Journal of Thermal Analysis, Vol. 37 (1991) 1239-1249

Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

THERMOANALYTICAL STUDY OF ELECTRICALLY AGED POLYETHYLENE

G. Liptay and G. Kenessey

INSTITUTE FOR INORGANIC CHEMISTRY, TECHNICAL UNIVERSITY OF BUDAPEST; H-1521 BUDAPEST, HUNGARY

(Received October 25, 1990)

Thermal analysis is found to be suitable methods to investigate the electrical aging of polyethylene.

Measurements by means of the derivatograph and isothermal thermogravimetric analysis as well as differential scanning calorimetry (DSC) were applied to measure the induced changes of the properties due to electrical aging.

The influences of the elctrical aging on the thermal analytical curves are discussed. New effects in the starting phase were also observed.

Polyolefines, used as electrical insulators, occupy an important place in the cable industry. Polyethylene (PE) was used usually at medium voltage levels of 10 to 35 kV for the insulation of power cables. Nowadays manufacturers try to use polyethylene to insulate high voltage wires.

The use of polyethylene as an insulating material is justified by a number of valuable properties: outstanding AC and DC insulation, very low dielectric loss and high dielectric strength.

The cable core insulation in the electric mains is exposed to several physical and chemical influences [1]. Two important aging factors are the electric field intensity and varying ambient temperatures.

Numerous methods are avaible to study the aging of insulating materials [2, 3]. Thermal analysis is well suited to study the changes of the structural and physical properties of PE [4]. These techniques are also often used to measure the thermal aging of polymers [5–8].

The electrical aging was previously examined mainly by other methods (e.g.: gas chromatography [9], mass spectroscopy [10], scanning electron

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

microscopy, UV- and IR-spectroscopy [11] e.t.c.), especially by electrical engineering methods [12–14]. It is generally accepted that electrical influences cause no changes in proportion to the thermal mechanism of aging [15].

Liptay and co-workers investigated electrically aged PE by simultaneous TG–DTG–DTA, isothermal thermogravimetry [16] and thermodilatometry [17]. It was pointed out, that the electrical aging seems to initiate degradation at a lower temperature and leads to a considerably increased oxidation.

This work attempts to extend the thermal methods to describe the aging of PE at constant electric field.

These results may give useful informations not only to the scientists but in the first place to the engineers working in the development of cable industry.

Experimental

Two types of PE, linear and cross-linked, were used for the examination of the electric aging. Both materials are used at medium voltage levels as insulating materials in Hungary.

Sheet test samples were aged in a special aging cell (Fig. 1) in homogeneous electric field (10 kV) for various times. The selected value of the electric field was small in order to avoid electrical discharges.

The measurements were carried out both by dynamic and static thermal

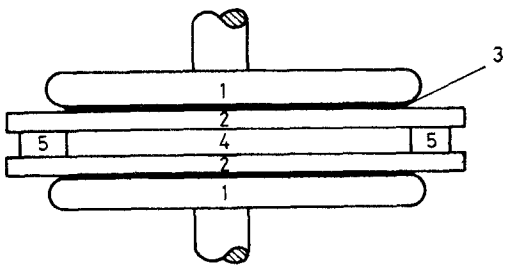

Fig. 1 Aging cell
1 – Electrodes, 2– Glass plates, 3 – Graphite conductor layer, 4 – Sample, 5 – Plastic distance keeper

methods. The dynamic thermoanalytical investigations were made by:

– Hungarian MOM–OD2 Derivatograph in a platinum crucible with a heating rate of 5 deg/min and a sample weight of 500 mg.

– Mettler DSC with a heating rate of 5 deg/min and a sample weight of 55±0.2 mg.

Isothermal thermogravimetry was used as a static method. Sample weight (1.0 g) changes were recorded at constant temperature *vs.* time.

All the examined sample weights were greater than the sensitivity of the applied methods demand to be able to describe quatitatively the differences between the weight and enthalpy changes of the samples. As it will be shown in the following in the case of DSC curves, only one part of the peak area was used for a comparison between the samples.

The investigation were carried out neither in oxygen nor in inert atmo-- sphere, but in air, in order to simulate the working conditions of outdoor PE insulators.

The samples were cut into small prisms of 1·1·2 mm in all methods.

Results

1. Dynamic measurements

A. Derivatograms of linear and cross-linked PE samples are shown in Figs 2 and 3 respectively. In the case of cross-linked PE (Fig. 3) standard sample under test conditions exhibited a perfect weight constancy up to 210° where a slight increase was observed well shown by the DTG curve. The weight increase was due to the oxidation of PE. The oxidation was followed by a slow oxidative decomposition and (break on TG and DTG curve) a fast degradation.

Oxidation and decomposition-degradation processes can be seen as exothermic peaks on the DTA curve. There was also a complex endothermic peak at approximately 105°, unaccompanied by a change in weight due to the melting of the crystalline phase. The DTA peak area was related to the degree of crystallinity [4].

The changes in weight are greater in the case of cross-linked standard samples (Table 1). This is due to the easy oxidation of the tertiary carbon.

Table 1 Oxidation weight increase of linear and cross-linked PE

Aging time, h	standard	2	9	67.5	130
Linear sample, %	0.05	0.45	0.35	0.25	0.15
Cross-linked sample. %	0.20	0.45	0.30	0.20	0.05

As a result of the electric aging volatile products releasing can be seen on the TG curve. The oxidation weight increase, increases in quantity up to

2 hours of aging and decreases continuously afterwards (see Table 1). The staring points of the decomposition processes are shifted to lower temperatures in the case of aged samples.

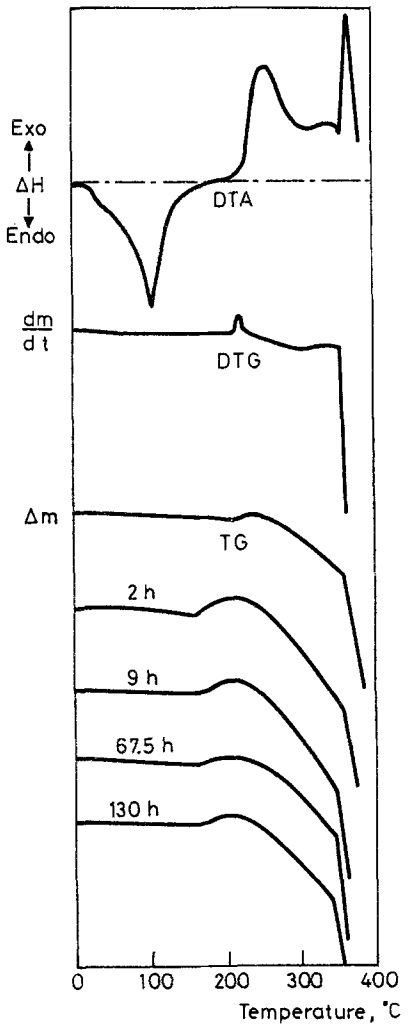

Fig. 2 Thermoanalytical curves of linear PE samples

We were unable to describe the electric aging of PE quantitatively in this way because of the slight changes in weight and enthalpy between the samples, only the trend of the changes were determinable.

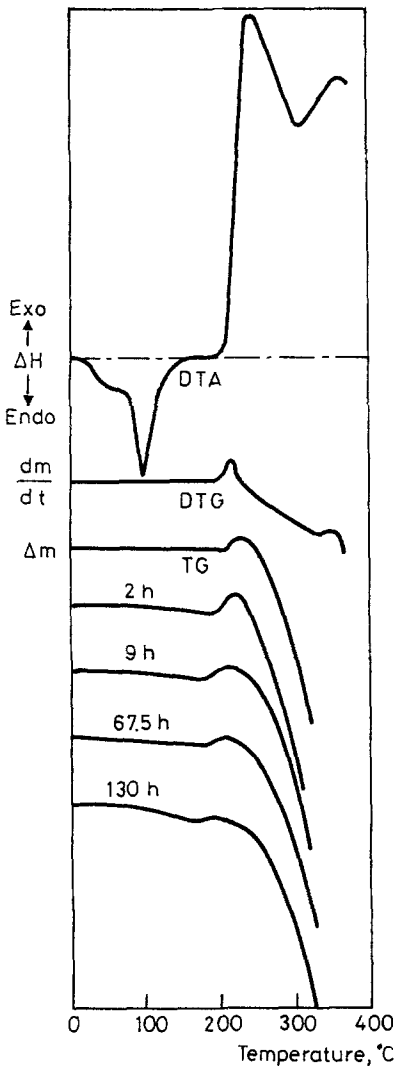

Fig. 3 Thermoanalytical curves of cross-linked PE samples

B. DSC curves of cross-linked samples are shown in Fig. 4. As can be seen on the DSC curve, the overlapping exothermic peaks immediately follow the complex endothermic peak of melting. The starting temperature of the thermooxidative processes was shifted down from 242° to 190° by the aging procedure.

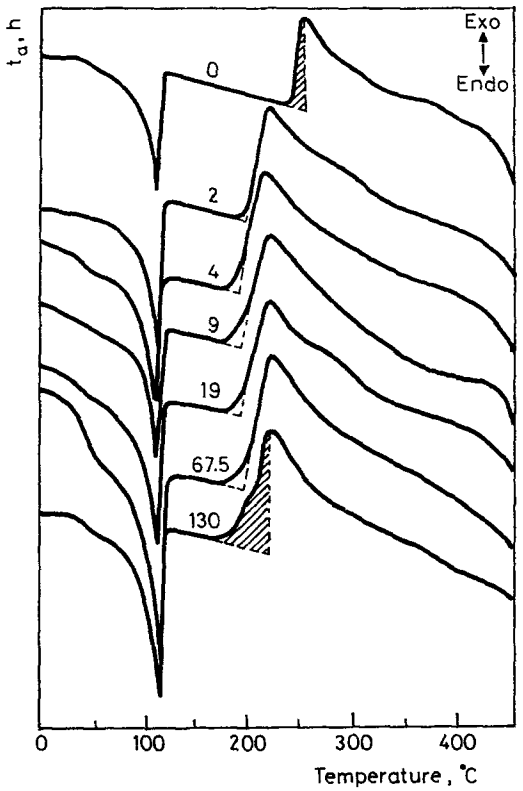

Fig. 4 DSC curves of cross-linked PE samples

Changes can be seen in the melting enthalpy between the standard and the aged samples (Table 2).

Table 2 Melting enthalpy of linear and cross-linked PE samples

Aging time, h	Standard	4	9	19	67.5	130
Linear PE, mJ / mg	103.7	107.2	108.6	108.1	107.7	107.4
Aging time, h	Standard	4	10	29	67.5	130
Cross-linked PE, mJ / mg	69.7	92.5	92.1	91.5	92.0	91.0

Because the consecutive, overlapping termooxidative reactions only the area marked by the lines (bordered by the extended base line, the perpen-

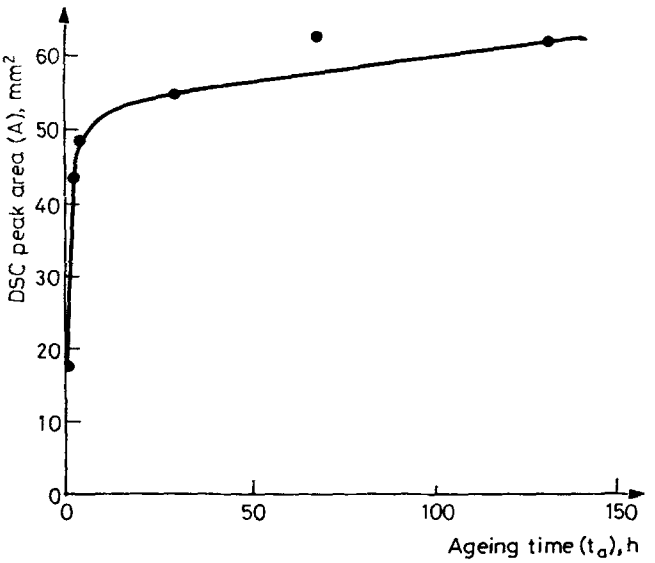

Fig. 5 DSC peak areas *vs.* aging time

dicular line from the peak maximum and by the curve) was used to describe the electric aging of PE. As will be shown in later testing, significant changes will occur in the starting phase of aging (See Fig. 5).

2. Static measurements

After an informative investigation carried out by dynamic methods. the samples were tested by isothermal thermogravimetry.

This was described previously [18], PE samples have shown the characteristics of the curve shape according to Fig. 6.

The beginning of the curve is characterized by the release of certain amount of volatile materials and some absorbed water loss (IWL = *i*nitial *w*eight *l*oss). This is followed by the oxidation of PE (WI = *w*eight *i*ncrease). Finally the material undergoes progressive degradation at the end of the oxidation process, as evidenced by the weight loss (WLO = *w*eight *l*oss from the *o*xidation maximum, EWL = *e*xtent *w*eight *l*oss during the measurement).

Isothermal thermogravimetric curves of cross-linked samples recorded at 170° are shown in Fig. 7.

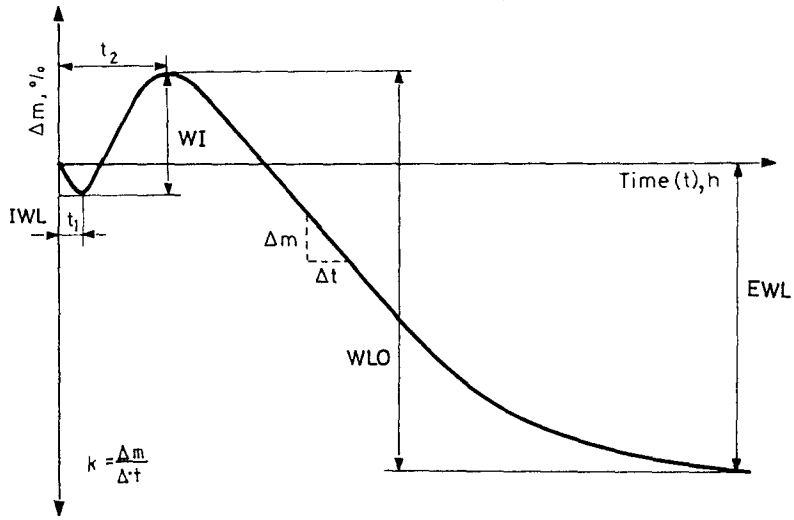

Fig. 6 Isotherm thermogravimetric curve of Pe. IWL – Initial weight loss; WI – Weight increase; WLO – Weight loss from oxidation maximum; EWL – Extent of weight loss during the measurement

All the caracteristic values (IWL, WI, WLO, EWL) show changes (See Table 3), which are evaluable quantitatively. These values are shown as a function of aging time in Fig. 8.

Table 3 Characteristic isothermal thermogravimetric values of cross-linked PE at 170°

Aging time, h	standard	2	4	10	29	67.5	130
IWL, %	0.24	0.35	0.47	0.24	0.28	0.38	0.28
WI, %	1.40	1.55	1.47	0.64	0.96	1.00	0.28
WLO, %	5.18	7.02	8.90	7.26	5.06	3.96	1.96
EWL, %	3.92	5.82	7.90	6.62	4.38	3.34	1.96

All the weight changes have sharp increases and a maximum at approximately 4 hours of electric aging. Afterward a fast decrease can be seen on the curves. Volatile products releasing (IWL) has a constant value after 10 hours of aging. Degradation weight losses (EWL, WLO) show a slow decrease after 30 hours.

It is conceivable, that thermoanalytically observable processes increase by the elctrical aging induced degradation up to 4 hours.

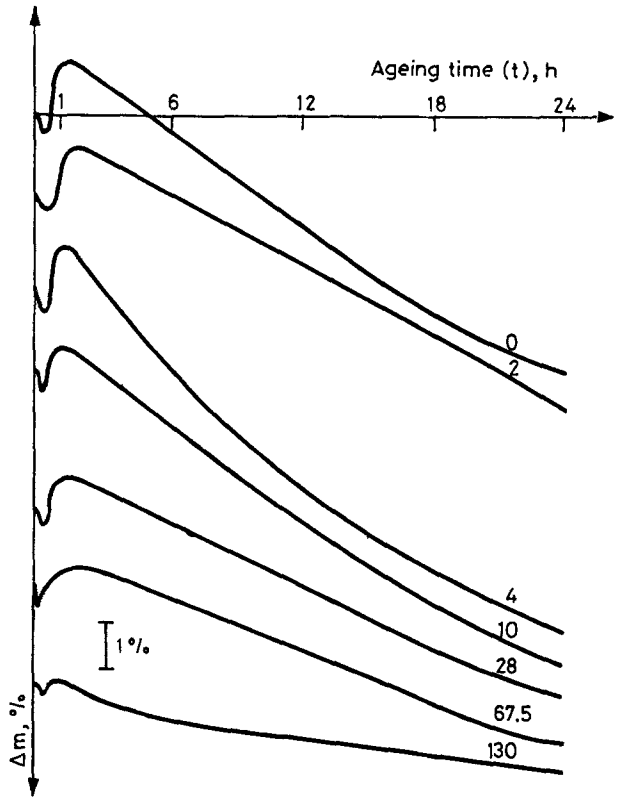

Fig. 7 Isotherm thermogravimetric curves of cross-linked PE samples

After 4 hours of aging these thermoanalytically observable processes begin in the aging cell. Volatile products evaporation and oxidation processes are able to proceed during the electric aging. These processes come to an end after approximately 10 hours.

Degradation processes also take place during the electric aging and have a continuous rate after 30 hours.

Discussion

Our measurements show that the electrical aging causes chemical changes in the insulation materials.

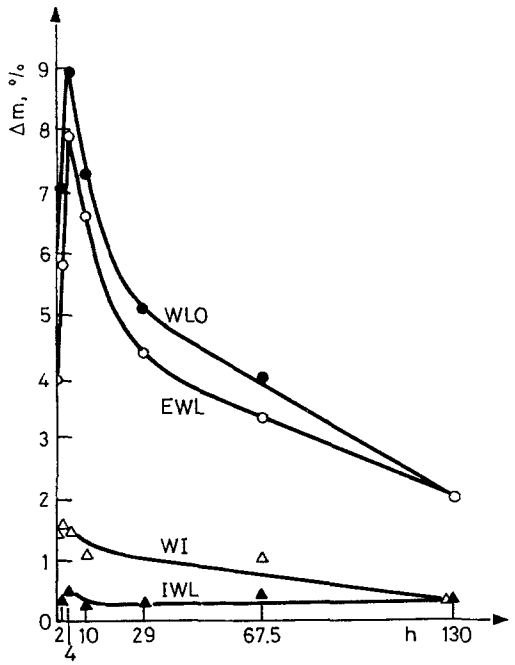

Fig. 8 Characteristic values (IWL, WI, WLO, EWL) of isotherm thermogravimetric curves *vs.* aging time

These effects can be followed by thermal analytical methods, especially by isothermal thermogravimetry.

Radical changes take place at the beginning phase of the electric aging. It is to be expected, that volatile materials evaporate and oxidation processes go on during the electrical aging as well as degradation.

Electric field causes physical changes in the insulation materials also. It can be investigated by measuring the melting enthalpy of the standard and aged samples in the case of PE.

These results may give useful informations to the engineers working in the development of the cable industry to planning and describing single and combined stresses tests on insulating materials.

With full knowledge of the results we intend to study the electric aging of polyethylene in the function of aging voltage. In addition to thermal and electrical aging of PE it would be useful to investigate the influence of other aging factors (e.g.: UV-radiation, ozone e. t. c.) using thermal analysis.

* * *

The authors wish to express theirs gratitude to Dr. Werner Ludwig (Department of Chemistry, Friedrich Schiller University, Jena) for the DSC measurements and for valuable discussions.

References

1 K. D. Walter, J. F. Johnson, and J. Tanaka: IEEE Trans. Electr. Insul., Vol. EI-13 (1978) 327.
2 J. Tanaka: IEEE Trans. Electr. Insul., Vol. EI-15 (1980) 201.
3 R. Blahnik, and M. Volkova: Elektrie, 33 (1979) 139.
4 W. Wrasidlo: Thermal Analysis of Polymers. Advances in Polymer Science Springer-Verlag, Berlin-Heidelberg-New York (1974)
5 D. J. Toop: IEEE Trans. Electr. Insul., Vol. EI-6, (1971) 2.
6 D. J. Toop: IEEE Trans. Electr. Insul., Vol. EI-7, (1972) 25.
7 H. A. Papazian: Journal Appl. Polym. Sci., 16 (1972) 2503.
8 P. Paloniemi: IEEE Trans. Electr. Insul., Vol. EI-7, (1972) 126.
9 M. Thibault et J. Galand: Rev. Générale de l'Élelectricité, 3 (1970) 247.
10 S. R. Smith, S. A. S. Smith, J. F. Johnson and J. Tanaka: IEEE Trans. Electr. Insul., Vol. EI-12, (1977) 442.
11 C. Mayoux: IEEE Trans. Electr. Insul., Vol. EI-12, (1977) 153.
12 D. W. Kitchin and D. S. Pratt: Trans. AIEE PAS, 81 (1962) 112.
13 R. M. Eichhorn: IEEE Trans. Electr. Insul., Vol. EI-12 (1976) 2.
14 R. M. Eichhorn: Conf. on Electr. Insul. and Dielectric. Phen., (1973), 290.
15 M. A. Bagirov and Z. G. Ahmedov: Plast. Mass., 2 (1975) 65.
16 G. Liptay, L. Ligethy, E. Brandt-Petrik: Thermal Anal. (Proc. 6th ICTA) Ed.: H. G. Wiedmann, Birkhäuser Verlag, Basel 1980, p. 427.
17 E. Karmazsin, P. Satre, R. Barhoumi, G. Liptay, L. Ligethy: J. Thermal Anal., 29 (1984) 1259.
18 G. Liptay, M. Lackó, L. Ligethy, E. Brandt-Petrik: Thermal Anal. (Proc. 7th ICTA). Ed.: B. Miller, John Wiley and Sons, Chichester 1982, p. 1356.

Zusammenfassung — Thermoanalyse erwies sich als geeignet, um das elektrische Altern von Polyethylen zu untersuchen.

Mittels derivatografischer und isothermer thermogravimetrischer Analyse und DSC wurden die durch elektrisches Altern verursachten Veränderungen der Eigenschaften untersucht.

Der Einfluß von elektrischem Altern auf die thermoanalytischen Kurven wurde diskutiert. Weiterhin konnten neue Effekte in der Startphase beobachtet werden.