●) the field distribution in hexane treated low density polyethylene AC poled (10^7 V/m at 60°C for 1 h).

$$C_2 = \frac{\alpha_x - \alpha_\varepsilon}{p} L$$

$$y = X/L \qquad i = \sqrt{-1}$$

where I_0 is the current at zero frequency, L the sample thickness, k the thermal diffusivity, I_L the pyroelectric current when the laser beam is incident on the sample face $X = L$, I_z the current when the laser beam is incident on the face $X = 0$, p the pyroelectric coefficient, ω is the angular frequency, α_p, α_x and α_ε are the relative temperature dependence of the polarisation, thermal expansion coefficient and permittivity respectively.

The polarisation can be determined with the known values of α_p $(=-0.25 \times 10^{-4}\ \mathrm{K}^{-1})$, α_x $(=2.8 \times 10^{4}\ \mathrm{K}^{-1})$, $\alpha_\varepsilon(=-6.8 \times 10^{-4}\ \mathrm{K}^{-1})$ and p $(=-1.0 \times 10^{-8}\ \mathrm{C \cdot m^{-2} \cdot K^{-1}})$. The value of $0.01\ \mathrm{C \cdot m^{-2}}$ was used for P_0 in the present case. It may be observed that the deviation of the spatial distribution of polarisation tends to increase from the central part of the sample thickness towards the two surface regions. The maximum deviation of polarisation from the value of P_0 in the surface regions occurs with the hexane treated samples for AC poling in comparison with the corresponding case for DC poling.

For the untreated samples, the injection of charge is reduced because of the presence of impurities in the polymer matrix. The deviation from (P_0) the mean value is lower because P is lower. Also, it can be observed that for DC stressed sample $P - P_0$ is higher on one side than on the other because of single injection.

In hexane treated samples the injected charges can be held in the polymer matrix at the empty sites, created by the removal of the impurities. Now, the AC stressed sample shows higher $(P - P_0)$ deviation from the mean value because the polarisation (P) is higher since the charge is injected on both half cycles.

4. Conclusion

Using organic solvent, like hexane, impurities such as low molecular weight aromatic molecules, which are present in the polyethylene matrix, can be removed. The result of this chemical treatment shows that there is a reduction in the permittivity and dielectric loss of the polymer. Also it can be observed that there is a reduction in intensity of the Raman spectrum in the disordered longitudinal acoustic mode region (DLAM) due to hexane treatment. By reducing the permittivity and the dielectric loss the effect of hexane treatment may increase the breakdown strength of the polymer which is strongly affected by the presence of the impurities.

The TSDC measurement shows that more charges can be injected during the polarisation in hexane treated samples than for the untreated case. These charges injected by the poling field can be localised in the empty sites created by the removal of low molecular weight dipolar impurities. The presence of an enhanced charge density in hexane treated samples was observed in the LIMM measurements as well.

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