

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Effect of Thermal Cycling on D.C. Conductivity and Morphology of Polyethylene

M. Salah Khalil^a

^a Dept. of Electrical & Electronics Eng., College of Engineering, Sultan Qaboos University, Muscat, Sultanate Of Oman

To cite this Article Khalil, M. Salah(1995) 'Effect of Thermal Cycling on D.C. Conductivity and Morphology of Polyethylene', International Journal of Polymeric Materials, 28: 1, 179 – 185

To link to this Article: DOI: 10.1080/00914039508012101

URL: <http://dx.doi.org/10.1080/00914039508012101>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Effect of Thermal Cycling on D.C. Conductivity and Morphology of Polyethylene

M. SALAH KHALIL

Dept. of Electrical & Electronics Eng., College of Engineering, Sultan Qaboos University, Muscat, Sultanate of Oman

(Received August 26, 1994)

The effects of long period repeated thermal cycling in the presence of d.c. electric field on the d.c. conductivity, morphology and degree of crystallinity of low density polyethylene (LDPE) were investigated. D.C. conductivity measurements indicate that a reasonable steady state conductivity could be achieved after a period of 10 days of thermal cycling between 80°C and 40°C in the presence of a d.c. electric field across the sample followed by another 10 days of conductivity measurements at constant temperature of 80°C. Crystallinity evaluation as well as morphological investigations using scanning electron microscopy (SEM) of etched surfaces of the material before and after thermal cycling and conductivity measurements show that the investigated material has undergone structural changes after that long period of thermal cycling and conductivity measurements. An attempt is made to correlate between the d.c. conductivity results and the observed structural changes in the material.

KEY WORDS D.C. conductivity, thermal cycling, polyethylene, morphology.

INTRODUCTION

It has been long realized that morphological structure of polymers may have a detrimental influence on the electrical properties of these materials. However, few attempts have been made to study the effects of polymer morphology on its electric strength.^{1–4} Less attention has been given, so far, to correlate between polymer morphology and d.c. conductivity and publications on this subject are sparse.^{5–7}

There are various reasons for this state of affairs: firstly, the measurement of d.c. conductivity of insulating polymers is beset with a number of difficulties due to the very small values of the measured currents and the difficulty in attaining steady state conductivity if such steady state is attained at all. In many of the works on d.c. conductivity in PE, conductivity measurements were made for relatively short periods of time (few hours) after application of the field.⁸ In such cases it is extremely difficult to assume that steady state conditions have been reached. Secondly, the involved difficulties in using the available structure characterization

techniques to observe representative microstructures and the uncertainties connected with the interpretation of such observations.

In certain cases, the investigated polymer itself may offer experimental obstacles due to its structure and reaction to the used techniques. Moreover, it has been shown that some of the features of morphologies reported in the literature might be artifacts resulting from the used techniques to prepare the surface of the sample for examination by electron microscopy.⁹⁻¹¹ Different methods and combination of techniques have been used to study the internal microstructure of crystalline polymers. These methods vary from polarized light microscopy, small angle light scattering (SALS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of etched surfaces and/or replicas of etched surfaces.¹²⁻¹⁵

The objective of the present work is twofold: firstly, to investigate the possibility of achieving steady state conductivity by thermal conditioning of the polymer in the presence of electric field and measuring the conductivity for long time periods after field application; secondly, to study the effect of this method of conditioning on the d.c. electrical conductivity and morphology of LDPE.

Morphological investigations were conducted using SEM of etched surfaces with carbon tetrachloride CCl_4 . Density measurements and evaluation of degree of crystallinity were used to complement the study.

EXPERIMENTAL DETAILS

Test samples were square plaques ($190 \times 190 \times 2$ mm) of LDPE (density 925 kg/m^3 , melt index 0.25 gm/10 min) made by pressing from pellets. Conductivity samples were discs of 175 mm diameter cut from the plaques and provided with conventional gold conductivity electrodes and guard rings deposited on the sample by vacuum evaporation.

Thermal cycling under d.c. electric field and d.c. conductivity measurements were made as follows. Test sample was first conditioned by putting it into vacuum (10^{-2} torr) at 40°C for 24 hours after which it was mounted in a test cell and immersed in silicone oil, where it was subjected to thermal cycling between 80°C and 40°C for 10 days. During this period a voltage of 50 kV d.c. was applied across the electrodes while the current flowing through the sample was monitored. At the end of the 10 days, the voltage was removed and the sample was short circuited for 48 hours. The same voltage was then applied again, and conductivity measurements were started at constant temperature of 80°C for another 10 days after which the voltage was removed and the sample was short circuited at 80°C . In order to check for the reproducibility of the conductivity measurements, the above procedure of thermal cycling followed by d.c. conductivity measurements was repeated again under the same experimental conditions described above. The temperature profiles during thermal cycling and conductivity measurements as well as the current-time dependency in each case are shown in Figure 1. The system used for d.c. conductivity measurements is described elsewhere.¹⁶

Structural and morphological investigations were conducted by (i) determination of sample density related to amount of crystallinity, (ii) SEM of etched surfaces

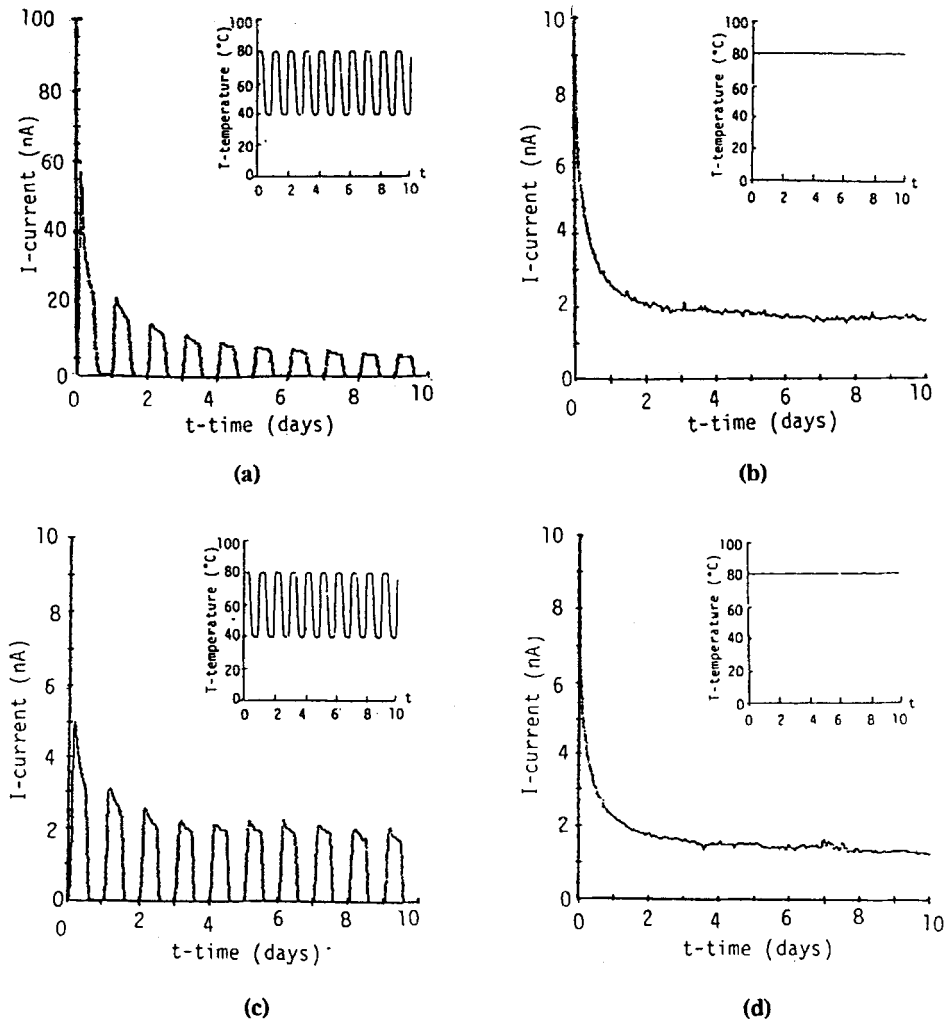


FIGURE 1 Current-time dependencies during thermal cycling and d.c. conductivity measurements at constant temperature 80°C: (a),(c) thermal cycling; (b),(d) d.c. conductivity [Inserts are the corresponding thermal profiles.]

using CCl_4 vapour. Two groups of samples were used for these investigations. The first group was taken from the corners of the square plaque from which conductivity disc was cut. In this case, the LDPE was not subjected to any electrical or thermal stresses after preparation by pressing from pellets. The second group was cut from the conductivity disc itself after it has been subjected to the thermal profiles and electrical stress during thermal cycling and conductivity measurements. For SEM investigations two samples were used from each group: one sample having the size of 10×10 mm and another having the size of 10×5 mm. The samples were embedded in a cold mounting resin and wet ground using standard metallurgical technique and then polished. Etching was effected using CCl_4 vapour to reflux on the surface of the sample for a short period (30–90 seconds) to avoid swelling of

the sample. Reprecipitation of the solvated resin on the sample polished surface was avoided by keeping the surface vertical in the vapour. The etched samples were then dried under vacuum for 24 hours and coated by 50 Å platinum layer. SEM was carried out using a JEOL-JSM-03 instrument.

RESULTS AND DISCUSSION

In Figure 1 are shown the current time dependencies during the periods of thermal cycling between 80°C and 40°C (a,c) and conductivity measurements at 80°C (b,d) respectively. The decay of current with time throughout each period is evident. In the first period of thermal cycling, Figure 1a, the current decayed from a maximum level of 57 nA to 5.4 nA. These values represent current levels at 80°C intervals of the thermal cycling period. At 40°C intervals the currents are found to be negligibly small. Figure 1b shows that the current decayed from a level of 12 nA to a level of 1.6 nA in 10 days after field application. In the second period of thermal cycling, Figure 1c, the current level at the 80°C intervals has decayed from 5 nA to 1.6 nA. Figure 1d shows that the current has decayed from 9 nA to 1.3 nA during the second period of conductivity measurements. Comparison between Figure 1b and Figure 1d indicates that a reasonable and reproducible steady state d.c. conductivity was achieved.

In Table I are given the density and the corresponding degree of crystallinity of the investigated LDPE before and after thermal cycling and d.c. conductivity measurements.

The degree of crystallinity X was evaluated from the densities of the samples before and after treatment using the formula:

$$X = \frac{v_a - v_m}{v_a - v_x} \times 100\%$$

where $v_x = 0.987 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$, which is the specific volume for the pure crystalline parts of the PE, $v_a = 1.160 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}$, which is the specific volume of the amorphous fraction of PE at 20°C, and v_m is the measured specific volume of the sample. (Specific volume is the reciprocal of density.¹⁷)

TABLE I
Density and degree of crystallinity of LDPE before and after thermal cycling and D.C. conductivity measurements

Sample	Density (kg/m ³)	Degree of crystallinity %
Before thermal cycling and conductivity measurements.	925	46
After thermal cycling and conductivity measurements.	920	42

From Table I it can be seen that the density, and consequently the degree of crystallinity were slightly reduced as a result of being subjected to the experimental conditions described above.

Figures 2a, 2b and 2c show SEM micrographs for the investigated LDPE before being subjected to the combined thermal and electrical effects described above. The micrographs reveal spherulitic structure, typical for LDPE as well as the lamellae accommodated within the spherulites.

Figures 2d, 2e and 2f show SEM micrographs for the same material after being subjected to repeated thermal cycling between 80°C and 40°C in the presence of the d.c. electric field and d.c. conductivity measurements at 80°C for a total period of 40 days. In this case, a quilt-like structure is observed (d), while no internal structure can be discerned (e,f). It appears that, in this case CCl₄ vapour treatment

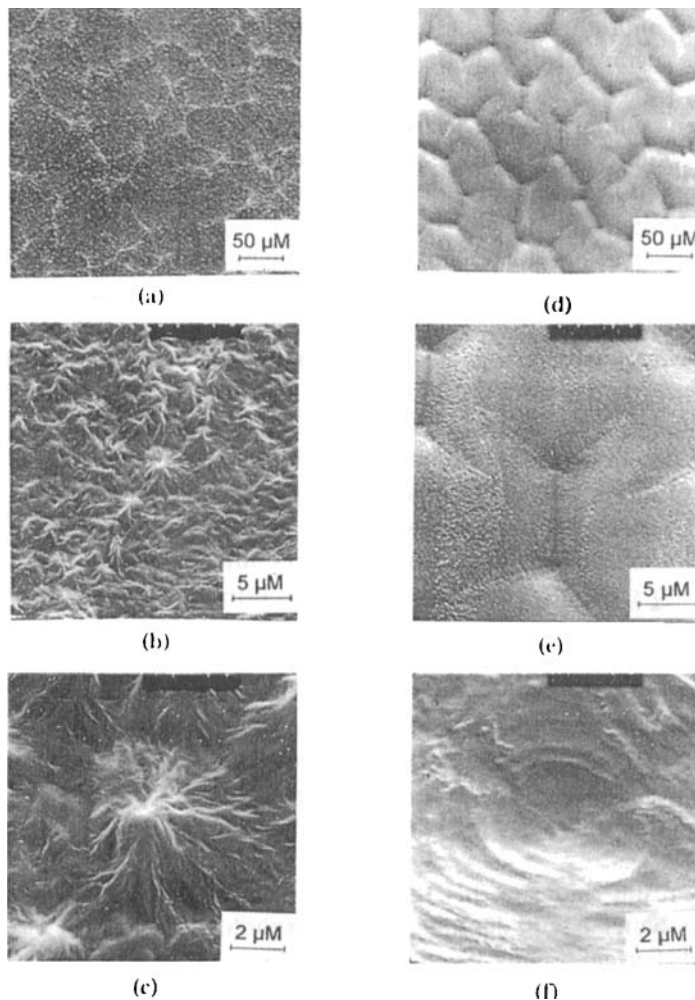


FIGURE 2 SEM of etched surfaces of LDPE. (a),(b),(c): Before thermal cycling and conductivity measurements (d),(e),(f): After thermal cycling and conductivity measurements.

has modified the surface of the sample by swelling and that the original polymer morphology could not be revealed.

Solvent etching using CCl_4 was used successfully to reveal the supermolecular structure for LDPE.^{12,13,15} The solvent selectively dissolves low molecular weight polymer in the amorphous regions leaving the crystalline regions unaffected. CCl_4 vapour is expected to attack different polymers with different degrees.

XLPE was reported before to react to CCl_4 vapour by swelling without revealing any structure. The pillow-like entities observed in that case are thought to be insoluble gel particles resulting from the cross-linking.⁹

The present observed reaction of the LDPE to CCl_4 vapour by swelling together with the observed reduction in its degree of crystallinity after it was subjected to the present experimental conditions suggest that the polymer has undergone chemical as well as morphological changes as a result of thermal cycling in the presence of electric field and long term d.c. conductivity measurements at 80°C. Changes of spherulitic structure of PE due to various heating cycles was reported before by other authors.^{12,20}

A full understanding of electrical conductivity in polymers would require the knowledge of a multitude of factors such as the nature and origin of charge carriers, the mechanisms of their generation and transport, and polymer structure and its influence on charge trapping and transport.

D.C. conductivity studies of polymers performed by many authors^{5-7,18-20} suggest the following: (i) In PE, conduction is mainly electronic in nature. (ii) Charge carrier injection at the electrodes is the most dominant mechanism responsible for generation of charge carriers. (iii) Although many measurements on PE are consistent with space charge limited conduction, effects of electrode processes and the properties of metal electrode-polymer interface cannot be excluded. (iv) The morphology of PE has an important influence on the d.c. conductivity of polymers due to the effects of morphological changes on charge carrier trapping.

The present results can be explained in the light of the above considerations. With d.c. field application, charge carriers will be injected at the electrodes, penetrate into the bulk and start to fill trapping sites. Injected charge carriers together with charges already in the polymer will form a space charge which will control the current flow. Such a space charge, and hence the flowing conduction current will be influenced by trapping and detrapping processes.

The observed slow decay of current with time in response to such d.c. field is a typical characteristic of electrical conduction in many polymers including PE. So far, there is no universally accepted explanation for such a behaviour. However, it was suggested that such a decay is relevant to the local states at the metal-polymer interface.¹⁸

The present results indicate that the degree of crystallinity of PE was reduced and that the polymer has undergone some morphological changes as a result of long periods of thermal cycling. Such morphological changes are expected to have changed the interspherulitic amorphous regions to which traps are associated. Consequently, polymer trapping sites were modified, and hence conductivity changes were observed. Changes of conductivity of PE were found to be associated not

only with the degree of crystallinity of the polymer but also with the type of morphological structure and size of spherulites.²⁰

Acknowledgments

The author is indebted to NKT Power Cables, Denmark for their support and permission to publish this paper. Thanks also go to the Dept. of Electrical Power Eng. Technical University of Denmark for providing the experimental facilities. The author is also grateful to the Danish Electrical Research Institute (DELRI) ELSAM and EL-KRAFT for supporting this work.

References

1. H. Wagner, CEIDP Ann. Report, 1974, pp. 62–70.
2. K. Yahagi and K. Isshi Ki, CEIDP Ann. Report, 1978, pp. 171–175.
3. S. N. Kolesov, *IEEE Trans. Electr. Trans. Insul.*, **EI-15**, 1980, pp. 382–388.
4. T. Fukuda, S. Irie and Y. Asada, *IEEE Trans. Electr. Insul.*, **EI-17**, 1982, pp. 386–391.
5. V. A. Kargin, N. G. Podosenova, G. P. Andrianova and B. I. Sazhin, *Polym. Sci. (USSR)*, **9**, 323–328 (1967).
6. B. I. Sazhin and N. G. Podosenova, *Polym. Sci. (USSR)*, **6**, 162–189 (1964).
7. M. Kryszewski, H. Kasica, J. Patora and J. Piotrowski, *J. Polym. Sci., Part C*, 243–260 (1970).
8. D. K. Das Gupta, M. E. Tindell, R. D. Wingrove and K. Joyner, *DECHMA-Monogr.*, **72**, 73–83 (1973).
9. S. Bamji, A. Bulinski, J. Denseley and A. Gorton, *IEEE Trans. Electr. Insul.*, **EI-19**, 32–41 (1983).
10. K. L. Naylor and P. J. Phillips, *J. Polymer. Sci., Polymer. Phys. Ed.*, **21**, 2012–2016 (1983).
11. J. Muccigrosso and P. J. Phillips, *IEEE Trans. Electr. Insul.*, **EI-13**, 172–178 (1978).
12. F. P. Reding and E. R. Walter, *J. Polym. Sci.*, **38**, 141–155 (1959).
13. J. S. Macki and A. Rudin, *J. Polym. Sci.*, **49**, 407–417 (1961).
14. R. H. Olley, A. M. Hodge and D. C. Bassett, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 627–643 (1979).
15. U. W. Gedde, *Morphology of Polymers*, 337–346 (1986).
16. M. Henriksen and H. S. Johanessen, Conf. Rec. 3rd Int. Symp. Electr. Insul., 1986.
17. L. A. Dissado and J. C. Fothergill, Peter Peregrins Ltd., London, U.K., 1992, Chapter 1, pp. 19–20.
18. T. J. Lewis, CEIDP Ann. Report, 1976, pp. 533–561.
19. P. Fischer, *J. of Electrostatics*, **4**, 149–173 (1977/1978).
20. M. Kryszewski, *J. Polym. Sci. Symposium*, 359–404 (1975).