Paper

Treeing in Extended Chain Crystal Polyethylene

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Extended chain crystal (ECC) polyethylene subjected to a high voltage exhibits some unique properties. Electrical trees were investigated using a needle to plate electrode system under a lightning impulse voltage application. The propagation direction of the trees was strongly influenced by the orientation of the ECC polyethylene. When the needle electrode was normal to the orientation, some linear trees with no branches always propagated along the orientation. When the needle electrode was parallel to the orientaion, the tree propagated as a single line without branching along the orientation. The current following tree formation was observed as intermittent sharp pulses in the wave tail of the applied voltage. The number of pulses was dependent on the peak value of the impulse voltage and on the sample's temperature. The tree inception voltage was also dependent on the sample's temperature. These experimental results are represented in the form of an Arrhenius plot for discussion the tree inception process in test samples.

Keywords: orientation, electrical tree, extended chain crystal, polyethylene, tree inception voltage

1. Introduction

Treeing breakdown is one of the most important issues in the use of polymers for electrical insulation. The investigation of the treeing in insulating materials has been the focus of many researchers. In general, the observation of trees in amorphous polymers is easy because of their transparency. Crystalline polymers are opaque, and therefore tree growth is difficult to be observed. Polyethylene (PE) is different in transparency. Low density polyethylene (LDPE), having lower crystallinity, is translucent because of less scattering elements, while high density polyethylene (HDPE), with its higher crystallinity, is opaque because of abundant scattering elements. Electrical trees in polyethylene (1) (2) have been extesively examined in LDPE, in HDPE and also in cross-linked polyethylene (XLPE).

The interesting behavior of trees in the polyethylene under heavy strain has been reported by Hayami (3). He showed that the propagation of electrical trees can be determined by mechanical strain in compressed or stretched samples. However, the detailed relationship between orientation and tree propagation has not heretofore been clarified.

Extended chain crystal (ECC) polyethylene (4) (5) can have a crystallinity greater than 0.95. Making ECC polyethylene highly oriented causes it to become transparent, thus facilitating the observation of tree growth. However, the properties of the electrical trees in ECC polyethylene are still not fully understood.

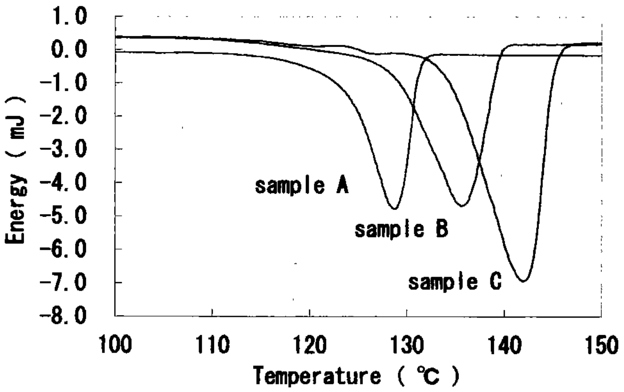
2. Sample ECC polyethylene

Polyethylene exhibits polymorphism, i.e., monoclinics and orthorhombics co-exist under normal atmospheric pressure (6). Under high pressure, hexagonals appears. When the hexagonals becomes orthorhombics, ECC is formed by lowering the temperature (7) (8).

A typical crystalline form of HDPE is FCC (folded chain crystal). In FCC, molecules are folded and reinserted at the surfaces of lamella crystals, which is called a re-entry model (9). The length in the C-axis (molecular axis direction) of FCC is approximately 10 to 20nm. In ECC, molecules are linearly extended, and the length in the C-axis of ECC reaches several microns.

The apparent melting points change according to crystal sizes (10). The larger crystals melt at higher temperatures. Figure 1 shows differential scanning calorimetery (DSC) data of polyethylene samples which were crystallized under different conditions. Sample A is a raw material (pellets). Sample B (a pressed sheet) is crystallized under atmospheric pressure at 95°C and Sample C is ECC polyethylene. The melting point of HDPE never exceeds 138°C. In ECC polyethylene, it is in the range of 138° to 142°C, and is higher than that of HDPE. The test samples used in the present study have melting points above 138°C.

HDPE consists of spherulites, but ECC polyethylene has a domain structure similar to that of liquid crystals. The cryofractured surface of random ECC polyethylene is shown in Fig. 3(a). We can clearly see the alignment



Sample A : HDPE (raw material)
Sample B : HDPE (crystallized under atmospheric pressure)
Sample C : ECC polyethylene (crystallized under 500MPa)
Sample weight is 1mg. Heating rate is 10 $^\circ C/min$.

Fig. 1. Melting points of polyethylene

of rod-like crystals and the formation of domains in this figure. Figure 3(b) shows the cryofractured surface of oriented ECC polyethylene. In Fig. 3(b) the domain structure is not clear, but an aligned fibril structure along the orientation is visible.

3. Experiments

To investigate the relationship between the orientation and the propagation of an electrical tree, three types of test samples were prepared as shown in Fig. 2.

Sample 1: Random ECC polyethylene
(Unoriented)
Sample 2: Oriented ECC polyethylene
(Orientation is normal to a needle electrode)
Sample 3: Oriented ECC polyethylene
(Orientation is parallel to a needle electrode)

Samples were prepared using the following steps. First, HDPE (HJ560:Japan Polychem) was hot pressed into plates. The a-plate was 2.5mm in thickness for sample 1, and the b-plates were 10mm in thickness for samples 2 and 3. Second, the b-plates were drawn by 600% at room temperature. Drawing the b-plates reduced the thickness to 2.5mm, and gave them fibril structures and strong orientation. The a-plate and the b-plates were cut into samples (10×10×2.5mm). In order to examine the tree under an impulse voltage application, a needle electrode (stainless steel with a 0.5mm diameter and a tip radius of approximately 10μm) was inserted into the centre of the sample. The direction of the needle was set normal to the orientation for sample 2 and parallel to the orientation for sample 3. Third, sample 1 was melted under 500MPa at 258$^\circ C$, and thereafter cooled to 241$^\circ C$ to crystalize the samples. All samples were crystallized under high pressure (500MPa) at 241$^\circ C$ for 10 minutes and then cooled to room temperature while maintaining the high pressure. In the samples obtained by this method, a microscope was used to observe the needle tips. No void were seen.

Molecular orientation (degree of orientation) was evaluated using Herman's orientation function(f) from the Raman spectra (11)(12). f means that the orientation is random when f=0 and complete when f=1. $f = 0.06$ for sample 1 and $f = 0.5$ for samples 2 and 3. Sample 1 was opaque. Samples 2 and 3 were transparent, and observation of their interiors was easy. $f = 0.5$ was sufficient to make ECC polyethylene transparent.

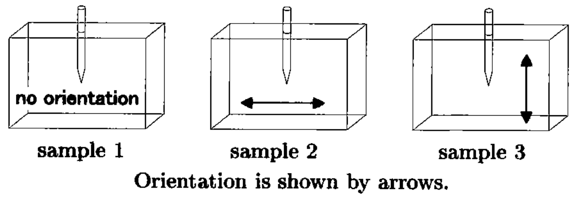
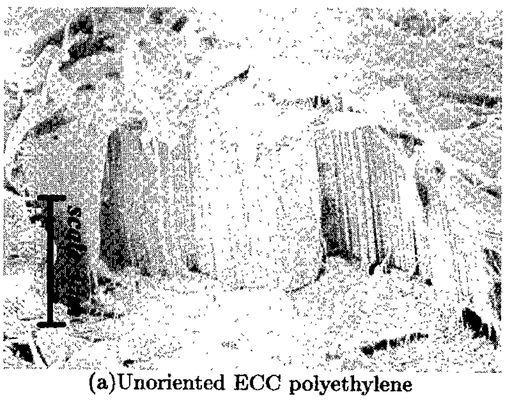
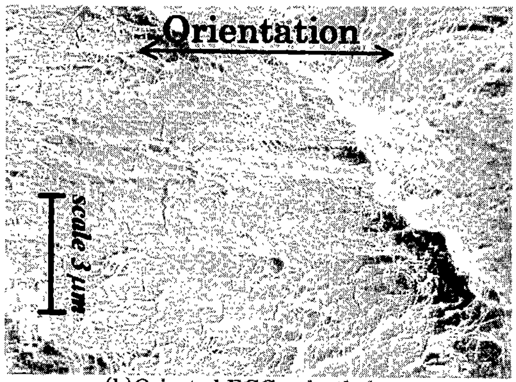


Fig. 2. Orientation of samples



(a)Unoriented ECC polyethylene
Crystallized under 500MPa,248°C



(b)Oriented ECC polyethylene
crystallized under 500MPa,241°C

Fig. 3. Cryofractured surface of ECC polyethylene

To prevent creepage discharges over the sample surfaces under the applied high voltage, the samples were sandwiched between transparent acrylic plates and were moulded using epoxy resin. A metallic counter electrode (a ground brass electrode 10mm in diameter) was placed on the opposite side of the needle tip. Gap spacing between the needle tip and the counter electrode was 5mm.

The experimental system employed in the measuring the tree is shown in Fig. 4. After a test sample was immersed in insulating oil (silicon oil), the lightning impulse voltage was applied to the needle electrode. Tree channels in the ECC polyethylene were observed through a polarized microscope. The current pulses following the formation of the tree were recorded through light intensity measurement using an LED

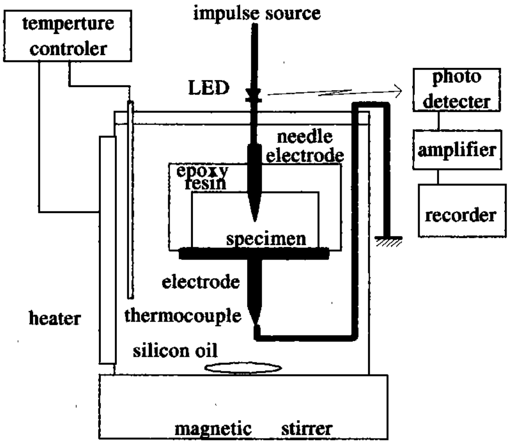


Fig. 4. Schematic diagram of a measuring system

circuit connected to the high voltage side. Two types of impulse voltages with different wave tails (1.2/50μs and 1.2/200μs) were used to examine the effect of wave tails on tree propagation and on the occurrence of current pulses. The temperature of the silicon oil was controlled within the range of $20^\circ C$ to $100^\circ C$ and the peak value of the voltage (V_m) was increased in 5kV increments. A new sample was used for each increase in voltage application.

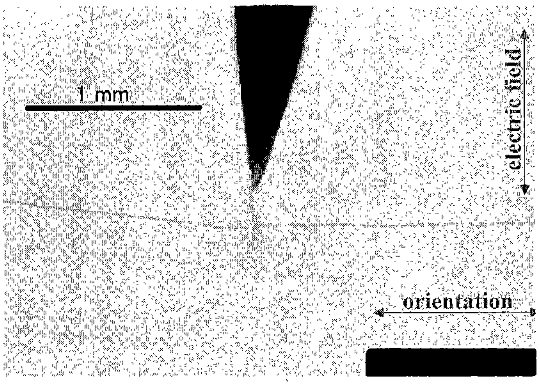
4. Result and discussion

It is known that, in general, an electrical tree in polyethylene propagates along an electric field toward a grounded counter electrode in random forms with a great deal of branching. This characteristic of trees is similar to that observed in sample 1 of the present study.

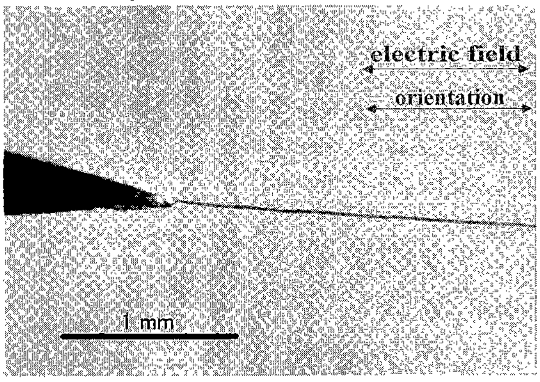
The trees in the oriented ECC polyethylene (samples 2 and 3) revealed a distinctive pattern in that the orientation of the samples determined the propagation direction of the trees as shown in Fig. 5. In the oriented ECC polyethylene, the trees assumed a simple form. When the needle electrode was normal to the orientation (sample 2), some linear trees with no branches propagated along the orienation (Fig.5(a)). When the needle was parallel to the orientation, the tree appeared as a single line with no branches (Fig.5(b)). This means that the direction of the tree propagation is strongly affected by the orientation in the ECC polyethylene.

On the other hand, the current following the formation of the trees appeared as intermittent sharp pulses. We paid special attention to the occurrence of current pulses in the oriented ECC polyethylene (samples 2 and 3). Basically, the formation of current pulses in sample 2 was approximately the same as that of sample 3, which meant that the cause of the pulses was the same.

Typical variations in the current pulses are shown in Fig. 6(a) and (b). These intermittent pulses were measured for the duration of wave tails (50μs and 200μs) at the different voltages. The first large current pulse, which occured immediately after the voltage application, appeared to have been a combination of injection current and charging current. After this large pulse, smaller intermittent current pulses were visible over a long period of the wave tail of the applied voltage.



(a)sample 2 (needle is normal to the orientation)



(b)sample 3 (needle is parallel to the orientation)

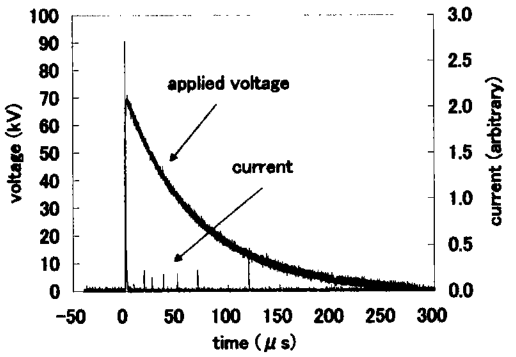
Allows: the direction of an electric field and an orientation

Fig. 5. Typical aspects of tree

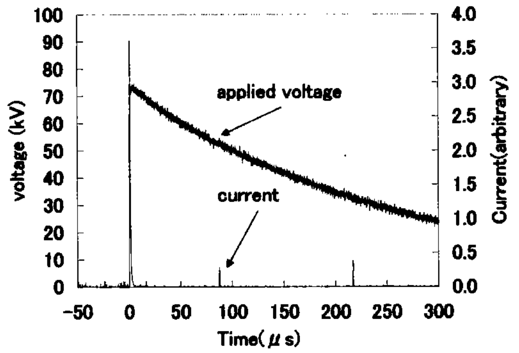
The occurrence of the intermittent pulses was strongly influenced by the V_m-values and by the duration of the wave tails of the applied voltage. It is thought that the occurrence of those pulses is related to the tree inception voltage, V_i. The number of current pulses, N, was counted for each applied voltage. Figure 7 shows the relationship between N and V_m. N-value increased almost linearly with increases in V_m, and it decreased as wave tail lengthened. As for tree inception, it is supposed that when one small intermittent pulse appears, tree formation has already began.

Based on this assumption, the tree inception voltage, V_i, is defined as the voltage which causes one intermittent pulse. This voltage can be estimated using the intersection of line $N = 1$ and the lines N vs. V_m as shown in Fig. 7(a). According to this method, the V_i-values were in the range of 25kV to 38kV at room temperature. The effect of the wave tails on $theN$ vs. V_m curve is shown in Fig. 7(b). This figure shows that the wave tail does not affect the V_i-value.

The occurrence of intermittent current pulses in the wave tail of the applied voltage can be explained as follows. It is thought that the tree is formed in the wave front of the applied voltage and the intermittent current pulses appear after the formation of tree channels. After the formation of tree channels, multiple charges will remain in the tree channels. These charges produce electric potential (V_c) between the electrodes. The



(a)1.2/50μs impulse voltage (V_m= 70kV)



(b)1.2/200μs impulse voltage (V_m= 70kV)

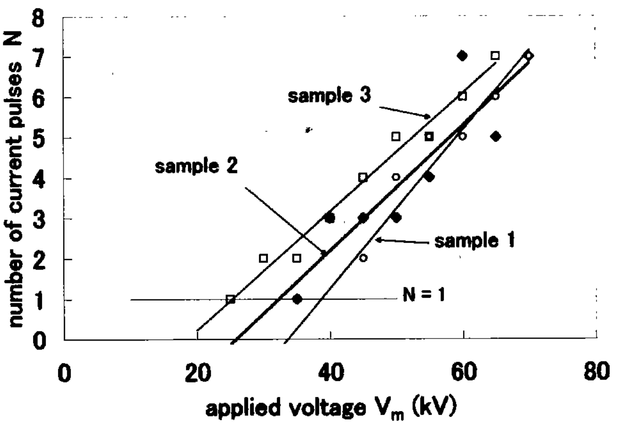
Sample 2 (the needle is normal to the orientation)
Temperature is 20°C. Number of current pulses (N) is counted for small pulses except for a large pulse at 0μs.

Fig. 6. Typical examples of current pulses accompanied by tree

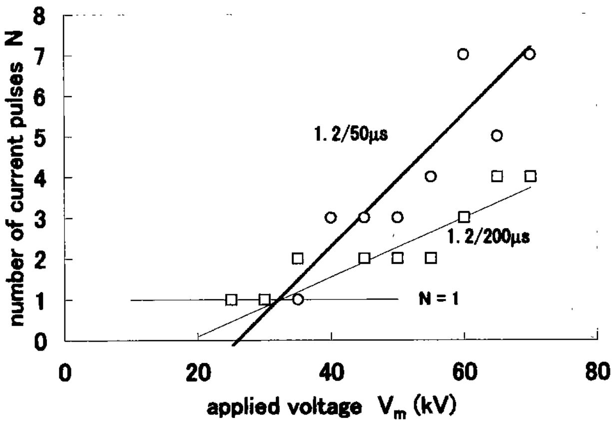
applied voltage, V, decays gradually in the wave tail. The potential difference between V and V_c causes the electric field to reverse direction which forces the removal of the charges based on the Coulomb force. This movement of the charge results in the occurrence of the current pulses. Actual tree length observed through a microscope is shown in Fig. 8. The relationship between L_m and V_m was also linear like the relationship between N and V_m. By this method the tree inception in opaque samples can be evaluated.

Furthermore, the effects of the samples' temperatures on the N-value and the V_i-value was examined within the range of 20°C to 100°C under the applied voltages with a fixed V_m (V_m=50kV) of 1.2/50μs. One possible explanation of the effect of the temperature on V_i can be related to the activation energy and Arrhenius plot as shown in Fig.10. There was a linear relation between N and V_m at each temperature. The N-values were presented in the form of an Arrhenius plot as shown in Fig.9, where T is the absolute temperature. There was a difference in the slopes of the test samples, in that, the slopes of samples 2 and 3 were approximately the same value (approximately -240), while the slope of sample 1 (approximately -450) was greater than those of the samples 2 and 3.

Tree channels in the sample 1 were sopposed to propagate ramdomly. In the oriented ECC polyethylene, the



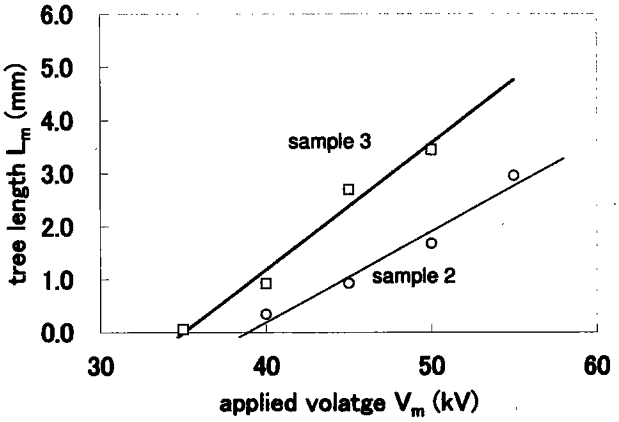
(a)Comparison in orientation
○ : Samples 1 (random without orientation)
◆ : Samples 2 (needle is normal to the orientation)
□ : Samples 3 (needle is parallel to the orientation)



(b)comparison in wave tails
sample 2(needle is normal to the orientation)

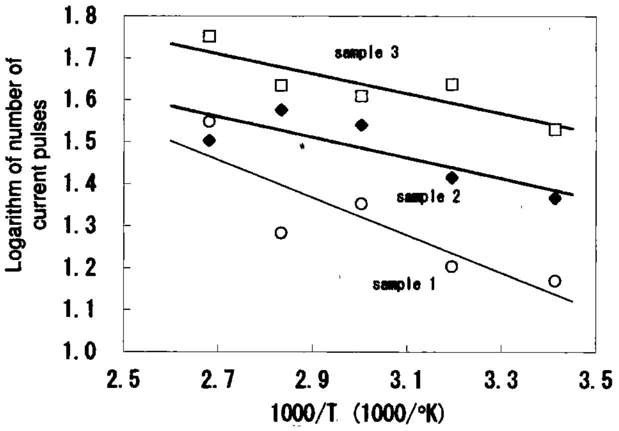
Sample temperature : 20°C
Applied voltage is 1.2/50μs or 1.2/200μs impulse.

Fig. 7. Relationship between N and V_m



temperature: 20 °C

Fig. 8. Plot of length of tree vs. applied voltage



V_m: 50kV (1.2/50μs)

Fig. 9. Arrhenius plot of number of current pulses vs. temperature

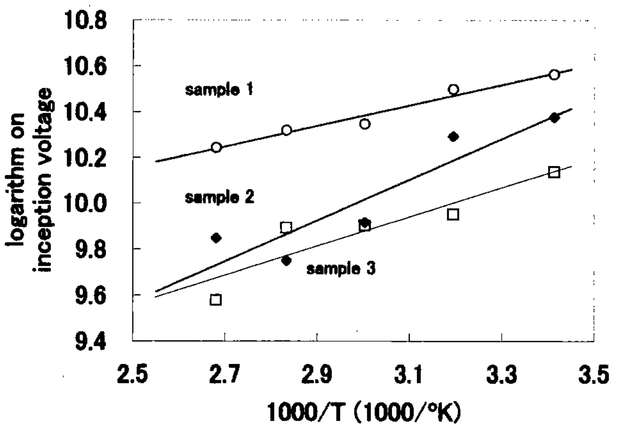


Fig. 10. Arrhenius plot of inception voltage vs. temperature V_m=50kV (1.2/50μs)

tree channels were straight without branches. The slope of the sample 1 was heigher than those of sample 2 and sample 3. This suggests that the occurrence of current pulses can be associated with the shape of tree channels, because the charge seemed to move more easily in straight channels.

As mentioned before, the tree inception voltage, V_i, can be determined by the intersection point of the line $N = 1$ and the line N vs. V_m. The effect of the temperature on V_i was also presented in the form of an Arrhenius plot as shown in Fig.10, where T is the absolute temperature. It is thought that V_i is influenced by physical conditions such as orientation and temperature. The slopes of the Arrhenius plots were positive for the three samples. The largest slope was obtained in sample 2 (slope=890). The smallest slope was in sample 1 (slope=450). The slope in the sample 3 was 635. This means that the V_i of sample 2 was the one most affected by the temperature.

The mechanical properties of ECC polyethylene can affect tree propagation. In oriented ECC polyethylene mechanical properties are strongly dependent on direction because of weak linkage between oriented crystals. The mechanical strength in the orientation direction is over 400MPa, compared with only several MPa in the transverse direction. This extreme direction dependancy seems to affect the propagation of both trees and inception voltage (V_i).

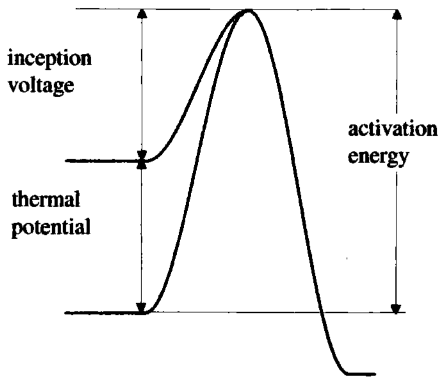


Fig. 11. Concept of tree inception voltage

Concerning the propagation of trees, the following mechanisms are assumed: (1) The ionization process due to the injection charges. (2) The decomposition of polyethylene and the increase of pressure due to the gases accumulated around the needle tip.

It is thought that the tree at the positive needle in the present study is based on the field ionization of solid molecules. In this case, the tree were likely to occur, compared with the negative needle case, while trees is essentially due to the charge injection process. This agrees with the polarity effect observed in LDPE (13).

We assume that the accumulated gases are forced to move in the direction of greatest weakness (the orientation direction). The energy consumed in the orientation direction is less than that consumed in the transverse dirention. This difference in mechanical strength is thought to be the reason that the tree travels along the orientation.

It is known that mechanical strength changes by temperature and follows Ahrrenius plots (14)(15). It was reported that in treeing breakdown in long time, the activation energy was related to the lifetime of solid materials (16). It is thought that the tree inception voltage was affected by the activation energy. In general, chemical reactions of solid materials occur when the energy of the corresponding systems override the activation energy. Figure 11 shows a concept employed to explain the tree inception voltage. Thermal energy increases the overall energy level of the system which means that the difference between the activation energy and the inherent energy of the system decreases. This energy difference is regarded as an indicator of inception voltage. This model agrees with the minus slope of the inception voltage to the temperature as shown in Fig.10.

5. Conclusion

Large samples of extended chain crystal (ECC) polyethylene were newly developed for this study, and the properties of electrical trees in ECC polyethylene were examined using a needle to plate electrode system under a lightning impulse voltage application. The major results can be summarized as follows:

(1) The tree propagation in ECC polyethylene was strongly influenced by the orientation. When the needle electrode was normal to the orientation, some linear trees with no branches propagated along the orientation. When the needle electrode was parallel to the orientation, the trees propagated in a single line without branching.

(2) Current pulses were observed as sharp pulses in the wave tails of the applied voltages. The relationship between the number of pulses, N, and the peak values of the applied voltages, V_m, was linear. The N-values increased with increasing temperatures. Those relationships were presented in the form of Arrhenius plots. For oriented samples, the slopes of the curves were approximetly the same. In random samples, the slope was steeper than that of the oriented samples.

(3) The tree inception voltage, V_i, was defined as the voltage which caused one small intermittent pulse. This voltage can be estimated using the intersection of line $N = 1$ and line N vs. V_m. The inception voltage was also presented in the form of an Arrhenius plot. The V_i-value decreased with increasing temperature. Tree propagation and tree inception voltage were sensitive to temperature.

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References

(1) P. Yan, Y. X. Zhou, and N. Yoshimura : "Influence of Morphology on Tree Initiation in Crystalline Polyethylene Films", *T. IEE Japan* **119-A**, No.11, pp.1342–1348 (1999)

(2) M. M. Rezinkina and O. L. Rezinkin : "Experimental Investigation of Treeing Growth in Polyethylene Insulation", IEEE Int. Conf. Conduct Breakdown Solid Dielectr., 6, pp.313–316 (1998)

(3) T. Hayami : "Effect of Mechanical Strain on Treeing-Resistance Property of Crosslinked Polyethylene", *T. IEE Japan*, **94-A**, No.12, pp.538–544 (1974-12)

(4) B. Wunderlich and L. Melillo : "Morphology and Growth of Extended Chain Crystals of Polyethylene", *Die Makromolekulare Chemie*, **118**, pp.250–264 (1968)

(5) B. Wunderlich and T. Davidson : "Extended-Chain Crystals. I. General Crystallization Conditions and Review of Pressure Crystallization of Polyethylene", *J. Polym. Sci. A2*, **7**, pp.2043–2050 (1969)

(6) J. M. Lagaron, S. Lopez-Quintana, J. C. Rodriguez-Cabello, J. C. Merino, and J. M. Pastor : "Comparative Study of the Crystalline Morphology Present in Isotropic and Uniaxially Stretched Conventional and Metallocene Polyethylenes", *Polymer*, **41**, pp.2999–3010 (2000)

(7) M. Yasuniwa, R. Enoshita, S. Taki, T. Ide, and T. Takemura: "Formation of ECC and High Pressure Phase in Polyethylene", *Rep. Prog. Polym. Phys. Jpn.*, **19**, p.199 (1976)

(8) M. Hikosaka, T. Seto, and S. Minomura : "Melting and Solid-Solid Transition of Polyethylene under Pressure", *J. J. Appl. Phys.*, **19**, pp.1763–1769 (1980)

(9) H. Tadokoro : "Reviews on Chain Folding in Polymer Crystals", *Koubunshi*, **32**, pp.202–207 (1983)

(10) A. Wlochwicz and M. Eder : "Distribution of Lamella Thickness in Isothermally Crystallized Polypropylene and Polyethylene by Differential Scanning Calorimetry", *Polymer*, **25**, pp.1268–1270 (1984)

(11) G. Yu. Nikolaeva, K. A. Prokhorov, P. P. Pashinin, and S. A. Gordeyev : "Analysis of the Orientaion of Macromolecules in Crystalline and Noncrystalline Area of Polyethylene by Means of Raman Scattering Spectroscopy", *Laser Phys.*, **4**, pp.955–958 (1999)

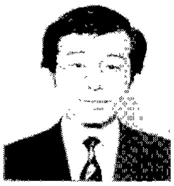
(12) N. Everall, J. Chalmers, and P. Mills : "Use of Polarized Resonance Raman Spectroscopy of a Polyene Probe and FTIR Dechroism to Probe Amorphous Phase Orientation in Uniaxially Drawn Polyethylene", *Appl. Spectrosc.*, **50**, pp.1229–1234 (1996)

(13) M. Kosaki, K. Kazuki, N. Shimizu, and K. Horii : "Treeing Phenomena of Polyethylene at Cryogenic Temperature Region", *T. IEE Japan*, **95-A**, pp.292–299 (1975)

(14) A. N. Zhurkov : "Kinetic concept of the Strength of Solids", *Int. J. Fract. Mech.*, **1**, pp.311–323 (1965)

(15) S. N. Zhurkov and V. E. Korsukov : "Atomic Mechanism of Fracture of Solid Polyethylene", *J. Polym. Sci. Polym. Phys. Ed.*, **12**, pp.385–398 (1974)

(16) L. Dissado : "The Physics of Electrical Aging in Semi-Crystalline Insulating Polymers", Proc. of the 32nd Symposium on Electrical and Electronic Insulating Materials and Applications in Systems, p.9 (2000)



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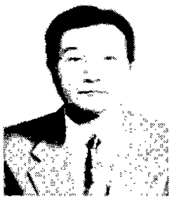

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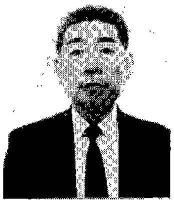

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