A New Estimation Method of Thermal History in Crosslinked Polyethylene

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The authors conducted differential scanning calorimeter (DSC) measurements of various crosslinked polyethylenes of known thermal history, and found close relationships between the DSC profiles and the thermal history. From the detailed investigation of these relationships the temperature and the period of heat treatment can be correlated into functions for the DSC profiles. Using these relationships, we can estimate the thermal history. Applying this method to actual cable, the results showed good agreement with the thermal history of the cable. It is concluded that this method is useful and beneficial for revealing the thermal history on crosslinked polyethylene insulated cables and for considering the thermal behaviors of the cable.

KEY WORDS Polyethylene, thermal history, estimation, DSC

1. INTRODUCTION

XLPE (crosslinked polyethylene) is widely used as a power cable insulator because of its excellent electrical and thermal properties. XLPE is a semi-crystalline polymer which under certain temperature conditions exhibits metamorphoses of crystalline structure, e.g. partial crystalline melting or recrystallization. The electrical properties of XLPE are also influenced by such metamorphoses.

In general, XLPE insulated cable suffers various thermal history in its production process and in field usage. This includes, for example, the thermal history at the metallic or plastic jacketing process and mold joint process of an installation, and thermal history due to variations of ambient field conditions, such as sunlight, thermal resistance of the soil, applied load variations and so on. In this thermal history, however, perfect agreement of real thermal history with expected values through simulation is rarely obtained, even though some of the processes like molding at joints are conducted under controlled thermal conditions. Moreover, simulations of the thermal history of cable used in the field have also been impossible because of fluctuations of the load.

In crystalline polymers like XLPE, it is well known that recrystallization occurs under heat treatment while the thermal characteristics also change.[1-2] This phenomena can be recognized with the DSC profile measured for specimens before and after heat treatment.[3-7]

There is a proposal for the estimation of thermal history in crystalline polymer using DSC profile differences,[6-8] and some reports refer to the thermal history in XLPE cables and XLPE itself despite some remaining imperfections.

Thermal history consists of two factors, namely, the temperature and the exposure period of the specimen. However no methods are established to estimate both items simultaneously with a DSC.

The authors conducted DSC measurements on various heat-treated XLPEs to establish a new estimation method of thermal history, including both the given temperature and period. Applying the method to XLPE cables, it was confirmed that the estimated thermal history obtained with this method exhibits good agreement with the actual thermal history given to cable insulation XLPE.

2. EXPERIMENTAL

In order to ascertain the DSC profile dependences due to the thermal history in XLPE, the following experiments were performed.

The XLPE sheet specimens of 0.5 mm thickness were prepared by compression molding using low density polyethylene (LDPE) of MFR = 3, density = 0.918 g/cm^3 with dicumyl peroxide (DCP) as a crosslinking agent. The following heat treatment was performed to give the thermal history for the specimens. The specimens were immersed in a fixed temperature water bath. The temperature of the sheet specimen reached the fixed temperature because of its small thickness. After a certain time they were removed from the water bath and immediately quenched in cold water. The heat treatment temperature and periods in these experiments were 50°C to 95°C and 5 sec to 5 days, respectively. The DSC measurements were done with a DSC 220 (Seiko Instruments Inc.) using approx. 2 mg of specimen in air atmosphere at a heating rate of 10°C/min.

3. RESULTS AND DISCUSSION

3.1. Results of DSC Measurement

DSC curves of specimens treated under various temperatures at some fixed period (60 min) are shown in Figure 1. In all specimens, the maximum endothermic peak is observed at approximately 105°C. This peak temperature is defined as P_m, which corresponds to the temperature of the main melting of crystal, and is said to be the melting point of XLPE in general. P_m is independent of the treated period and thus a constant value in this experiment. And furthermore, two subsidiary peaks in the DSC curve are observed in heat-treated specimens. One is the hump in the DSC curve observed at a slightly higher temperature than that of the heat treatment. The other is a small change of the DSC curve observed as a small concave at a lower temperature than the former. The peak-top of the former and the latter are defined as P1 and P2, respectively. In Figure 1, P1 and P2 can be observed in the specimen treated above 50°C and 79°C, respectively, and both of the peaks shift to higher temperatures with an increasing temperature of the heat treatment. The
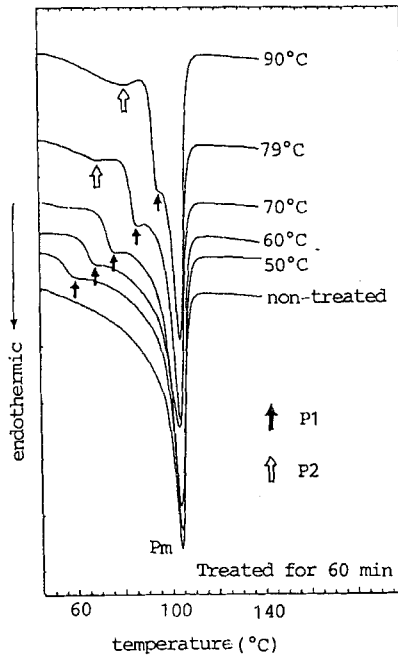
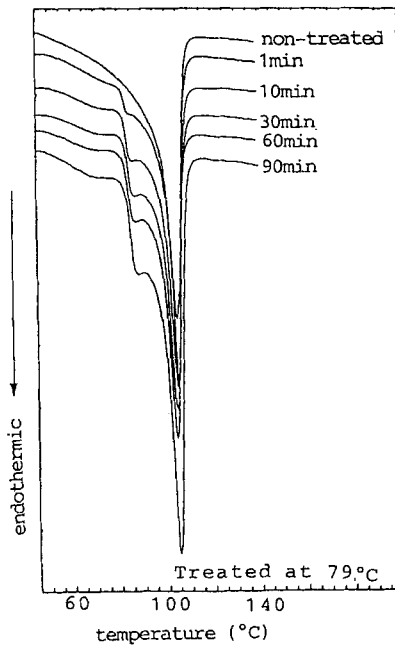FIGURE 1 The DSC curves of heat-treated XLPE sheets, at various temperatures.

FIGURE 2 The DSC curves of heat-treated XLPE sheets, for various treatment periods.

intensity of the two peaks also rise with the increase of the treated temperature. The intensity of P2 is smaller than P1. For heat treatment below 79°C, P2 is not observed in DSC curves.

Figure 2 shows the DSC curves of heat-treated specimens for various periods of heat treatment at constant temperature. Two subsidiary peaks are observed. The temperature of P1 shifts with the increase of the periods of heat treatment, but P2 shifts lower. The intensity of the two peaks grows stronger with an increase of the period. No P2 is observed for a period of less than 5 sec. That is to say, P1 is recognizable at more than 50°C, 15 sec, and P2 is recognizable at more than 79°C, 15 min. It is clear that P1 and P2 are closely connected with temperature and the period of heat treatment. And analysis of the thermal data in Figures 1 and 2 was made to develop a method for estimating the thermal history.

The dependencies of the temperature of P1 and P2 on the period of each treated temperature are summarized in Figure 3, in which T_{P1} and T_{P2} represent the temperature at peak P1 and P2, respectively. T_{P1} and T_{P2} are proportional to the logarithm of the treated period at each treated temperature. The slope and intercept
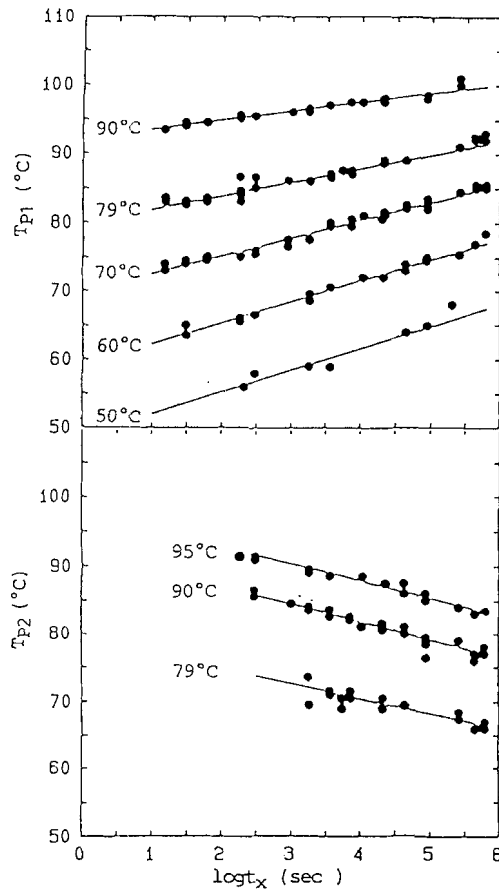
FIGURE 3   Relations between T_{P1}, T_{P2} and t_x.

of each line are also dependent on the treated temperature. Taking the slope of each line of T_{P1} and T_{P2} data as S_1 and S_2, and the corresponding intercepts as T_{P1}^0 and T_{P2}^0, respectively, the relations are shown in Figures 4 and 5.

These results are expressed by the following equations.

$$T_{P1} = S_1 \log t_x + T_{P1}^0 \tag{1}$$

$$T_{P2} = S_2 \log t_x + T_{P2}^0 \tag{2}$$

$$S_1 = A_1 T_x + B_1 \tag{3}$$

$$S_2 = A_2 T_x + B_2 \tag{4}$$

$$T_{P1}^0 = C_1 T_x + D_1 \tag{5}$$

$$T_{P2}^0 = C_2 T_x + D_2 \tag{6}$$

where

t_x $\quad$ = treated period
T_x $\quad$ = treated temperature
A_1, A_2 = slope of S_1, S_2 data
B_1, B_2 = intercept of S_1, S_2 data
C_1, C_2 = slope of T_{P1}^0, T_{P2}^0 data
D_1, D_2 = intercept of T_{P1}^0, T_{P2}^0 data

3.2. Estimation of Thermal History

Springer *et al.*'s investigation[8] of the thermal behavior of polyethylene refers to the relation between the endothermic profile and the annealed temperature. But in the paper only an approximate estimation is made, and no similar approach was
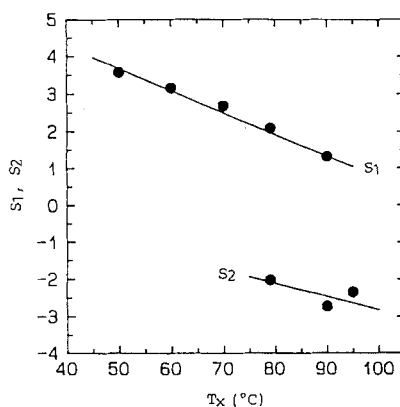

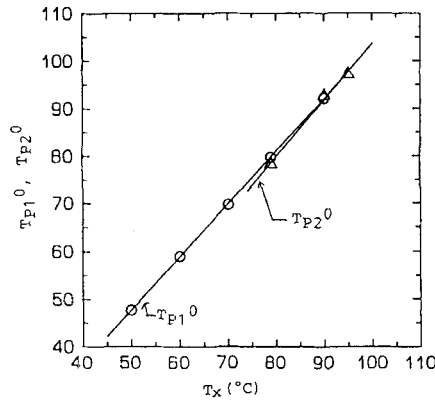FIGURE 4 Relations between S_1, S_2 and treated temperature (T_x).

FIGURE 5   Relations between $T_{P_1}^0$, $T_{P_2}^0$ and treated temperature (T_x).

attempted for the anneal period. So the development of a new estimation method is warranted.

Our intention is to develop a new method that gives more complete thermal information including temperature and period, T_x and t_x.

From Equations (1), (2), (3), (4), (5) and (6), the following equations are obtained.

$$aT_x^2 + bT_x + c = 0 \tag{7}$$

where

$a = A_1C_2 - A_2C_1$
$b = T_{P1}A_2 - T_{P2}A_1 + A_1D_2 - A_2D_1 + B_1C_2 - B_2C_1$
$c = T_{P1}B_2 - T_{P2}B_1 + B_1D_2 - B_2D_1$

and

$$d(\log t_x)^2 + e \log t_x + f = 0 \tag{8}$$

where

$d = A_2B_1 - A_1B_2$
$e = T_{P2}A_1 - T_{P1}A_2 + A_2D_1 - A_1D_2 + B_1C_2 - B_2C_1$
$f = T_{P2}C_1 - T_{P1}C_2 + D_1C_2 - C_1D_2$

By solving the equations, T_x, t_x can be calculated. This means that temperature T_x and period t_x of heat treatment can be obtained by substituting T_{P1} and T_{P2} data, which are obtained from DSC measurements, into the above equations. Obtained parameters in this experiment are listed in Table I.

Errors in this method are caluated from Figures 3, 4 and 5, and are listed in Table II.

The applicable region of this method is limited to the range of the appearance of both of the peaks. From Figures 3, 4 and 5, the applicable range is from 50°C

TABLE I

Parameters in XLPE

A_1	A_2	B_1	B_2	C_1	C_2	D_1	D_2
−0.056	−0.022	6.5	−0.43	1.1	1.2	−7.7	−16

TABLE II

Errors in T_x, t_x

T_x	$\log(t_x/t_A)$
<3°C	<0.5

t_A = actual time.

to 95°C in terms of the temperature, and more than 15 sec in terms of the period. When either the temperature or the period of thermal history is known, it is possible to estimate the other condition using Equations (7) and (8). In this case, the applicable range is expanded to 15 sec and 50°C, respectively.

4. CONSIDERATIONS

4.1. Mechanism of P1 and P2 Generation

In general, the thickness of polyethylene crystal increases with heat treatment. According to the experimental results of Statton,[9–10] this increase at isothermal crystallization can be expressed by:

$$L(t) = L_0 + K \log t \qquad (9)$$

where

$L(t)$ = thickness of crystallite after heat treatment for t hours
L_0 = thickness of crystallite before heat treatment
K = rate constant of crystallite thickening

On the other hand, the melting temperature of the crystal with a thickness of L, $T_{m(L)}$, is given by Leung[11] as follows:

$$T_{m(L)} = T_m^0(1 - (2\delta_e/\Delta H)(1/L)) \qquad (10)$$

where

$T_{m(L)}$ = observed melting temperature of the crystal
T_m^0 = equilibrium melting temperature of the crystal
δ_e = surface energy on folding plane of molecular chain of crystal
ΔH = heat of fusion per unit volume of the crystal
L = crystal thickness in molecular chain direction

Equation (9) means that the thickness of the crystal, which is composed of crystallite, increases with the treated period. And Equation (10) means that the melting point also rises with the increase of crystal thickness. So, the melting point becomes higher in accordance with an increase of the heat treatment period.

This phenomenon occurs even when polyethylene is treated under its main melting point (105°C) because polyethylene is composed of various lengths of crystals that have their own corresponding melting temperature.

Under heating at some fixed temperature, crystals that have a lower melting temperature than the heated temperature can be melted. As shown in Figure 6, treated polyethylene shows P1 and P2 which appear at slightly higher and lower temperature of heat treatment, respectively. This means that the amount of crystals that can melt at the treated temperature decreases and the crystals that have a higher melting point increase, namely, thickening of the crystals occur during the heat treatment, so that the endothermic peak P1 appears. P2 is thought to represent the lower limit of recrystallization occurrence. Consequently, P1 is observed at a higher temperature than the treated temperature, and P2 appears below the treated temperature, moving to an even higher and lower temperature with an increase of the treated period, respectively.

4.2. Influence of Crosslinking

In order to confirm the influence of crosslinking to the parameters obtained above, thermal measurements for LDPE (non-crosslinked) were performed under the same conditions in XLPE. Parameters are listed in Table III.

The fact that the parameters related to P1 are approximately equal indicates that the thickening of the crystal is not influenced by the degree of crosslinking.

On the other hand, in terms of the parameters that relate to P2, there are observed differences between XLPE and LDPE. It is surmised that this phenomenon is
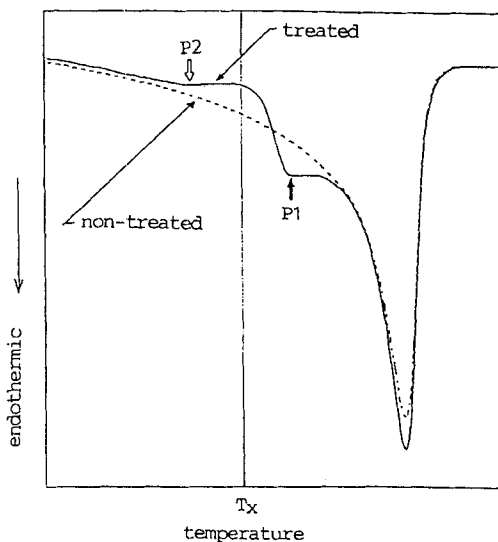

FIGURE 6   Schematic illustration of P1 and P2.

TABLE III

Parameters in XLPE and LDPE

	XLPE	LDPE
A1	−0.056	−0.056
A2	−0.022	−0.0099
B1	6.5	6.7
B2	−0.43	−1.4
C1	1.1	1.1
C2	1.2	1.0
D1	−7.7	−5.2
D2	−16	−4.1

related to the restriction of molecular chain mobility caused by crosslinking. In practical use for the estimation of thermal history in XLPE cables, the value obtained in this research can be used, because the degree of crosslinking in cable is constant.

5. APPLICATION TO PRACTICAL POWER CABLES

The thermal history was estimated for 66 kV 1 × 250 mm² XLPE power cable that was immersed in a 90°C oil bath for 2 hours and then cooled in air. DSC measurements were made on the outer and inner insulation layer of the sample taken from the cable. The DSC chart is given in Figure 7. Comparing with Figure 1, the shape of P1 is more sharp. The temperature estimates are 92°C and 93°C for the inner and outer insulation layer, respectively. It is confirmed that the result is equal to the temperature measured in dummy cable using thermocouples.

The estimated periods of 1.7 and 2.9 hours for the inner and outer layers are considered in good agreement with the immersed period, given the experimental errors in Table II. It can thus be said that estimation of thermal history is successfully achieved.

In XLPE power cables, the thermal conditions, including time and temperature, are not rapid heating and cooling, but gradual heating and cooling on the order of an hour. This differs from the sheet samples, which have large volume and heat capacity. From the result in Figure 7, however, it is deduced that the difference in heating and cooling rate rarely affects the estimation results. In order to certify the influence of the heating and cooling rate on thermal data, gradual heating and cooling history were applied to sheet specimens so that T_{P1} and T_{P2} were nearly the same as those with rapid heating and cooling, even though the shape of P1 changes to a sharp peak from the shoulder-like curve, showing the same pattern observed in Figure 6.

Understanding the thermal history quantitatively is also important in the prediction of cable life because insulation materials deteriorate with heating over time. In this way this method can be of great benefit to the cable industry.
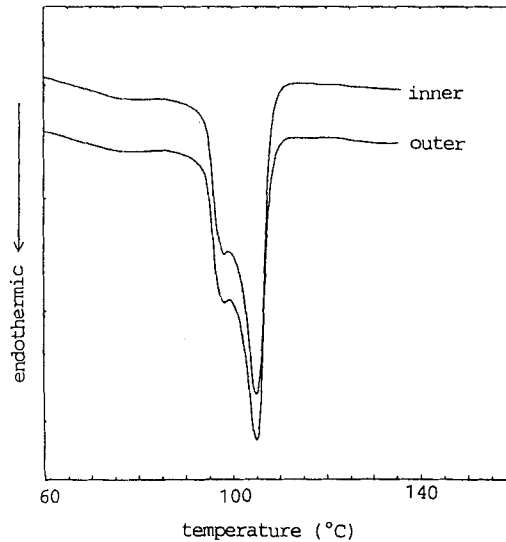
FIGURE 7   The DSC curves of XLPE insulations.

6. CONCLUSIONS

In order to develop the estimation method of thermal history in XLPE cables, DSC measurements were made.

From the DSC measurement of heat treated XLPE, relations between the treated temperature and the period were represented by equations.

Solving the equations, it became possible to estimate the thermal history, both of temperature and period, in XLPE power cable using the DSC measurement.

Applying the developed estimation method to practical high voltage XLPE power cable, good agreement with the expected value was obtained.

This method is regarded as widely applicable for the estimation of thermal history.

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