論　文

Relation between Spherulites and Water Trees in Polypropylene

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Polypropylene (PP) material has many kinds of crystal types, its spherulite size is large, and its spherulites can be easily controlled by heat treatment. Consequently, in this paper, using PP as specimens, a water needle is respectively inserted into spherulite region and amorphous region to observe patterns and growth of water trees. All of experimental results indicate that a water tree is more easily formed in amorphous regions than in spherulites. This can be well explained by the mechanical mechanism of water treeing. Also, some new experimental phenomena were found and discussed.

1. Introduction

Semi-crystalline polymers such as polyethylene (PE) and polypropylene (PP) have been widely used as insulation materials for wires and power cables. The crystalline morphology of these materials is spherulites which are formed during cooling process from melted state. A lot of examples and much research work have verified that spherulites in the polymeric insulation play an important role in water treeing.[1-6] However, as far as water treeing is concerned, the acting mechanisms are not well understood, and new studies are necessary to clarify the relationship between spherulites and water treeing phenomena. In fact, understanding the role of spherulites is closely related to understanding water treeing itself.

As well known, the spherulite size of some semi-crystalline polymers (such as PE and PP) can be modified by heat treatment, by the addition of nucleating agents, or by the molecular weight. The molecular chain structure of polyethylene is not only linear, but also very flexible. That is to say, the crystallization ability of PE is superlative. Consequently, it is very difficult to control the size and number of spherulites in PE by means of heat treatment method. Besides, PP material has many kinds of crystal types, its spherulite size is larger, and can be easily controlled by heat treatment. Accordingly, in this paper, using PP as specimens, a water needle is respectively inserted into spherulite region and amorphous region to observe patterns and growth of water trees.

2. Experimental Conditions and Methods

2.1 Prepartions of Specimens

Figure 1 shows specimen configuration. Polypropylene film, 25 μm thick, was used as samples. Ten pieces of the PP film were laminated, and a copper needle with its diameter of 170 μm and with the radius of the needle tip of 2 to 5 μm was inserted into the laminated film specimen. Subsequently, the laminated film specimen was sandwiched between two pieces of cover glass (24 mm× 24 mm), placed in a isothermal box, and heated to 200°C. A 5 kg steel block was pressed on the specimen for 20 s. Then, switching off the isothermal box, the specimen was gradually cooled in the isothermal box. Over a temperature range of 95-100°C (depending on the experimental requirements), the specimen was taken out of the isothermal box, and rapidly cooled to room temperature. After that, the copper needle was slightly withdrawn to produce a small gap between the needle tip and surrounding PP material. The small gap was filled with tap water (the conductivity of tap water is equal to 3.6×10^2 μs/cm) under vacuum to ensure good penetration of tap water into the small gap. The water-filled gap acted as water needle electrode during the formation of water trees. Silver paint was coated on one-side surface of the specimen, and used as ground electrode. The distance from the ground electrode to the tip of water needle was 1.5 mm.

2.2 Experimental Conditions and Methods

In general, the distribution and size of spherulites in PP material depend on the cooling conditions from melted state. The temperature at which a specimen is taken out of the isothermal box is defined as "taking out temperature." The range of taking out temperature for PP material is 95-100°C. When a specimen is taken out of the isothermal box at higher "taking out temperature" (98°C), spherulites in the specimen are sparse in the distribution and smaller in the size, as shown in Fig. 2(a). On the contrary, on condition that a specimen is taken out of the isothermal box at lower "taking out temperature" (95°C), spherulites in the specimen are saturated, as illustrated in Fig. 2(b).

Experimental conditions are as follows: A water

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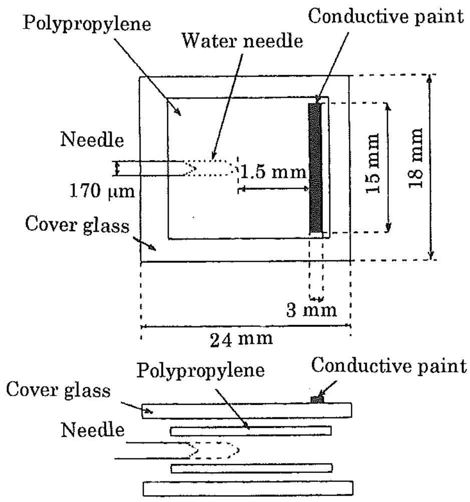

Fig. 1 Specimen configuration.

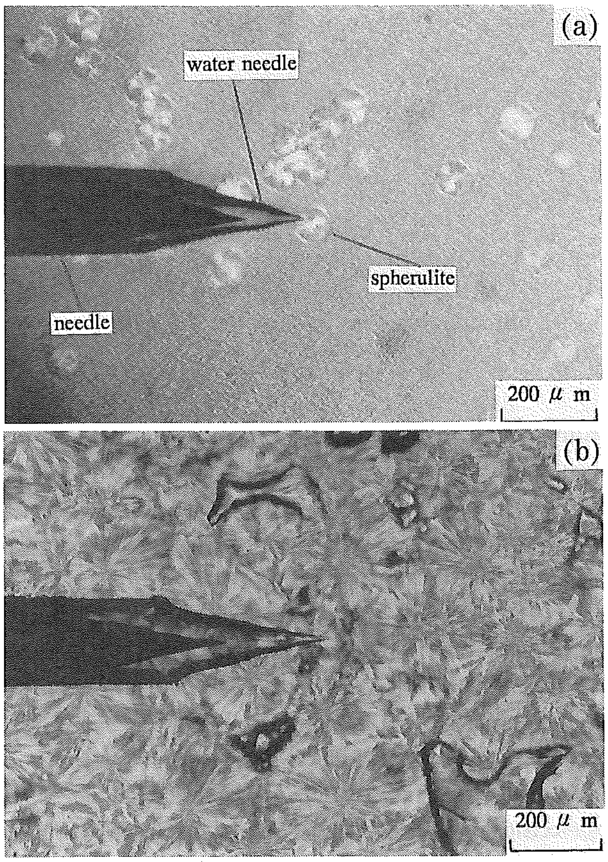

Fig. 2 Distribution of spherulites at different "taking out temperature."
(a) 97°C, (b) 95°C.

needle is inserted in a spherulite. A water needle is inserted in a amorphous region. Spherulites are saturated in specimens.

In order to avoid the occurrence of flashovers, the specimens were immersed in insulation oil. A.C. voltage of 6.3 kV was applied between the water needle and ground electrode. Methylene blue was used to dye the specimens for the observation of water trees.

3. Experimental Results and Analyses

3.1 The Structure of Spherulites in Some Semi-crystalline Polymers

A semi-crystalline polymer (such as PP) is composed of amorphous regions and a great number of small spherulites (rather than a single crystal), as shown in Fig. 3. A spherulite consists of crystalline lamellae and uncrystallizable molecules. In accordance with crystallography, the molecular chains fold in the direction of the c-axis, a lamella grows along the directions of b-axis, and the orthogonal direction to b- and c-axes is a-axis. Consequently, amorphous regions in PP polymer include two portions: one portion is amorphous regions between spherulites; the other is non-crystalline regions inside all spherulites. In a PP specimen with saturated spherulites, the amorphous regions between spherulites include two portions: one portion is the boundary regions between spherulites; the other is the interstices formed at the points of impingement of three or more spherulites.

3.2 A Water Needle Was Inserted in a Spherulite

It was found that a water tree is initiated and grown from the side of the water needle (outside of the spherulite), not from the tip of water needle, as shown in Fig. 4. It is well known that a spherulite has an ordered structure and high density, whereas a amorphous region

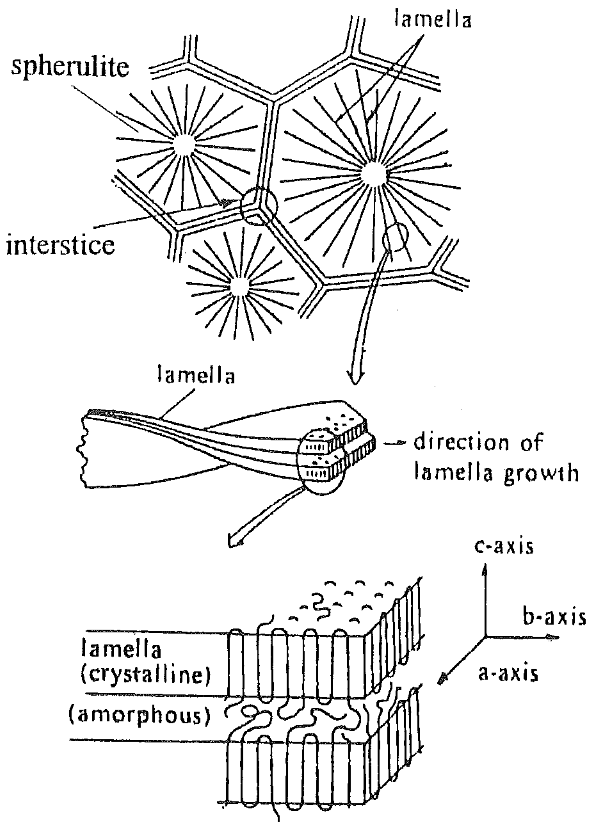

Fig. 3 Fine structure of polypropylene.

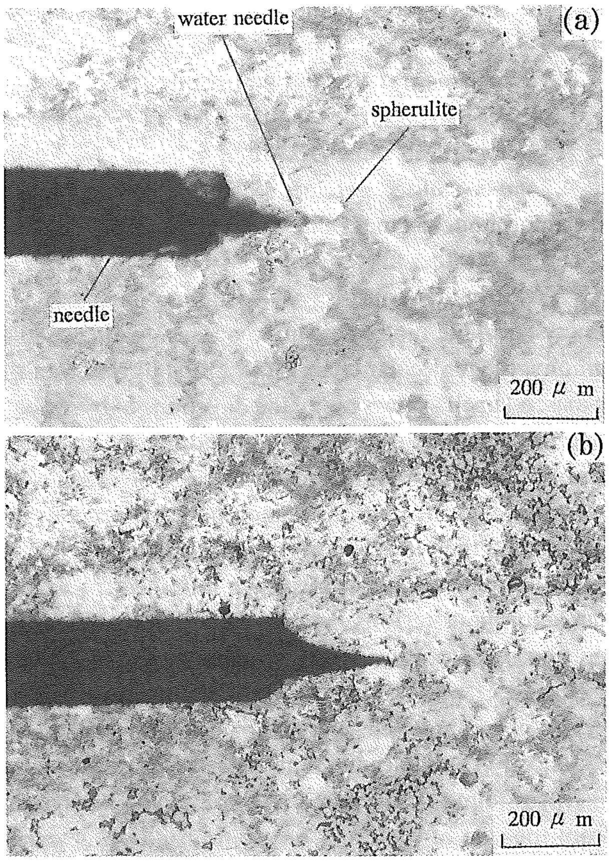

Fig. 4 A water needle was inserted in a spherulite (applied voltage: 6.3 kV; duration: 240 h).
(a) before dyeing, (b) after dyeing.

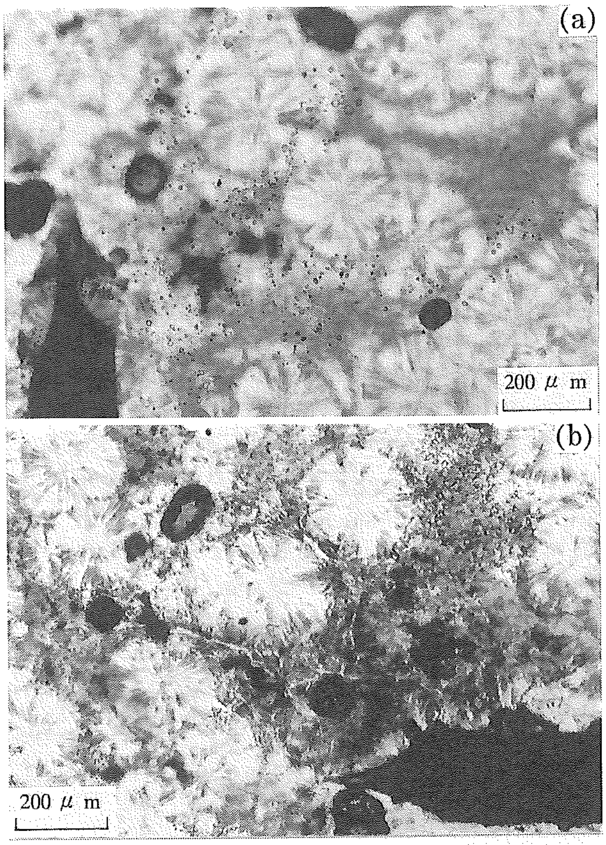

Fig. 5 A water needle was inserted in a amorphous region (applied voltage: 6.3 kV; duration: 240 h).
(a) before dyeing, (b) after dyeing.

between spherulites has low density. This indicates that a water tree is more easily formed in amorphous regions than in spherulites.

3.3 A Water Needle Was Inserted in a Amorphous Region

Figure 5(a) shows that before dyeing there exist numerous water-filled voids in amorphous regions between spherulites. After dyeing, it was found that a water tree was initiated from the tip and side of the water needle, and grown in the amorphous regions around spherulites, as illustrated in Fig. 5(b).

3.4 Spherulites Are Saturated in Specimens

When spherulites are saturated in a specimen, the amorphous regions between spherulites become very small. In this case, the growth of water tree was restricted to some extent, but its branches became a few and thicker, and some spherulites in water tree region were partially destroyed, as shown in Fig. 6.

3.5 New Phenomena

3.5.1 Transient Tree

Before giving the definition of transient tree, let us briefly introduce the basic characteristics of water tree and electrical tree. The basic features of water trees are simply listed in the following: Water trees are initiated from defects such as contaminants and voids in the insulation, as well as protrusions on interfaces between insulation and semi-conductive shield. Water trees are known to disappear on drying of the insulation, reappear on rewetting, and are rendered permanently visible by various water-soluble dyes, most commonly, methylene blue. The growth of water trees is normally not attended by detectable partial discharges. Consequently, there are no carbonized paths or channels in water trees. Under certain circumstances, a water tree may transform into or initiate an electrical tree. The fundamental characteristics of electrical trees are mainly described as follows. Electrical tree is an aging phenomenon producing in polymeric materials under application of electrical stress. An electrical tree is composed of a great number of micro-channels in which partial discharges take place. These micro-channels are carbonized by the partial discharges, which enables the electrical tree region to be black in colour. As a result, an electrical tree can be directly observed without any dyeing.

During the experiments, special trees were found which were initiated from the tips of electrical trees or from the tips of water trees. A special tree consists of microchannels, and its area is dark brown, not black in

Fig. 6 Spherulites were saturated (applied voltage: 6.3 kV; duration: 240 h).

Fig. 7 A transient tree (applied voltage: 6.3 kV; duration: 120 h).

colour, as shown in Fig. 7. Moreover, after removing electric field, the colour of the special tree gradually became pale and light with the lapse of time. In the aspect of the structure, the special tree is similar to an electrical tree, being composed of micro-channels. But the both kinds of trees are different in colour. On the other hand, no carbonization was observed in the special tree. At this point, the special tree is also similar to a water tree. In general terms, the special tree is not only similar to electric tree and water tree, but also different from the both kinds of trees. Therefore, the special tree is defined as "Transient Tree." The mechanism on formation of the transient tree will be further discussed in the Section **4.2**.

3.5.2 Coexistence of Transient Tree and Water Tree

In the case of highly applied voltage (7.0 kV), treeing photographs before and after dyeing were taken using the same sample, as shown in Fig. 8(a), (b). It was found that before dyeing there only exists a transient tree in a sample, and after dyeing there coexist the transient tree and a water tree. The water tree was initiated from the water needle tip, while the transient tree was grown from the copper needle tip.

3.5.3 Partial Breakdown due to Treeing

As illustrated in Fig. 9, transient trees were initiated and propagated from the side of needle, not from the tip of water needle, and a partial breakdown phenomenon took place at the tip of a transient tree. This phenomenon can be explained in the following: The electric field at the tips of transient trees which consist of transparent channels increases with the growth of transient trees. As soon as the electric field at the tips of transient trees reaches breakdown strength of PP material, the partial breakdown takes place.

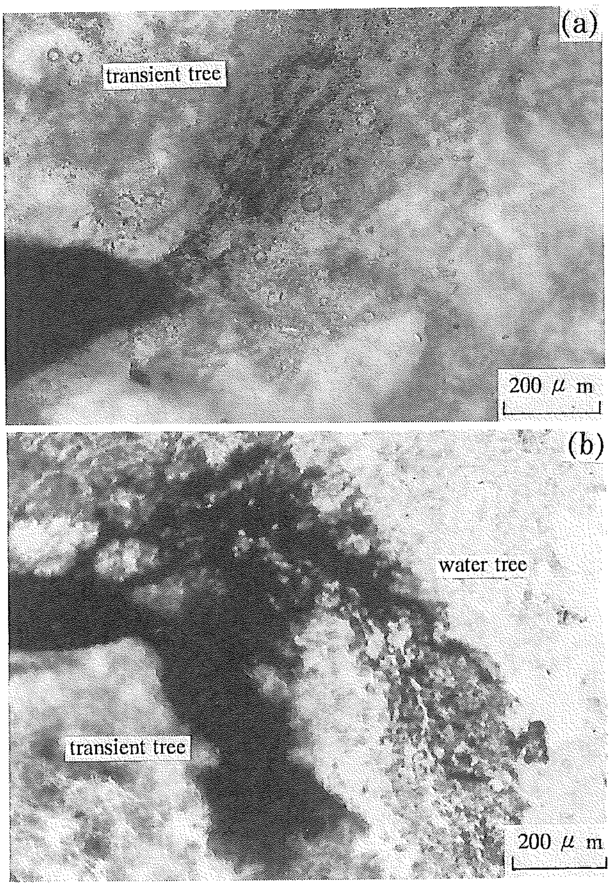

Fig. 8 Coexistence of transient tree and water tree (applied voltage: 7.0 kV; duration: 240 h).
(a) before dyeing, (b) after dyeing.

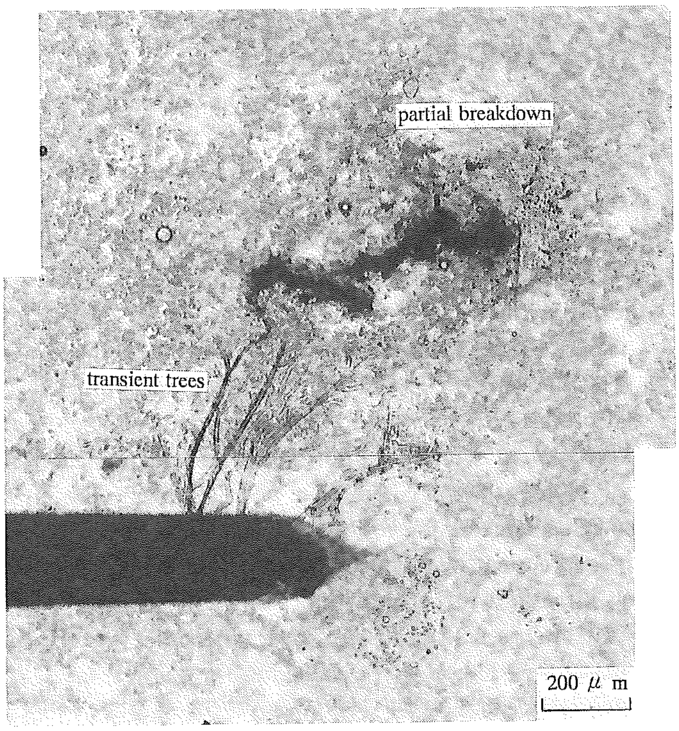

Fig. 9 A partial breakdown phenomenon due to treeing (applied voltage: 6.3 kV; duration: 216 h).

4. Discussions

4.1 The Effect of Spherulites on the Growth of Water Trees

It is observed from Fig. 4 that a water tree was initiated and grown from the side of the water needle (outside of the spherulite), not from the tip of water needle. Also, Fig. 5 shows that a water tree was initiated from the water needle, and grown in amorphous regions around spherulites. It is well known that in semi-crystalline polymers, amorphous regions appear not only between spherulites, but also between the lamellae of the spherulites. When spherulites are saturated in a specimen, the boundary regions between spherulites almost become zero. In this case, it is found from Fig. 6 that some spherulites in the water treeing region were partially destroyed, and it is not observed that some branches of the water tree penetrated spherulites. This experimental result denotes that the growth of a water tree in amorphous regions between lamellae of spherulites is restricted. In general terms, all of the above results indicate that a water tree is more easily initiated and grown in amorphous regions than in spherulites. What is the mechanism?

There seems to be a consensus among experts in the field that water treeing does not obey a single mechanism but rather a complex combination of various mechanisms, the relative dominance of which depends on material morphology and the specific combination of aging stresses. Thus, in some circumstances the chemical or electrochemical effects might prevail whereas in others the electromechanical mechanism may be the dominant one.[4] The destruction of spherulites in treed region reveals the importance of mechanical phenomena in water treeing. Such a damage clearly results from the action of local forces which are able to stretch the tie molecules and possibly to change the conformation of the macromolecules. The local forces originate from: (1) forced injection of hydrated ions into the polymer, and (2) electrostatic pressure induced by coulomb forces.[7–10] In both cases, the local forces have the fatigue effect which should be compared to the phenomena observed in fracture mechanics of polymer under dynamic loads. The formation of crazes, cracks and finally the time to failure, not only depend on the load amplitude, but also on the total number of cycles. Although no theoretical mechanical model corresponding to the precise geometry of a water tree is present available, a comparison with what is known from fracture mechanics makes the fatigue interpretation realistic. Some authors[1,4] consider that the water absorbed by the polymer during water tree growth is confined mainly to the amorphous regions of the polymer, indicating that the local fatigue forces appear not only in amorphous regions between spherulites, but also in amorphous regions between lamellae of spherulites. Accordingly, we consider that the amorphous regions between spherulites are more easily damaged by these local fatigue forces than the amorphous regions between lamellae of spherulites. The reasons are as follows:

(1) Impurities and uncrystallizable polymer molecules are known to generally segregate in the boundary regions between spherulites,[5] although impurities with good solubility in the polymer could be found in the amorphous regions between lamellae inside the spherulites. This implies that the amorphous regions between spherulites are looser than the amorphous regions between lamellae. In other words, the amorphous regions between spherulites have weaker resistance to a mechanical stress in comparison with the amorphous regions between lamellae.

(2) It is well known that there exist the tie molecules between the lamellae of semi-crystalline materials. In these materials, the tie molecules contribute to the mechanical resistance of the polymer to the dynamic electromechanical forces induced by the alternating electric field. This indicates that the amorphous regions between the lamellae have stronger resistance to the mechanical stress than the amorphous regions between spherulites.

On the basis of the above analyses, it is reasonably considered that water trees more easily grow in the amorphous regions between spherulites than in the amorphous regions between lamellae. That is to say, the amorphous regions between spherulites are weaker pathways for water treeing.

4.2 The Mechanism on Formation of Transient Tree

It is found from Fig. 7 that transient trees were initiated from the tips of branches of the formed electrical tree. The whole area of the formed electrical tree is dark black, indicating that the electrical tree has been seriously carbonized, and has high conductivity. As a result, H.V. electrode is extended to the tips of branches of the electrical tree. It is also observed from Fig. 7 that the branches of the electrical tree become thicker, and curvature radii of their tips also become larger. This enables the electric field at tips of the branches to decrease so markedly that partial discharges can not take place at the tips of the branches. Nevertheless, under the action of electric field, water can be migrated to the tips through micro-channels existed in the electrical tree. Consequently, two kinds of the local forces, as described in Section **4.1**, still exist at the tips of branches of the electrical tree. These local forces cause crazes or microcracks inside the PP material extremely close to the tips of the branches of the electrical tree. During the formation of the crazes or microcracks, the scission of molecular chains take place unavoidablely, and some kinds of radicals are formed. The formed radicals make the crazes or cracks become hydrophilic, so that the migration of water into these crazes or cracks is further improved. Finally, under the action of these local forces, the crazes or cracks are developed into microchannels. That is to say, transient trees are formed.

5. Conclusions

In this paper, using PP as specimens, a water needle was respectively inserted into spherulite region and amorphous region to observe patterns and growth of water trees. All of experimental results indicate that a water tree is more easily initiated and grown in amorphous regions than in spherulites. This can be well explained by the fatigue effect of local forces. Also, some new phenomena (such as transient trees, coexistence of transient tree and water tree, and partial breakdown due to treeing) were found.

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