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論　文

Investigation on Tree Initiation and Morphology of Polyethylene Films

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The electrical tree initiation voltage of polyethylene films after annealing was investigated. The thickness of lamellae, diameter of spherulites and change of melting behavior were also monitored. It was found that the tree initiation voltage increases with the thickness of lamellae. Differential thermal analysis reveals that the tree initiation voltage also increases with the melting point of samples, which indicates that the higher tree initiation voltage is related to the higher thermal stability. It was considered that the thermal stability is inherently related with the thickness of lamellae. Therefore the thickness of lamellae is one of the important factors that affect the tree initiation voltage.

1. Introduction

It is well known that for semi-crystalline polymers, treeing degradation is influenced by morphology.[1–3] Major results of recent investigation show that the tree initiation voltage is greatly influenced by crystallinity of polymers, the higher is the crystallinity, the higher is the tree initiation voltage.[4–6] Research for influence of lamellae on the tree initiation indicates that tree path is virtually parallel to lamellae. Because tree is regarded to initiate from the center of spherulite, which consists of lamellae and amorphous region between lamellae, it has been suggested that the tree initiation is related to internal properties of spherulite.[7,8] However, influence of morphological structure on tree initiation is not clear yet, especially the influence of thickness of lamellae on tree initiation has not been paid enough attention.

In this paper, polyethylene (PE) samples have been prepared by different annealing conditions. It was discovered that the morphology changes with varying annealing condition even though the same PE sample was used. For example, the thickness of lamellae of high density polyethylene (HDPE) can be changed from 122Å to 165Å, resulting in the melting point changed from 397 K to 407 K. Low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) demonstrated almost the same change after annealing. The tree initiation voltage of PE films has been measured. Based on the concept of thermal stability, the tree initiation properties have been studied. The importance of the thickness of lamellae in spherulite during the tree initiation processes has been stressed.

Key words: thermal stability, lamella, morphology, electrical tree, polyethylene

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2. Experimental

2.1 Preparation of samples

The properties of LDPE, LLDPE, and HDPE samples without additives used in this experiment are listed in Table 1. Film samples with a thickness of 100 μm were prepared by hot pressing method. A copper needle electrode with 30 μm diameter was put between two pieces of films, which has 30° needle tip angle and 2 μm curvature radius of the needle tip. Each of the sample with a needle electrode was sandwiched between two pieces of cover glasses, and then placed in an oven preheated at 180°C that was higher than the melting point of PE, pressed by a 5 kg steel block, and kept for 20 min at this temperature so as to make the samples melt. Then these samples were subsequently treated by different annealing conditions as shown in Table 2. Conditions 1～3 are different in cooling rate, and conditions 4～6 are re-heated at 90°C to re-crystalline the samples with different annealing time. The structure of sample with electrode is schematically shown in Fig. 1. A silver electrode was evaporated on one piece of cover glass in vacuum. The silver electrode is vertical to the needle with a 1±0.1 mm distance from the needle tip.

2.2 Measurement of morphological parameters and tree initiation voltage

Morphological parameters of PE such as crystallinity, thickness of lamellae were measured by using infrared spectrophotometer (IR-435, P/N 204-03000, Shimadzu Corp.) and X-ray diffraction analyzer (RAD-1A). Melting point was measured by differential thermal analysis (TG/DTA 320 Seiko Corp.) method. Spherulites were carefully examined by microscope (Nikon) and microphotography color TV camera (IK-1590N, Nakamura Physic Industry Ltd.) before and after tree initiation test, as well as the size of them was carefully measured. The average value of the diameter of spherulites observed was taken as the spherulite diameter in

Table 1 Polyethylene samples used in the experiments.

Samples	Density (g/cc)	Melt index (g/10 min)	Melt point (°C)
LDPE	0.92	3.2	110
LLDPE	0.92	1.0	106
HDPE	0.95	0.9	129

Table 2 Annealing processes of PE samples.

Conditions	Annealing processes
1	Samples were preheated at 180°C for 20 min, and then were cooled to 30°C at a cooling rate of 50°C/s.
2	Samples were preheated at 180°C for 20 min, and then were cooled to 30°C at a cooling rate of 5°C/s.
3	Samples were preheated at 180°C for 20 min, and then were cooled to 30°C at a cooling rate of 0.003°C/s.
4	The samples annealed by annealing condition 3 were again heated to 90°C, and then were held at this temperature for 1 h.
5	The samples annealed by annealing condition 3 were again heated to 90°C, and then were held at this temperature for 2 h.
6	The samples annealed by annealing condition 3 were again heated to 90°C, and then were held at this temperature for 6 h.

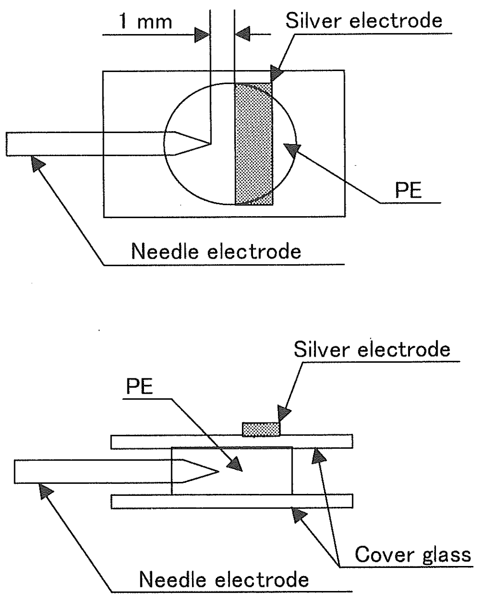

Fig. 1 Schematic structure of the sample.

this paper.

Samples for tree initiation experiment were put into sample holder with silicone oil to prevent flashover or discharge along the sample's surface. AC 50 Hz ramp voltage with rising rate of 300 V/s was applied to the samples. A microscope was used to observe the tree

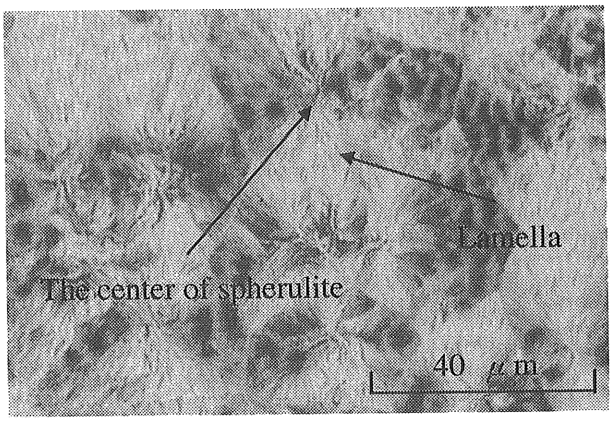

Fig. 2 The microphotograph of lamellae in the spherulite of HDPE.

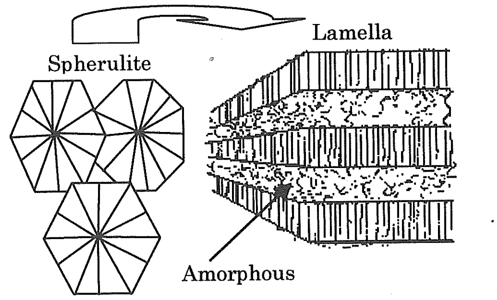

Fig. 3 Schematic representation of the detail structure of lamellae in a spherulite.

initiation. When a tree of 10 μm in length was observed, the corresponding applied voltage was defined as "tree initiation voltage." Tree initiation voltages of twelve samples annealed at a same condition were measured. The tree initiation voltage mentioned in this paper is the average of these twelve values.

3. Results

Tree initiation is greatly influenced by the morphology of semi-crystalline polymers.[4-8] Morphological properties and microstructure of crystalline should be made clear before any discussion of electrical tree characteristics.

3.1 Morphology

Partially crystallized polymers, such as PE, contain internal superstructures called spherulites. The spherulites possess a laminar structure, and can be observed through the polarizing microscope. Figure 2 is the microphotograph of spherulites of HDPE film treated with annealing condition 6. It was observed that tracks of white lines are visible in the spherulites. These white lines are referred to as lamellae.[9] It is obvious that the spherulites consist of lamellae that radiate from the center outward. Lamellae is regular, thin platelets approximately 10～20 nm thick.[10] The molecular chains within each lamella fold back and forth on themselves. This structure, aptly

Table 3 Diameter of spherulites and its standard deviation of PE treated with different annealing conditions (Unit: μm).

Samples	Annealing conditions					
	1	2	3	4	5	6
LDPE	8.0±0.7	9.7±1.0	20.3±2.3	20.8±1.4	20.3±2.0	20.8±2.2
LLDPE	10.6±2.3	13.5±2.6	19.8±2.3	20.7±3.7	21.0±3.3	21.0±3.2
HDPE	3.0±1.1	10.0±2.2	36.6±2.8	36.8±4.4	36.6±4.2	36.6±3.9

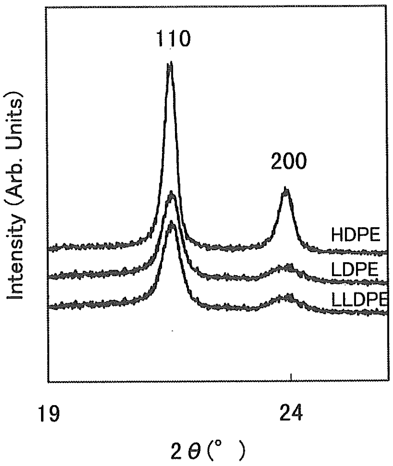

Fig. 4 X-ray diffraction patterns of HDPE, LDPE and LLDPE samples.

termed the chain-fold model, is illustrated schematically in Fig. 3. Each lamella consists of numerous molecules; however, the average chain length is much greater than the thickness of the lamellae.

Samples of different morphological structure are available after processed by different annealing conditions.[4,11–12] The diameter of spherulites of PE samples after annealing is shown in Table 3. The results corresponding to annealing condition 1~3 show that the diameter of spherulites increases with the decrease of cooling rate. However, it shows no significant changes in diameter after the film samples was treated with annealing condition 4, 5, and 6.

Thickness of lamellae, as an important parameter of morphology of PE, can be obtained with X-ray spectrum. Figure 4 shows the X-ray diffraction patterns of HDPE, LDPE and LLDPE samples. The thickness of crystallites (lamellae) that is perpendicular to the 110 plane is calculable with the X-ray wavelength, the peak width in radian and the Bragg angle of 110 plane. One of the remarkable differences between these curves are the peak width ΔW at half maximum which indicate the crystallite size. The thickness of lamellae, which increases with the decrease of ΔW, can be calculated based on the X-ray diffraction patterns.[5]

The relationships between the annealing conditions and the thickness of lamellae before and after re-crystallizing are shown in Figs. 5 and 6, respectively. It was found that the thickness of lamellae decreases with

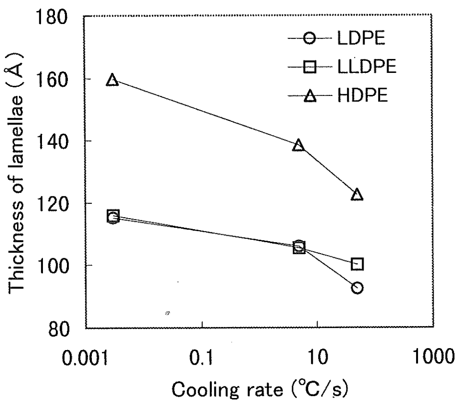

Fig. 5 Relationships between the cooling rate and thickness of lamellae.

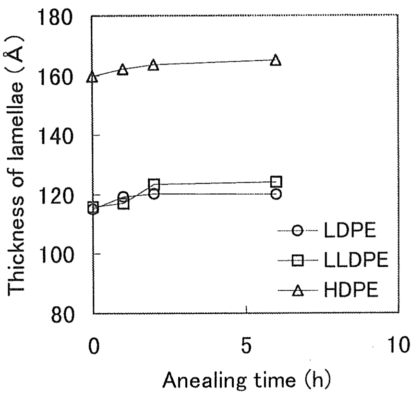

Fig. 6 Relationships between the re-crystallizing treating time and thickness of lamellae.

the cooling rate, and increases with the re-crystallizing time.

3.2 Tree initiation

The tip of needle electrode is almost surrounded by lamellae because it usually serves as center of spherulite during the crystallizing process in PE. Figure 7 is the typical microphotograph for HDPE sample with a needle electrode whose tip is in a spherulite. The annealing condition is 6. The overall diameter of the spherulite is about 40 μm which is a typical size in HDPE under normal industrial production conditions.

Dependence of tree initiation voltage on the annealing conditions is shown in Fig. 8. The tree initiation voltage of HDPE samples tends to increase with the decrease of the cooling rate, and also, with the increase of re-crystallizing time. LDPE and LLDPE demonstrated a similar change in tree initiation voltage after annealing.

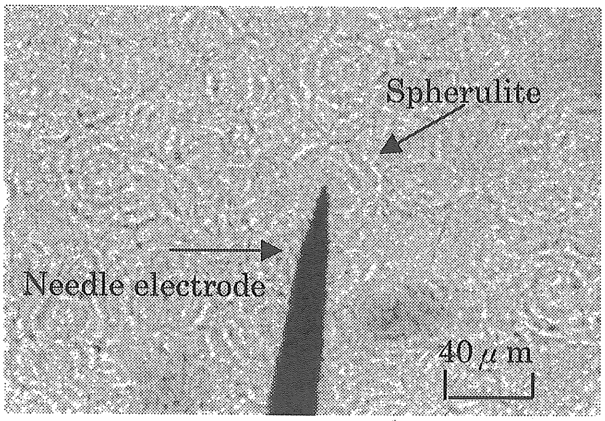

Fig. 7 Microphotograph of HDPE sample with a needle electrode.

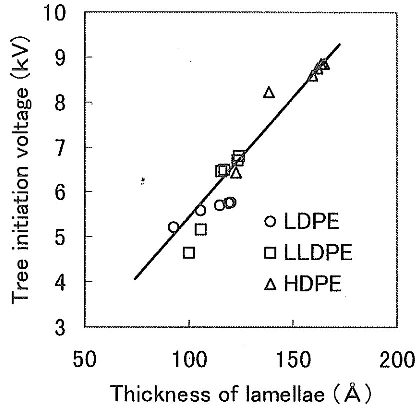

Fig. 9 Relationships between the thickness of lamellae and tree initiation voltages.

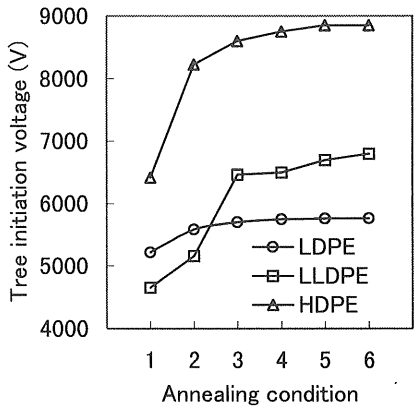

Fig. 8 Relationships between the annealing conditions and tree initiation voltages.

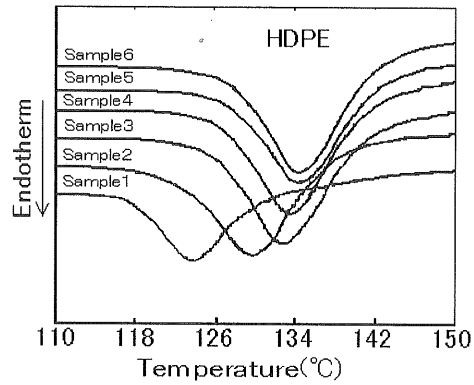

Fig. 10 DTA spectra of HDPE samples annealed under different conditions.

Considering the influence of annealing conditions on the morphological parameters as shown in Figs. 5 and 6, it was presumed that the tree initiation is inherently related with the morphological parameters, that is, the thickness of lamellae. This has been testified by experimental results as shown in Fig. 9. The tree initiation voltage increases with the increase of thickness of lamellae. It is interesting that the tree initiation voltages of three kinds of PE sample are on the same line, no concerning with the fact that the three kinds of PE have a lot of differences in chemical structure and morphology. This result furthermore demonstrates that the tree initiation is inherent related to the thickness of lamellae. After re-crystallizing, the change of the size of spherulite is invisible as shown in Table 3. Related to the fact that the tree initiation voltage increases after re-crystallizing, we presumed that the tree initiation shows independence of the size of spherulite.

3.3 Melting behavior

Figure 10 shows the DTA thermogram for HDPE samples. HDPE samples treated by different annealing conditions 1, 2, 3, 4, 5 and 6 were designated as samples 1, 2, 3, 4, 5 and 6, respectively. The peak of the endotherm curves could be attributed to the thermal stability of crystalline regions of PE films.[13] The melting point of samples can be easily obtained from the temperature corresponding to the peak point. It is worth noting that the melting point is not a constant after treating by different annealing condition. As shown in Fig. 10, for HDPE samples 1, 2, 3, 4, 5 and 6, the melting point increases from about 124°C to 134°C. The same phenomenon can also be observed in the case of LDPE and LLDPE.

Figure 11 shows the relationship between the tree initiation voltage and melting point of PE. With the increase of melting point, the tree initiation voltage increases. From this result, we assumed that the tree initiation is some how related to the thermal stability of PE samples.

4. Discussion

4.1 The mechanisms of tree initiation

AC tree phenomena observed at the site of strong localized electric field has been wildly studied because it is the important factor controlling the long time breakdown process of polymer insulating systems.[14] Tree phenomenon is a complex process influenced by many factors. The exact mechanism is not clear so far. Two

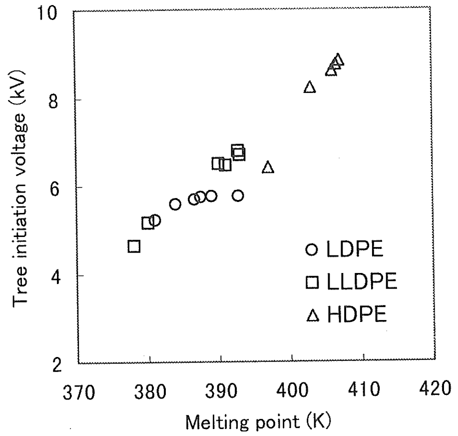

Fig. 11 Relationships between the tree initiation voltage and melting point of lamellae.

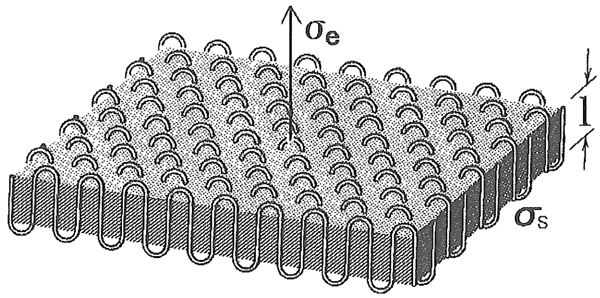

Fig. 12 Schematic representation of detail structure of lamellae.

major kinds of processes are conceivable. One is such that the injected charge carriers are trapped to form space charge and enhance the electric field. The other is a process of micro-void formation initiated by the attack of polymer chains by high-energy charge carriers. Some sub-processes also can not be ignored such as Joule heating and oxidation.[15] In a word, it is well accepted that initiation of an electrical tree requires damaging the dielectric in the direction of the field over a distance in the range of 1 to 1.5 μm no matter which process is in action.[16] In fact, all processes are not independent and they produce a complex effect on tree process, simultaneously.

Tree initiation caused by collision between electrons and polymer molecular chains has been investigated previously.[17,18] When external electrical field was applied to the samples, the electrons in the bulk or injected from the needle electrode would be accelerated. The excited carrier will attack C-C bond of PE. When the energy of charge carriers that attack the polymer chains is large enough, the C-C bond is cut and tree initiation will occur. Generally, because the mean free path in crystalline region is smaller than that in amorphous region, the tree initiation resistance increases with the increase of the thickness of lamellae. This mechanism provides a reasonable explanation for the result of tree initiation voltage increases with the increase of the thickness of lamellae as shown in Fig. 9.[19]

As shown in Fig. 11, tree initiation voltage also increases with the increase of melting point. This result indicates the possibility of the influence of a Joule heating sub-process on the tree initiation as reviewed.[15] When the electric field is applied to the sample, injection and extraction of charges take place at the needle tip, which results in a flow of electric current. Local heating due to electric current concentration is considered to take place once per positive or negative half cycle. When the balance between heating due to current concentration and heat dissipation is lost, a thermal runaway will occur in the affected point and partial thermal defect, which may be the precondition of the tree initiation, will be formed. In this sense, Joule heating also plays an important role in tree initiation and thus the increase in thermal stability is beneficial to tree resistance.

4.2 Thickness of lamellae and thermal stability

According to the forgoing considerations, one would consider that the different tree initiation voltages under different annealing conditions are due to different morphological structure and can be related to thermal stability. The key problem is that what relationship between the thermal stability and thickness of lamellae is. As will be discussed later, the higher melting point of polymer is due to increase in thickness of lamella. The structure of lamella is schematically shown in Fig. 12. If σ_e is the free energy of interface between the folded surface and liquid, while σ_s is the free energy of the side surface of the lamella, the energy difference ΔG between the lamella and liquid can be expressed as:[10]

$$\Delta G = 2v_a\sigma_e + c\sqrt{v}l\sigma_s - v_a l\Delta g \tag{1}$$

where σ is the thickness of single crystal, Δg is the change rate of free energy of fusion per unit volume and v_a is the molecular chain number of folded surface. At the melting point T_m, the energy difference is $\Delta G=0$. Generally, σ_s is far smaller than σ_e and the second term in the right hand side of Eq. (1) can be neglected. When $\Delta g=\Delta h\cdot(T_m{}^0-T_m)/T_m{}^0$, the relationship between the melting point T_m and the thickness of lamella l can be described as:

$$T_m = T_m{}^0(1-2\sigma_e/l\cdot\Delta h) \tag{2}$$

where $T_m{}^0$ is the melting point of an infinitely thick crystal and Δh is the melting enthalpy per unit volume. This result indicates that the melting point increases with the increase of the thickness of lamellae. In other word, the thermal stability increases with the increase of the thickness of lamellae.

Figure 13 shows the relationship between the melting point of PE crystalline and the reciprocal number of thickness of lamellae measured in the present work. It is

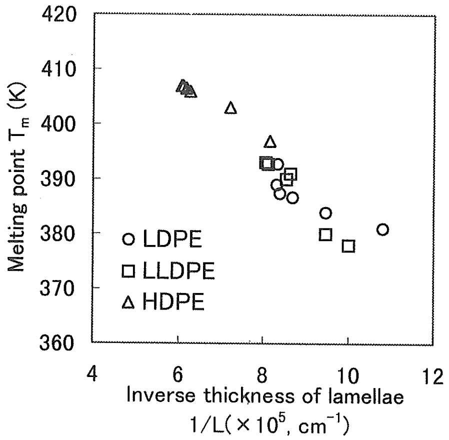

Fig. 13　Relationship between the melting point of PE crystalline and the reciprocal number of thickness of lamellae.

found that the melting point is proportional to the reciprocal number of thickness of lamellae. This indicates that the melting point increases with the increase of the thickness of lamellae. The experimental result is well correlated with the theoretical one. Relating with the results shown in Figs. 9 and 11, it can be reasonably concluded that the tree initiation voltage enhances with the increasing thickness of lamellae.

Considering the effect of lamellae on tree initiation, it was found that the increase in thickness not only decreases the efficient collision due to the decreases of free volume, but also increases the thermal stability, which need more energy to create a partial thermal defect for tree initiation. Thus it is reasonable that the tree initiation voltage increases with the increase of thickness of lamellae.

5. Conclusions

The relationship between tree initiation voltage, thermal stability and the thickness of lamellae in PE, including LLDPE, LDPE and HDPE has been discussed in detail. The main results of this study are summarized as follow:

1) The thickness of lamellae changes with annealing process. The slower is the cooling rate, the larger is the thickness of lamellae of PE. The thickness of lamellae increases after re-crystallizing, while the diameter of spherulites shows no significant change after re-crystallizing.

2) Melting point is not a constant value with different annealing conditions. This can be due to the change of the thickness of lamellae.

3) The thickness of lamellae considerably influences the tree initiation. The tree initiation voltage increases with the increase of the thickness of lamellae.

4) It is believed that tree initiation is a complex process. With the increase of the thickness of lamellae, the mean free path of electrons near the needle tip decreases. That leads to the increase of invalid collision in polyethylene, finally increasing the tree initiation voltages

5) The thermal stability of polymer is one of the important factors that influence the tree initiation. The thermal stability is inherently related to the thickness of lamellae. The increase of the tree initiation resistance can be related to the increase of the thermal stability.

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