

Extinction of Spherulites and Improvement of Polyethylene Properties by the Use of Lithium Carbonate

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SUMMARY

Polyethylene (PE) consists of nonpolar molecular chains having simple structural units. Physically, this polymer is so stable and flexible that it is widely used for insulation of electric wires and power cables, as well as for fabrication of various molded products. The crystalline texture and the presence of spherulites are major factors determining the mechanical and electrical properties of polyethylene.

For the purpose of improving these properties of PE, the spherulites are eliminated completely by heat mixing of PE with Li_2CO_3 . PE processed in this manner is free of spherulites, has a uniform structure and excellent electrical, mechanical, and thermal properties, such as short treeing length, high dielectric breakdown strength, and high tearing impact strength. © 2004 Wiley Periodicals, Inc. *Electr Eng Jpn*, 148(2): 22–38, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/ej.10296

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1. Introduction

Polyethylene (PE) consists of simple nonpolar molecular chains and has a two-phase structure comprising spherulites surrounded by an amorphous phase. The spherulite size is usually nonuniform and the amorphous phase is distributed unevenly. The crystalline phase is formed by flat crystals (lamellae) made up of continuous crystalline trans chains extending from the nucleation centers with kinks at regular intervals converging toward the outer circumference. The spaces between lamellae are filled by amorphous tie molecular chains. Various structural

amorphous molecular chains, impurities, microvoids and other irregularities present between adjacent spherulite interfaces are generally considered to be factors contributing to the growth of AC treeing [1]. When a mechanical impact force is applied to polyethylene, the stress is concentrated on the amorphous parts causing their plastic deformation. As a result, crevices, voids, and microcracks appear, which can cause the formation of cracks and other defects [2].

As can be seen from the above, the amorphous phase is the weak point of PE from the standpoint of electrical and mechanical properties and measures proposed for dealing with this problem include introduction of structural additives that do not react with PE or the use of blending agents [3]. These measures make it possible to reduce the size of spherulites and homogenize PE, thus limiting the propagation of the ac treeing and the formation of cracks due to stress concentration.

The authors performed infrared analysis of PE samples prepared by introducing various inorganic powdered substances with subsequent kneading treatment over a long time. It was found that samples with lithium carbonate as additive show a strong infrared absorption for the 1078 cm^{-1} band. As the processing time becomes longer, spherulites in such samples are reduced in size and eventually disappear.

Follow-up experiments consisting of the admixing of dozens of different substances to PE and PP, performed to check the condition of spherulites, confirmed that only lithium carbonate additives to PE can eliminate spherulites. This happens because the lithium carbonate treatment results in a reduced crystallization while the physical processing in the case of admixture of inert structural nucleation substances to PE, PP, and other materials results in an increased crystallization.

Absorption for the 1078 cm^{-1} band is attributed to amorphous gauche chains of PE. Coincidentally, it is the same band as the infrared absorption by lithium carbonate, and, as is explained below, we believe that it is related to

the extinction of PE spherulites. Observations by means of polarizing microscope show that in samples with lithium carbonate as an additive, spherulites are reduced in size and instead a large number of thick ribbon-shaped crystals consisting of lamellae with kinks directed inside the crystal body are formed [4]. Moreover, it was confirmed that on increasing the time of the kneading treatment, both spherulites and ribbon-shaped crystals disappear, resulting in a completely homogeneous PE.

A clear advantage of this method, compared to methods in which additives remain in the finished product as structural nucleation elements, is that spherulites remain eliminated even after lithium carbonate used for their extinction is removed after completion of the treatment, thus making it possible to obtain materials that do not contain foreign substances.

Methods of PE treatment using lithium carbonate can be roughly divided into two categories: the additive treatment and the contact treatment, in which the additive agents are removed after treatment completion rather than remaining in PE as additive agents. The latter method consists simply in bringing lithium carbonate in contact with molten PE. PE produced according to this contact method is referred to below as the improved PE and most of the tests described in this paper were carried out using this material.

Another simple method of PE processing, which does not involve the kneading of PE with admixed lithium carbonate, consists in multiple cycles of hot rolling of PE followed by cooling. This method offers full extinction of spherulites and its detailed description is given in Section 5.2.

We also examined the progress of spherulite extinction by means of IR absorption by blending PE with silica, aluminum silicate, and other substances characterized by high absorption in the infrared spectrum, including absorption by lithium carbonate for the 1078 cm^{-1} band.

We report also on improvements in such weak areas as electrical, mechanical, and thermal strength of the amorphous phase by means of the homogenization by treatment with lithium carbonate. PE used in this study was low-density PE (LDPE) and cross-linked PE (XLPE); the extinction of spherulites was also confirmed in MDPE, HDPE, and LLDPE.

2. Lithium Carbonate Characteristics in the Infrared Absorption Spectrum

We discuss the extinction of PE spherulites in relation to the treatment only with lithium carbonate. These findings have been partially reported in Ref. 5; here we provide more detailed explanations.

Figure 1 (a) shows two types of conformation of the carbon chain C–C bonds in PE as a function of the inner

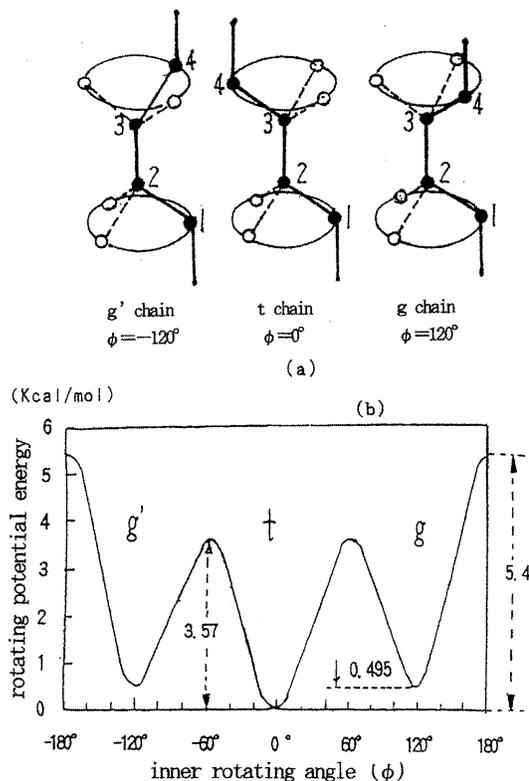


Fig. 1. Rotational potential energy of the C–C bond as a function of inner rotating angle.

rotating angle (ϕ) and Fig. 1(b) shows potential energy of the short carbon chains in *n*-butane (C_4H_{10}). The middle diagram of Fig. 1(a) depicts the most stable state when the 1–2 segment chain and the 3–4 segment chain linked by the 2–3 segment chain are positioned at the greatest possible distance from each other (inner rotating angle $\phi = 0^\circ$). Such crystalline chains are called trans (t) chains and Fig. 1(b) shows distribution of potential energy as a function of the inner rotating angle. Microcrystals of PE are formed by t-chains connected to each other forming continuous trans chains (ttt · · ·). Spherulites are formed by layered lamellae consisting of a large number of microcrystals, which, due to the kinking, aggregate into ribbon-shaped crystals, and amorphous tie molecular chains joining these crystals.

The right and left diagrams in Fig. 1(a) show carbon-to-carbon bonds, in which the 1–2 segment chain and the 3–4 segment chain are rotated to $\phi = \pm 120^\circ$ forming a quasi stable state. These conformations are called gauche (warped: g, g') chains. As seen in Fig. 1(b), due to the repulsion between methylene radicals ($-\text{CH}_3$) connected by carbon atoms, potential energy of gauche chains is only 0.495 kcal/mol; however, there are 3.57 kcal/mol potential energy barriers between t-chains and g- and g'-chains re-

stricting free rotation. But it is known [6] that, due to the thermal motion, t-chains can easily overcome these barriers only in one direction, from t-chains to g-, g'- chains, thus causing the transitions.

These transitions to gauche chains can be regarded as defects of a single crystal of PE. Figure 2(a) shows the most stable continuous trans chain and when a gauche chain is connected to this trans chain, a kinked chain shown in Fig. 2(b) is formed, or if two kinks are added, a doubly kinked chain is obtained [shown in Fig. 2(c)]. Energy necessary for the doubly kinked chain is not greater than 1.4 kcal/mol and it is assumed that it can be produced by thermal excitation [7, 8]. Here, the transition from t-chains to g- and g'-chains in the additive-treated PE is referred to as the gauche transition. It is considered that the gauche transition produces defects in a part of the lamellae, which results in the destruction of the ribbon-shaped crystals of the spherulites outer layers, thus reducing their size. On the other hand, the kneading treatment eliminates spherulites and ribbon-shaped crystals resulting in a more homogeneous PE.

Treatment with lithium carbonate leads to the formation of carbonyl radicals ($\dot{C}C=O$) in the middle and at a part of the ends of the PE molecular chains [9]. It was found that this results in the formation of large amounts of cross-linked gels [10], which can be considered to cause the growth of the gauche chains.

Considering the above-mentioned results, we think that additives used for the extinction of PE spherulites by increasing the formation of gauche chains must simultaneously satisfy the following two conditions (referred to below as Conditions 1 and 2):

(1) Thermal excitation of gauche chains must cause absorption for the 1078 cm^{-1} band.

(2) They must contribute to the formation of molecular chains producing a cross-linked gel causing defects in a part of the lamellae.

Methods supporting the provision of the thermal excitation of gauche chains of Condition 1 consisting in

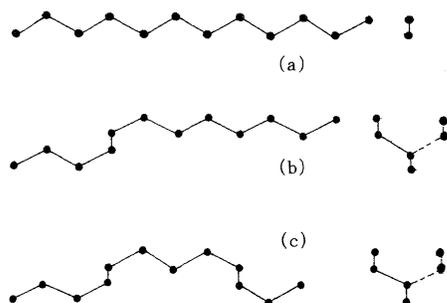


Fig. 2. A kinked chain and doubly kinked chains.

blending PE with various chemical compounds together with lithium carbonate treatment are explained in detail in Sections 4.5 and 5.9. Condition 2 at the present time consists in gel formation by the lithium carbonate treatment and is described in Section 5.2.

Here, we discuss the IR absorption spectra of PE, lithium carbonate, and various substances admixed for spherulite extinction measured for the purpose of examination of the thermal excitation of gauche chains under Condition 1.

Figure 3 shows IR absorption spectra of (a) PE, (b) lithium carbonate, (c) sodium carbonate, and (d) silica measured by infrared spectrometer IR420 (Shimadzu Seisakusho, Ltd.). Infrared frequencies (in cm^{-1}) are plotted along the horizontal axis, and the transmission factor data (in %) are plotted along the vertical axis.

Small circles in the spectrum shown in Fig. 3(a) indicate typical absorption points of PE molecules obtained by Wedgewood and Seferis [11]. Wave numbers (cm^{-1}) corresponding to these points are shown in the left column of Table 1(a). The 1894 cm^{-1} band corresponds to absorption by the continuous trans conformations (ttt... chains) of the crystalline phase (C) forming the spherulites. The 2016 cm^{-1} band corresponds to absorption by molecular conformations consisting of crystalline phases connecting four or more t-chains and amorphous phases (A + C). However, this feature is not clearly displayed in the actual measurements.

In addition, there is absorption by amorphous molecular chains (A), including strong absorption for the 1078 cm^{-1} band caused by the wagging vibrational oscillations of CH_2 in gauche chains [12]. Absorption by oscillation of the C-C lattice (g and t) is insignificant and can be disregarded.

Large circles in the spectrum shown in Fig. 3(a) indicate wide absorption areas caused by superimposed spectra of multiple molecular chains, such as methyl radicals and methylene radicals. Absorption data for these radicals are given in Table 1(b). Absorption spectrum of lithium carbonate shown in Fig. 3(b) has absorption for the 1078 cm^{-1} band and in two areas marked by large circles: the $870 \pm 50\text{ cm}^{-1}$ band and the $1430 \pm 20\text{ cm}^{-1}$ band attributed to carbonates. Their absorption data are given in the right column of Table 1. The only band common for the absorption by PE and lithium carbonate is 1078 cm^{-1} ; they are marked by arrows in Figs. 3(a) and 3(b).

Unlike lithium carbonate, sodium carbonate does not contribute to the reduction or extinction of spherulites in PE. Its spectrum is shown in Fig. 3(c). In this case, the arrow at 1078 cm^{-1} does not suggest absorption, but rather points to a band spectrum of carbonates in general. This suggests that oscillations of carbonate molecules causing strong absorption for the bands other than the 1078 cm^{-1} band

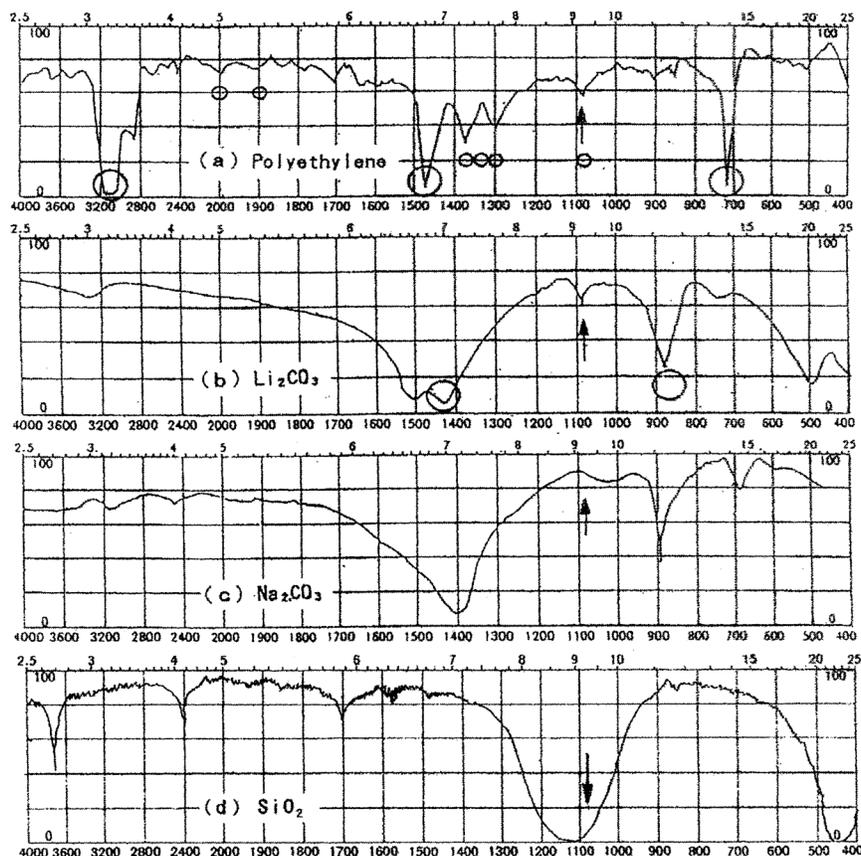


Fig. 3. Infrared absorption spectra of polyethylene, Li_2CO_3 , Na_2CO_3 , and SiO_2 .

Table 1. IR absorbed spectrum of polyethylene and Li_2CO_3

PE molecular chain			Li_2CO_3	
cm^{-1}	phase, intensity	conformation of molecular chain	cm^{-1}	intensity
1078	A, s	g (gauche), g and t	740	m
1303	A, ss	g, gtg or gtg'	870 ± 50	CO_3^- , s
1352	A, s	g, gg gtg or gtg'	1078	s
1368	A, ss	(t)n...ggtg... (t)m gtg or gtg' gttg or gttg'		
1894	C, m	tttt... (continuous trans)	1430 ± 20	CO_3^- , ss
2016	A+C, m	\geq tttt		

(a) IR absorbed spectrum of PE and Li_2CO_3

ss: very intense s: intense m: medium

cm^{-1}	intensity	linkage group
720 ~ 725	ss	$-\text{CH}_2-$
1460	s	$-\text{CH}_3$
1470	s	$-\text{CH}_2-$
2850		$-\text{CH}_2-$
2925		$-\text{CH}_2-$
2960		$-\text{CH}_3$

A: amorphous
molecular chain
C: crystalline
molecular chain

(b) absorbed spectrum of $-\text{CH}_2-$ and $-\text{CH}_3$

typical of lithium carbonate do not participate in reduction and extinction of PE spherulites.

Figure 3(d) shows the band spectrum of silica (SiO_2) contained in the siloxane compound (Si-O-Si), which displays a very strong absorption in the vicinity of the 1078 cm^{-1} band. Compounds featuring similar spectra include such silicates as aluminum silicate, kaolin, and talc. Additive treatment of PE using such compounds does not eliminate spherulites, but it was found that by blending these substances having a strong absorption at 1078 cm^{-1} with lithium carbonate, the thermal excitation of gauche chains increases, thus suggesting a considerable promotion of their formation. Detailed description of this treatment method is given in Sections 4.5 and 5.9.

Lithium carbonate strengthens gauche chains and thus accelerates gauche conformation of molecular chains and absorption for the 1078 cm^{-1} band. Therefore, the absorption can serve as a criterion of the treatment's effectiveness. Hence, the absorption rate for the 1078 cm^{-1} band measured by the baseline method [13] can be used as the quantitative measure of the proportion of gauche chains in PE. Below, it is denoted as Dg.

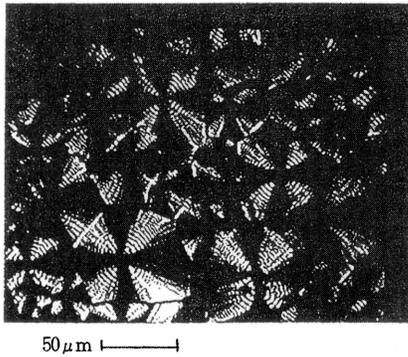


Fig. 4. Extinction rings of LDPE.

Reduction of spherulites in PE by lithium carbonate depends on the kneading temperature: D_g becomes higher and the number of gauche chains increases as the kneading temperature is increased. Detailed description of this processing method is given in Section 5.1.

It was also confirmed that the treatment of polypropylene also belonging to the olephine group does not result in the absorption by molecular chains for the 1078 cm^{-1} band or in spherulite extinction.

PE spherulites can be obtained by heating a sample on a cover glass by a gas lighter to $350\text{ }^\circ\text{C}$ and keeping it in the molten state for 2 seconds with subsequent cooling. In a polarizing microscope, spherulites can be observed as dark shapes in the form of Maltese Crosses. In a sample with spherulites placed between two cover glasses, one can observe concentric extinction rings [14] having the same period as the kinks of the ribbon-shaped crystals. Such spherulites in LDPE are shown in Fig. 4. Extinction rings in this figure are projected images of spherulites and, by compensating for distortions based on nine extinction rings, the kink period of ribbon-shaped crystals was calculated to be $2.760 \pm 0.184\text{ }\mu\text{m}$.

Figure 5 presents photographs taken by polarizing microscope ($\times 400$) showing samples at various stages of the treatment for quality improvement consisting of the kneading with lithium carbonate described in Section 3 showing gradual size reduction and extinction of spherulites. Untreated samples of both LDPE and XLPE (kneading treatment time 0 min) are characterized by clusters of large spherulites. The treatment leads to the reduction of spherulites and, as can be seen, samples kneaded for 25 min have a structure made of multiple connected white dots. The average distance between these white dots is $2.8\text{ }\mu\text{m}$, which is almost the same value as the kink period found in the configuration shown in Fig. 4. It is understood that these white dots are ribbon-shaped crystals rearranged due to the breakdown on spherulites. This suggests that in the

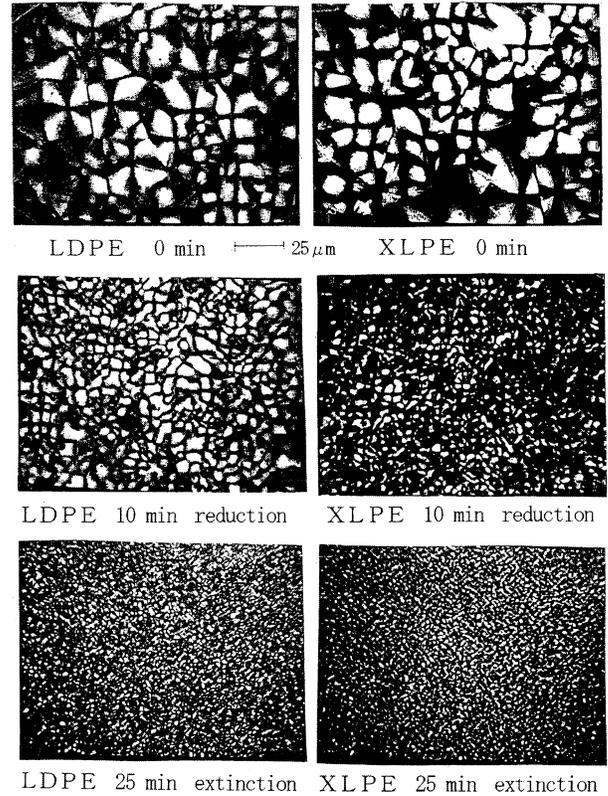


Fig. 5. Polarizing microscope photographs showing reduction and extinction of spherulites in improved PE.

process of PE kneading, spherulites are reduced in size and eliminated, resulting in the formation of ribbon-shaped crystals and microcrystals producing homogenized PE.

3. Preparation of Samples

PE samples for the treatment with additives and for the quality improvement processing were prepared from LDPE (NUC760) for power cables manufactured by Nippon Unicar Co., Ltd. XLPE samples were prepared using LDPE (HFDJ4201) manufactured by the same company as the base with addition of peroxide cross-linking agents. These PE grades have considerably higher viscosity and density (M.I: 3.2; density: 0.922) than previously reported M6545 PE (M.I: 45; density: 0.915) produced by Asahi Chemical Industry Co., Ltd. [15–18]. Samples were homogenized by mechanical kneading.

PE samples were processed in a mixer with heated twin rollers (HR-3 type: diameter 45 mm, length 100 mm) made by Nitto Hannoki Co., Ltd. placed in a nitrogen-filled vessel (O_2 content 1.4%). The processing was carried out under the following conditions: 7 g of PE was charged in

the vessel, the rollers temperature was 170 °C for LDPE and 130 °C for XLPE, gap between the rollers was 0.5 mm, and the rollers' rotation speed was 10 rpm for both types of PE. Finished samples obtained in the process of kneading were in the form of pellets with admixed additives. At both ends of the rollers, stoppers made of silicone rubber are provided whose purpose is to prevent the leakage of PE.

Additives can be removed by a mesh filter but this method is too difficult to be implemented in the laboratory conditions, so the contact method was used, namely, bringing the molten PE into contact with hard balls of lithium carbonate (diameter approximately 2 mm) using the heated twin roller mixer. Graphic representation of this method is shown in Fig. 6. Eighty balls of lithium carbonate and 7 g of PE are placed in the 0.5-mm gap between the heated rollers. After the PE has melted, the rollers start to rotate so that the material to be treated is pulled inside where molten PE comes in floating contact with lithium carbonate balls. The treated PE is removed from the roller surface and converted into pellets.

Lithium carbonate balls are not destroyed in the gap between the rollers, which is confirmed by the fact that lithium carbonate is not found in the material that underwent contact treatment by examination under the polarizing microscope ($\times 400$) and that no absorption for the $870 \pm 50 \text{ cm}^{-1}$ band characteristic for carbonates is present in the IR absorption spectrum.

Since the size reduction of spherulites and their extinction due to the propagation of PE gauche chains are implemented by contact between PE molecular chains and lithium carbonate and since the treatment takes place in the gap between the rollers, the processing time can be reduced, for example, by one-half by rotating the rollers two times faster.

Lithium carbonate is a nonhygroscopic substance having density of 2.10 and melting point of 618 °C. It is used as an ingredient in pottery glazes, fuel cell electrolytes, and partitions in lithium batteries, among others.

Molded samples having thickness of 1 mm and higher were fabricated by compression molding by charging LDPE pellets into the molds with subsequent heating at

175 °C for 15 min. XLPE samples were fabricated by molding pellets at 140 °C for 15 min with subsequent cross-linkage treatment at 200 °C for 20 min. In order to eliminate multiple “sinks” caused by cross-linking process from the XLPE films having thickness of 0.3 mm or less prepared on the heated twin roller mixer, they were heated between two thin metal plates.

Films used for the measurements of IR absorption spectra having thickness of 0.1 mm were fabricated on the heated twin roller mixer. Absorbance was measured by converting the film thickness divergence to 0.1 mm.

4. Test Methods

In order to check the effect of the improvement of homogeneity of the amorphous phase due to the contact treatment, we investigated the influence of the kneading treatment time on the electrical, mechanical, and thermal properties of PE samples by comparing them to the original material. Especially important was to check the mechanical strength of the amorphous phase of PE, which in previous reports was generally considered to be a weak point. In order to determine the ability of the improved PE to withstand mechanical impact, model samples were prepared for the impact destruction tests. These tests, along with the tests for the occurrence frequency of the corona pulses, have shown substantial improvements, especially with respect to cross-linked PE. We also examined accelerated formation of gauche chains due to the presence of silica, aluminum silicate, and other compounds contained in samples with admixed lithium carbonate showing strong absorption in the infrared spectrum, including absorption for the 1078 cm^{-1} band. These tests are described below.

4.1 Tests for electrical insulation properties

The effect of the treatment on the electrical characteristics of the improved materials was determined by testing them for the following electrical characteristics: dielectric breakdown, treeing, and water tree formation.

For the dielectric breakdown test, a 0.5-mm-thick PE sample having a diameter of 50 mm was placed on a spherical electrode having a diameter of 12.5 mm. The electrode with the sample was submerged in silicone oil and a voltage of 50 Hz rising at a rate of 3 kV/s was applied to the sample. Breakdown voltage was determined as the average value of measurements on five or six samples. If in the case of LDPE the original sample is made of pellets without kneading, then on its surface crystalline formations may appear due to the stretching effect, which results in an increased dielectric breakdown strength. Therefore, the samples were preliminarily treated in the heated twin roller mixer at 170 °C for 10 min.

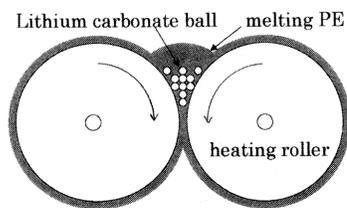


Fig. 6. Cross section of mixer with heated twin rollers.

Treeing tests were performed by puncturing the PE sample with a treeing needle having a tip radius of 3 μm (made by Ogura Industrial Jewels Co., Ltd.) and placing the sample in a set of needle–plane electrodes in silicone oil. The test consisted in application of a 50-Hz 8 to 12 kV voltage to the electrodes for 20 min. The tree growth was determined as the maximum length of the tree formed in the sample from the needle tip as registered by the microscope camera. However, when the needle puncture is made at room temperature, there appear microcracks caused by the expansion of voids and crevices due to the swelling produced by the pressure stress. As a result, tree breakdown develops in a short time. In order to eliminate the swelling, the sample is punctured with the needle at 120 °C, after which the sample was kept at 120 °C for 30 min and then at 130 °C for 30 min with subsequent cooling to room temperature in order to relieve the stress around the needle tip.

The water tree tests were performed using 1-mm-thick PE samples. A water needle electrode was prepared on one side of the sample by puncturing the surface with the treeing needle to a depth of 0.5 mm and adding salted water having conductivity of 4 $\Omega\text{-m}$; the electrode on the opposite side of the sample was made by applying a conductive paint. A voltage of 100 kV was applied to electrodes for 100 hours. After this, the samples were cut by a microtome into 40- μm -thick slices, which were placed into a methylene blue dye for 5 min at 70 °C. The tree growth was measured by observing tree propagations by means of a microscope camera ($N = 4$ to 7).

4.2 Tests for mechanical properties

Tests for mechanical properties of high polymers include tensile strength tests, compressive tests, tests for impact-initiated bending, tear tests, and rubbing tests. In this study, we performed stress–strain tensile tests for PE films of improved quality and especially the impact destruction tests based on the tearing strength to check the effect of homogenization of the amorphous part of PE.

During tensile tests by stretching at room temperature, PE exhibits characteristics of ductile materials, which break after a considerable stretching due to the necking caused by the unraveling of the amorphous phase of PE. During tests at low temperatures and during fast stretching, PE exhibits fragility and crack formation.

Modulus of elasticity and yield stress of PE were determined from stress–strain characteristics plotted using dumbbell-shaped film samples (0.2 mm thick, 5 mm wide, 20 mm long) stretched at a rate of 5 cm/min in a tank maintaining constant temperature of 25 °C.

Impact destruction tests on the improved quality samples were conducted using film samples having a cut on one

side. In these tests, the stress is concentrated at the cut even at room temperature and low stretching speed, thus creating crevices and microcracks in the amorphous part of PE [19]. Further development of cracks leads to rupture of samples. Based on these brittle fracture tests, the impact destruction strength was determined by finding, from the relationship between the film thickness and the maximum tear strength, the tear strength [20] T_c (kg/mm). These samples were made from PE film in the form of a dumbbell 0.2 mm thick, 10 mm wide, 20 mm long having a 2-mm cut made at one side of the sample. The tensile stress was applied at a rate of 20 cm/min at 25 °C.

4.3 Preparation of model samples for impact destruction and partial discharge tests

As mentioned above, impact forces in the form of a shock, bending, vibrations, stretching, and so on, applied to molded parts of electric wires or cables can result in fragmentation, cracking, or deformation of affected parts, which results in appearance of crevices and microcracks. There are indications that creation of crevices and microcracks generates a strong partial discharge that quickly develops into a tree discharge leading to breakdown. Tests on the impact destruction strength can be implemented as the falling ball method, flexural fatigue method, and other methods using naked-eye observations for evaluation. Since the creeping deformation in PE is difficult to determine by the naked eye, special model samples characterized by small deformation were prepared to investigate the partial discharge.

Since, as mentioned in Section 4.1, the insertion of the needle at room temperature in the sample in the treeing tests results in the formation of crevices and microcracks, model samples were made in the form of a disk with multiple depressions made by the treeing needle at room temperature.

LDPE model samples shown in Fig. 7(a) were constructed in the form of disks 2 mm thick and 40 mm in diameter having 200 depressions made by the treeing needle to a depth of 1 mm within a circle having a diameter of 15 mm. Conductive paint electrodes were applied to both sides of the samples and the depressions were filled with a conductive material. A 1- to 3-kV AC voltage (50 Hz) was applied to the samples generating at least 5 pc of CPS, which was measured by a CNT-21 corona pulse rate meter (made by Ando Electric Co., Ltd.). For the observation by microscope, depressions were carefully filled with a silver paste.

CPS generated at the depressions made by the needle in the XLPE model samples similarly to the LDPE samples amounted to only one-fourth of that observed in the LDPE samples. Since it was especially difficult to determine CPS

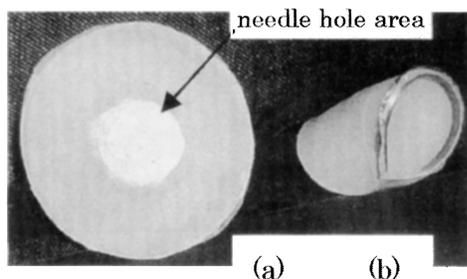


Fig. 7. Samples for impact destruction tests.

in samples of improved quality, samples having depressions were bent to add bending stress. As shown in Fig. 7(b), such samples are bent 180° to form a U-shape with the surface having depressions facing inside. Each sample was bent ten times along the entire circumference. This made it possible to clearly establish that the number of CPS increased three-fold.

4.4 Tests on heat treatment and thermal deformation temperature

Melting point of fully crystalline LDPE is 141 °C; that of commercially available PE is 105 to 111 °C; operating temperature is 100 °C; temperature of compression molding is 135 to 177 °C; temperature for injection molding is 149 to 316 °C; arc withstand temperature is 133 to 316 °C; point of thermal decomposition in vacuum is 406 °C.

In order to check the effect of spherulite extinction due to the heating over a long period of time in the course of the improvement treatment, LDPE original samples and samples prepared by the kneading treatment for 40 minutes were heated at different temperatures for 30 minutes in the nitrogen atmosphere, after which their IR absorbance, D_g , and degree of crystallinity, X (%), were measured.

All types of molded products have a drawback in that during their use they can be deformed even at temperatures considerably lower than the PE melting point. Therefore, evaluation of practical heat resistance is carried out according to the standard tests for the thermal deformation temperature. Such tests include bending under load tests and cantilevered stretching tests. However, these tests are not suitable for our purposes since they require large samples and a high temperature range. In this study, we used the Vicat softening temperature test (JIS K-7206:1999), which can be performed using small samples.

An indenter in the form of a steel needle having a cross-sectional area of 1 mm² was placed perpendicularly against a small sample (thickness 4 mm, area 10 × 10 mm). The indenter was loaded with a lead weight creating a force

of 10 N and the entire assembly was placed in a silicone oil bath where it was heated at a rate of 50 °C/h. Depth of the indenter penetration due to the softening of the sample was measured at each temperature by a dial gauge, and the Vicat softening temperature (VST) was determined as the temperature at which the depth of penetration is 1 mm. Since the temperature control in this test is to be carried out at ±0.5 °C, temperature of the stirred silicone oil was measured by an IC sensor and controlled in the follow-up mode by an immersed heater against the reference input signal of 50 °C/h.

4.5 Promotion of gauche chain formation by silica blending

As can be seen in Fig. 3(b), infrared transmission factor of lithium carbonate for the 1078 cm⁻¹ band is rather high. This means that Condition 1 consisting of the thermal excitation of gauche chains is not sufficiently satisfied. On the other hand, as can be seen in Fig. 3(d), silica has a very strong infrared absorption in the vicinity of the 1078 cm⁻¹ band, namely at 1110 cm⁻¹, and due to thermal losses its infrared transmission factor is almost zero. Since this infrared spectrum is of the band type including a strong absorption at 1078 cm⁻¹, blending silica with the lithium carbonate additive enhances Condition 1 for the promotion of gauche chains because the contact of the blend with PE molecular chains contributes to a stronger thermal excitation of gauche chains.

We also checked reduction and extinction of spherulites in LDPE by the following silicates having similar spectra (in parentheses, absorption frequencies in cm⁻¹ are provided for reference) when they are blended with lithium carbonate. It was established that silicates can be arranged in the following order based on their efficiency in promotion of gauche chain formation: silica (1110) > aluminum silicate (1085) > kaolin (1050) > talc (1015) > quartz (1085). However, we found that the PE kneading treatment with addition of only these silicates fails to produce gel, that is, it does not satisfy Condition 2 for the formation of gauche chains and extinction of spherulites.

In order to find an optimal, from the standpoint of gauche chain formation, ratio of these blending agents with respect to lithium carbonate, we checked characteristics of spherulite extinction by adding 0.25 to 1% of these silicates to PE containing 1% by weight of lithium carbonate with subsequent kneading in the heated twin roller mixer. Obtained results suggest that the optimal content of silicates in the blend is 0.5% by weight and the same content (0.5%) is optimal for aluminum silicate.

After that, we determined characteristics of spherulite diameter and absorption by gauche chains, D_g , as a function of kneading time for PE with addition of 1%

by weight of lithium carbonate, to which silica, aluminum silicate, or lithium carbonate was blended in amounts of 0.5% by weight.

Particle sizes of additives and blending agents were 10 μm for lithium carbonate, 5 μm for silica, and 3 μm for aluminum silicate. Samples for these tests were prepared from pellets made by adding these preliminary powdered components to the molten PE with subsequent mixing.

5. Test Results and Discussion

Test results provided below represent average values of characteristics, such as curves of dependence on the kneading time. In cases where two sets of data are plotted against the same horizontal axis, the data are separated by shifting respective symbols slightly to the left and to the right. Since there is a strong discrepancy of the data due to insufficiently homogenous state of the amorphous phase of the samples, we want to draw attention to the overall improvement effect compared to the original material (0 minute treating time).

5.1 Dependence of sample quality on the treatment temperature

Infrared absorption by gauche chains (D_g) in PE treated with lithium carbonate becomes higher and spherulite extinction accelerates as the kneading temperature is increased. The kneading temperature must be higher than the temperature of PE fluidity (140 $^{\circ}\text{C}$) but lower than 175 $^{\circ}\text{C}$ to prevent PE autoxidation in the nitrogen atmosphere.

Figure 8 presents D_g as a function of the kneading time in the course of improvement treatment of LDPE in the heated twin roller mixer for temperatures (a) 140 $^{\circ}\text{C}$, (b) 160 $^{\circ}\text{C}$, and (c) 175 $^{\circ}\text{C}$. Spherulites are extinct almost

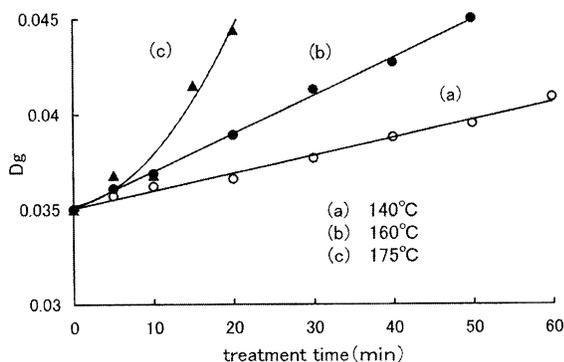


Fig. 8. Infrared absorbance of gauche chains in improved PE as a function of the treatment time at various temperatures.

completely when D_g is 0.04, that is, spherulite extinction is achieved in 80 min for sample (a), in 30 min for sample (b), and in 15 min for sample (c). Therefore, all subsequent processing was conducted at 170 $^{\circ}\text{C}$.

5.2 Reduction and extinction of spherulites in improved PE

Below, in Section 5.3 we discuss tests on the AC breakdown voltage tests and in Section 5.4 we discuss tests on the tree growth. Number of samples prepared for each test varied from 10 to 20. A polarizing microscope was used to measure diameter of spherulites in samples prepared for the examination of the effect of kneading time and to observe the formation of ribbon-shaped crystals appearing in the process of spherulite destruction.

Diameter of spherulites was determined as a diameter of the largest spherulites selected from four to five thin strips cut from the same sample and placed on the cover glass next to each other. Figure 9(a) shows diameter of

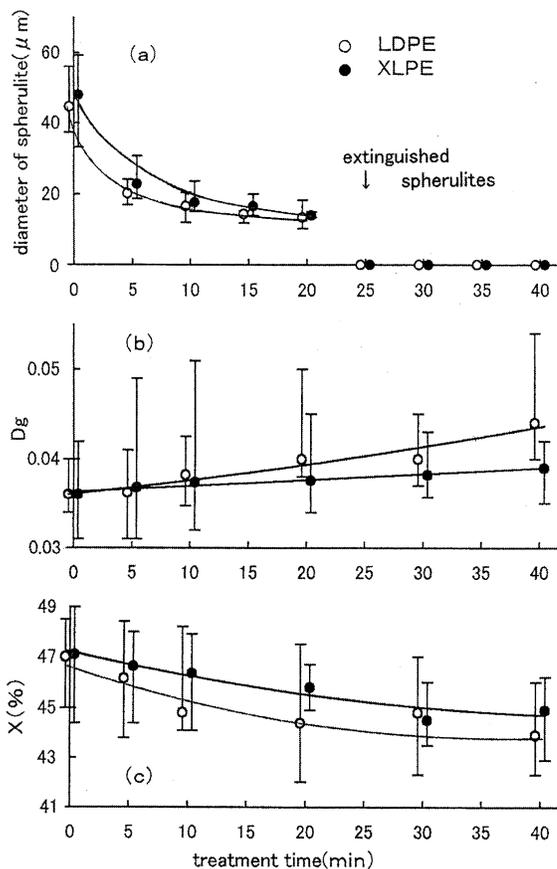


Fig. 9. Diameter of spherulites (μm), absorbance of gauche chains, D_g , and degree of crystallinity X (%) in improved PE as a function of treatment time.

Table 2. Characteristics of carbonates and lithium compounds used as additives or contacting agents in PE

Compounds used as additives or contact agents	Spherulites	Gel fraction (%)	D _g	D _K	X (%)
(1) PE (without additives)	present	0.1	0.034	0.00	45.01
(2) Li ₂ CO ₃ (additive)	absent	13.4	0.042	0.022	41.02
(3) Li ₂ CO ₃ (cont. agent)	absent	11.1	0.043	0.028	40.61
(4) Na ₂ CO ₃ (additive)	present	6.1	0.037	0.017	44.03
(5) Cs ₂ CO ₃ (additive)	present	5.4	0.035	0.017	42.96
(6) Rb ₂ CO ₃ (additive)	present	3.5	0.033	0.007	44.71
(7) LiF (additive)	present	5.6	0.036	0.013	43.64
(8) LiCH ₃ COO (additive)	present	5.6	0.036	0.012	43.74
(9) LiCl (additive)	present	5.2	0.033	0.015	43.21

spherulites as a function of the kneading time demonstrating reduction and eventual extinction of spherulites.

Spherulites become virtually extinct after 25 minutes of kneading treatment and multiple narrow ribbon-shaped crystals are formed in both LDPE and XLPE. In approximately half of the XLPE samples used for the plotting of characteristics shown in Fig. 9(a), spherulites are extinct after only 15 or 20 minutes.

However, since in order to achieve a homogeneous structure of PE it is not sufficient to eliminate spherulites but also to reduce the size of ribbon-shaped crystals, the treatment time was increased to 40 to 50 min. In addition, during the treatment, the speed of the rollers was doubled, from 10 rpm to 20 rpm, which resulted not only in spherulite extinction but also in achieving a fine homogeneous structure.

Figure 9(b) demonstrates an increase of the infrared absorption D_g by gauche chains in the same samples as in Fig. 9(a). Figure 9(c) shows that the degree of crystallinity X (%) is reduced [21]. These characteristics are almost identical for both XLPE and LDPE, except that in XLPE, due to cross-linking, the changes take place at a slower rate.

Samples prepared from LDPE with addition of lithium carbonate in the amount of 1% by weight and processed as mentioned above by multiple repetitive heating and cooling cycles without kneading were examined under a polarizing microscope. It was established that the smallest diameter of spherulites was of the order of 5.5 μm and they were formed by two ribbon-shaped crystals (kink period 2.76 μm). It was also found that if the processing cycle is repeated about 20 times, then the width of the ribbon-shaped crystals decreases from 2.75 μm to 1.44 μm [22].

Next, we checked the samples for Condition 2 for the PE spherulite extinction mentioned in Section 2, namely, the presence of carbonyl radicals in PE molecular chains and formation of cross-linked gel fraction. Data shown in Table 2 relate to characteristics of LDPE samples contain-

ing additives of carbonate and lithium series (1% by weight) prepared under the same conditions. These samples were examined for the presence (or absence) of spherulites, absorbance by carbonyl radicals D_K, and gel fraction content (%) [5].

According to the data of Table 2, Condition 1 for the spherulite extinction (absorption at the 1078 cm⁻¹ band) is satisfied only in cases (2) and (3) for samples treated with lithium carbonate. The content of gel fraction in these samples is almost two times higher than in other samples and absorption by carbonyl radicals D_K is the highest, indicating that these samples are the only ones satisfying Condition 2. They also have a higher infrared absorbance D_g by gauche chains due to the extinction of spherulites and, therefore, the lowest degree of crystallinity X%.

It was also confirmed that peroxides used as cross-linking agents form strong links due to covalent bonds but they do not contribute to absorption for the 1078 cm⁻¹ band and have no effect on spherulite extinction.

5.3 Characteristics of the AC breakdown voltage

Figure 10 shows characteristics of dielectric breakdown strength of improved PE as a function of the treatment time. Dielectric breakdown strength characteristics are practically the same for LDPE and XLPE; after treatment for 30 minutes, breakdown strength of LDPE becomes 1.22 times higher than that of the original material and breakdown strength of XLPE becomes 1.25 times higher, which suggests a better homogenization.

Figure 10 also shows data concerning the dielectric breakdown strength of PE containing 1% by weight of lithium carbonate additive having particle size of 10 μm after treatment for 30 minutes. Dielectric breakdown strength of LDPE with additives is 0.92 and that of XLPE with additives is 0.9 of the dielectric breakdown strength of

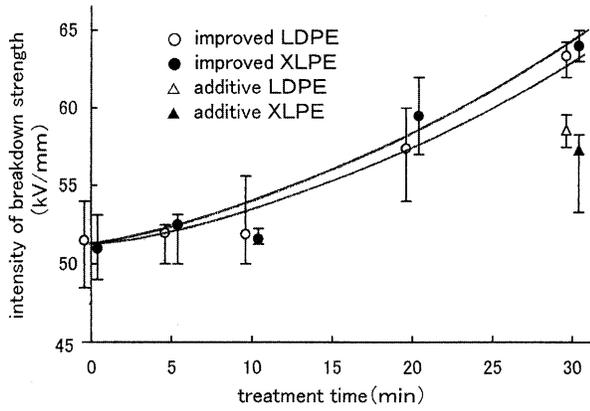


Fig. 10. Dielectric breakdown strength of improved PE.

improved PE samples. This shortcoming is caused by the presence of lithium carbonate particles as a foreign substance reducing the homogeneity of the samples.

5.4 Characteristics of treeing length

Figure 11 shows treeing length as a function of the treatment time. The tests were performed on samples made from improved PE with a needle-plane electrode system. The needle electrode was made by a treeing needle inserted to a depth of 2 mm. Treeing length (mm) characteristics as a function of the treatment time were measured by placing samples in a silicone oil tank and applying 50-Hz 8-kV voltage for 20 minutes. Treeing length characteristics of XLPE and LDPE are almost identical, and treated samples demonstrate a substantial quality improvement compared to the original PE: treeing length of the samples treated for 30 minutes is shorter by 40%, and that of samples with 1%

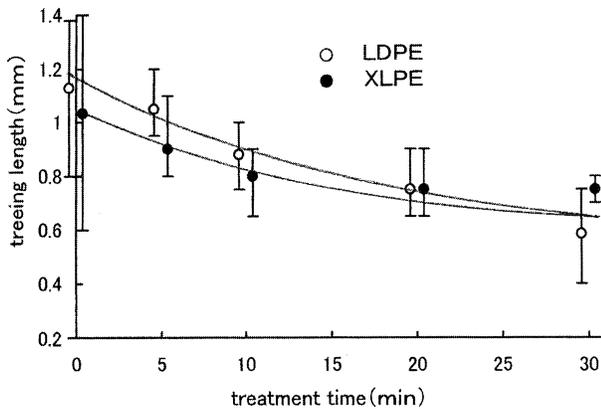


Fig. 11. Characteristics of treeing length in improved PE.

of lithium carbonate additive is improved by almost the same amount.

Figure 12 shows characteristics of treeing length of the original PE and improved PE (after treatment for 30 minutes) depending on the applied voltage. Voltage of 8, 10, and 12 kV was applied for 20 minutes. In all samples, the branching is observed at 8 kV and partial discharges occur near the tip of the needle electrode at 10 and 12 kV due to increased discharge energy forming a tree pattern similar to a green alga ball shape. An increased pressure of the dissociation gas suppresses the partial discharge at the tips of tree branches, thus limiting the treeing length [23].

5.5 Characteristics of watertreeing length

Figure 13 shows characteristics of watertreeing length in improved PE as a function of the treatment time. Watertreeing length was determined using samples with the waterneedle-plane electrode set applied to them placed in salted water for 100 hours. As can be seen from the test results, the watertreeing length of improved samples that underwent kneading treatment for 30 minutes was reduced to 62% for the LDPE samples and to 56% for the XLPE samples of the watertreeing length of the original PE. Since

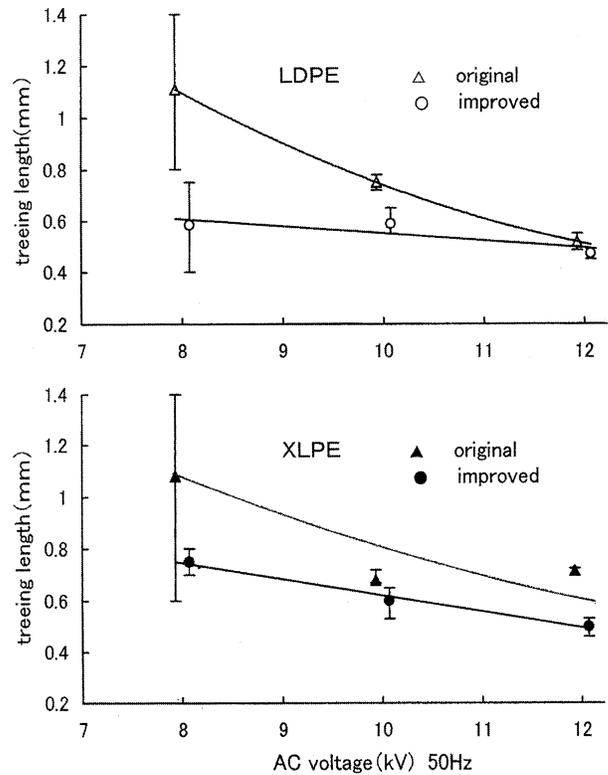


Fig. 12. Treeing length as a function of applied voltage.

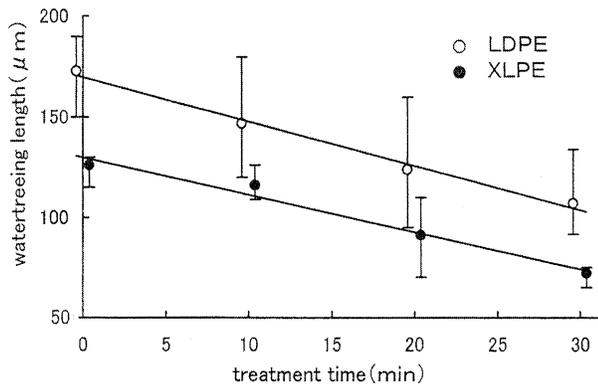


Fig. 13. Characteristics of watertreeing length in improved PE.

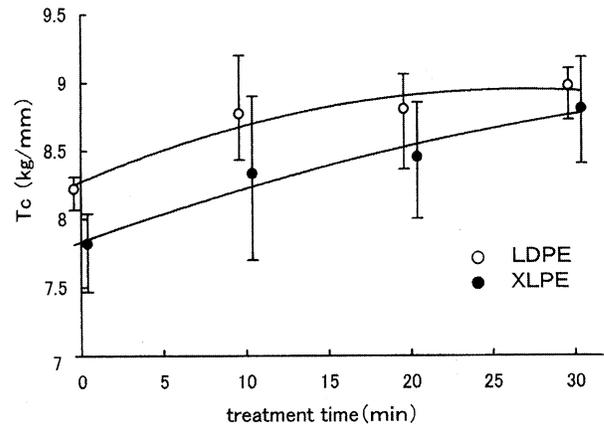


Fig. 14. Tear impact strength of improved PE.

plastic deformation at the time of making the water needle is lower in the case of XLPE, watertreeing length in XLPE samples is smaller than in LDPE samples.

5.6 Characteristics of the impact destruction strength

Table 3 shows modulus of elasticity, yield strength, and tear strength T_c of original samples and samples from PE treated for 30 minutes.

Tear strength, T_c , is the brittle fracture strength corresponding to the impact destruction strength. This value was obtained as the average value of measurements made on about 10 film samples.

Tear strength ratios (in %) based on the T_c characteristic (assuming the value of the original LDPE to be 100%) are given in the column labeled "Tear strength ratio." It is known [24] that cross-linking of PE results in a reduced tear strength: in the example shown in Table 3, it is 95%. Tear strength of improved PE is increased to 107%. Tear strength of improved LDPE is increased to 109%, and that of improved XLPE is 113%, if the tear strength of the original sample is 100%.

Figure 14 shows tear strength T_c of improved PE as a function of the treatment time. T_c of original XLPE is

lower than that of LDPE, but after treatment for 30 minutes, T_c of LDPE and XLPE become almost the same. Therefore, one can say that although cross-linking usually reduces the impact strength, it can be substantially increased by the treatment.

These conclusions are supported by the data on the improvement of impact strength characteristics reported by Ohlberg and colleagues [25] who demonstrated that fast cooling of LDPE leads to a smaller spherulite size and to an increased impact strength.

5.7 CPS characteristics of model sample for impact strength tests

Figure 15 shows characteristics of the partial discharge CPS produced by crevices and microcracks as a function of the treatment time, with the applied voltage as the parameter. CPS is reduced due to the improvement treatment, which results in a considerable suppression of the treeing discharge.

Compared to the original LDPE samples, CPS of samples after treatment for 30 minutes is considerably reduced. For example, at 2 kV, from 600 CPS to 40 CPS, that is, to only 6.7%.

Table 3. Mechanical properties and tear strength ratio of improved PE

Sample	Modulus of elasticity (kg/mm ²)	Yield strength (kg/mm ²)	Tear strength, T_c (kg/mm)	Tear strength ratio (%)	
LDPE (original)	7.64	0.88	8.22	100	
LDPE (improved)	8.72	0.96	8.97	109	
XLPE (original)	8.19	0.81	7.82	95	100
XLPE (improved)	9.26	0.83	8.80	107	113

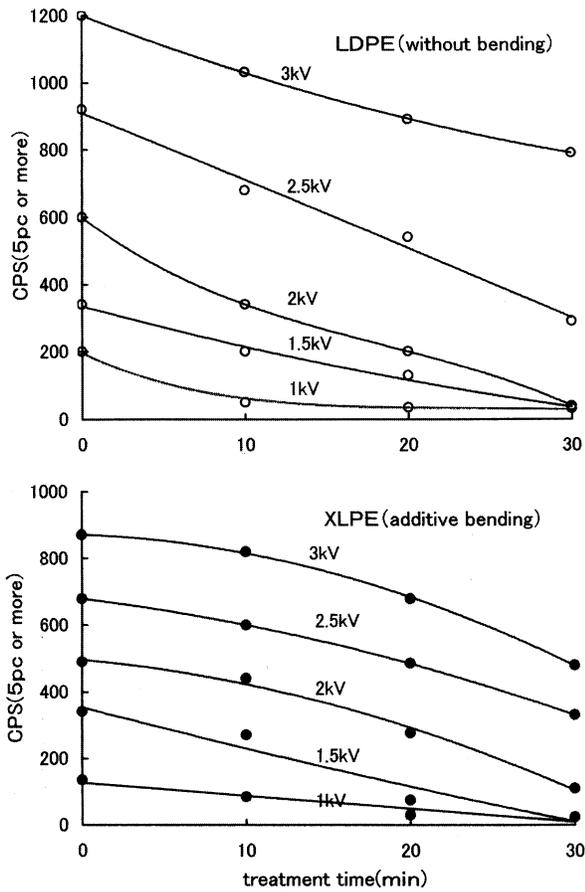


Fig. 15. Characteristics of partial discharge CPS in samples modeled for impact tests.

Since, as mentioned in Section 4.3, XLPE has extremely small crevices and microcracks, its CPS is 3 times greater when the bending stress is added. Because of this, at 2 kV, CPS of samples that were treated for 30 minutes is 22.4% lower than the original sample (from 490 CPS to 110 CPS), which indicates a higher degree of homogeneity.

5.8 Tests for the heat treatment and thermal deformation temperature

Figure 16(a) shows infrared absorbance by gauche chains, D_g , of the original samples and LDPE samples after 40-minute treatment as a function of the heating temperatures. In the tests, the samples were heated at each temperature for 30 minutes. At temperatures above 200 °C, D_g of improved PE starts to slightly decrease, thus indicating that spherulites remain extinct.

D_g of the original LDPE remains almost unchanged, indicating an excellent thermal stability of PE.

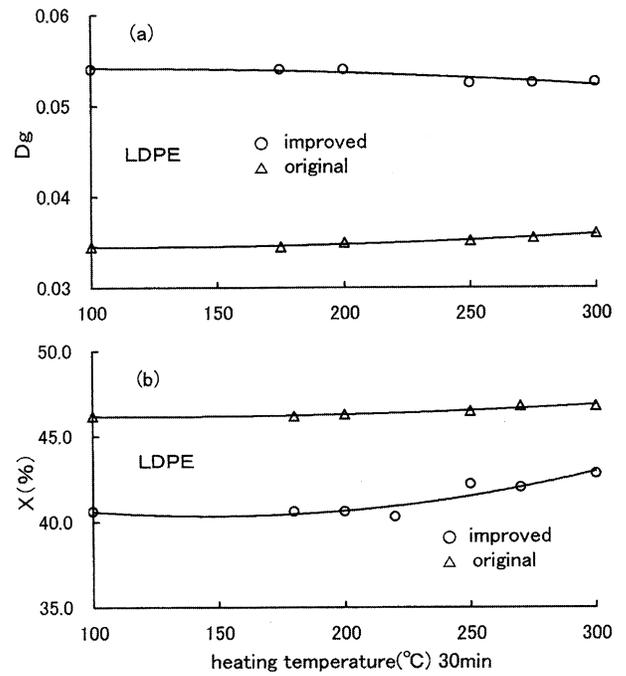


Fig. 16. Characteristics of improved PE as a function of heating temperature.

Figure 16(b) shows degree of crystallinity X (%) of the original and improved PE. Crystallinity of improved samples increases due to the decrease of D_g . From the above, it is clear that the effect of spherulite extinction in PE remains in force up to 300 °C.

Figure 17 presents characteristics of thermal softening of the improved PE samples in terms of thermal softening temperature as a function of the invasion quantity (mm) of the needle indenter with the treatment time (min) as the parameter. VST of the original LDPE (untreated, 0 min) at an invasion quantity of 1 mm is 91.6 °C, which is practically identical to that of LDPE treated for 30 min (91.65 °C). Even at lower invasion quantities, the increase of thermal softening temperature in treated samples is insignificant.

In contrast, thermal softening temperature of XLPE rapidly becomes higher as the treatment time is increased. While VST of the original PE is 92.4 °C, that of PE treated for 30 minutes is 95.9 °C, that is, its thermal softening temperature is 3.5 °C higher. The softening temperature becomes higher over the entire range of the invasion quantity increase. Compared to the original XLPE (0 min) the thermal softening temperature of the XLPE treated for 30 minutes is 11.0 °C higher at an invasion quantity of 0.1 mm and 13.0 °C higher at 0.2 mm, indicating a positive combined effect of cross linking and homogenization.

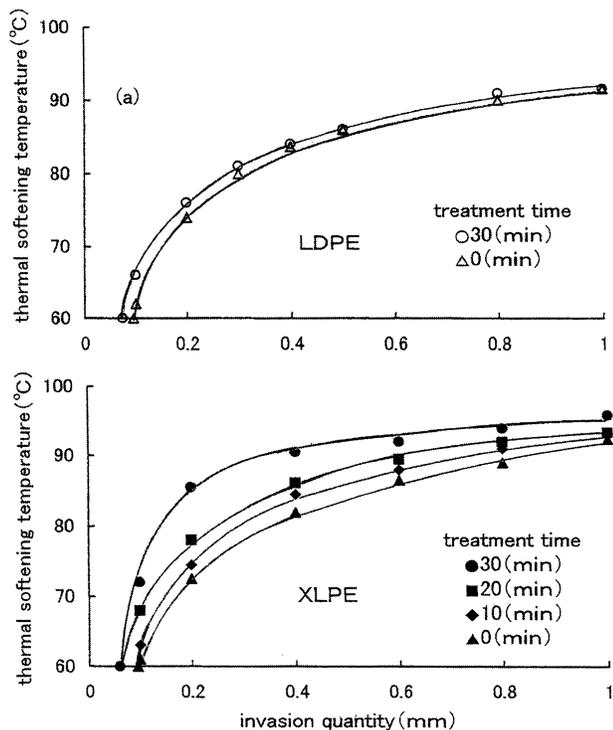


Fig. 17. Characteristics of thermal softening of improved PE.

5.9 Effect of accelerated formation of gauche chains due to compounding silica

A shortcoming of PE treatment with lithium carbonate to form more gauche chains is the low infrared absorption by PE gauche chains for the 1078 cm^{-1} band. In order to increase the absorption, 0.5% each of aluminum silicate and silica are blended into LDPE with lithium carbonate additive in the amount of 1% by weight. Film samples having thickness 0.1 mm were prepared from this material and tested for absorption by gauche chains at 1078 cm^{-1} within the band of $900\text{ to }1200\text{ cm}^{-1}$.

Infrared transmission factor of pure PE pellets shown as spectrum *a* in Fig. 18 is 76% at 1078 cm^{-1} suggesting that the infrared absorption by gauche chains is rather low. Spectrum *b* represents infrared transmission factor of PE with lithium carbonate additive in the amount of 1% by weight. In this case, transmission factor is 73%, that is, the infrared absorption is slightly higher than that of pure PE pellets. Spectrum *c* is the infrared transmission factor of PE blended with aluminum silicate (61% at 1078 cm^{-1}) and spectrum *d* is the infrared transmission factor of PE blended with silica (52% at 1078 cm^{-1}), which has the highest infrared absorption. In addition to infrared absorption for the 1078 cm^{-1} band by gauche chains, spectrum *d* also has absorption by silica at 1110 cm^{-1} .

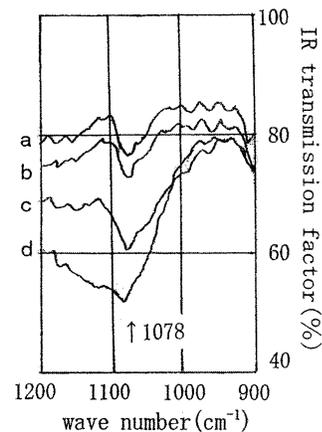


Fig. 18. Characteristics of IR transmission factor of various compounding agents.

This suggests that the blending of silica during the PE treatment with lithium carbonate promotes formation of gauche chains. Figures 19 (1) and (2) show dependence of spherulite diameter on the treatment time in the double roller mixer for PE with various amounts of the compounding silica. Curve (a) in Fig. 19 (1) is a characteristic of samples with lithium carbonate additive in the amount of 1% by weight without the compounding silica indicating that spherulites become extinct after the treatment for 57 minutes. Characteristics (b), (c), and (d) are for the same material as (a) but with silica compounded in amounts of 0.25, 0.4, and 0.5% by weight, respectively. From these characteristics, one can see that with an increase in the silica content, spherulite diameter decreases faster and the time required for spherulite extinction becomes shorter. Spherulite extinction is especially fast (only 17 minutes) in samples containing 0.5% of silica by weight [characteristic (d)]. This is 30% of the spherulite extinction time of samples (a) (57 minutes). Figure 19 (2) shows characteristics of samples with increased amounts of compounding silica: (d) 0.5%, (e) 0.7% and (f) 1% by weight. As can be seen in characteristics (e) and (f), the effect of treatment with lithium carbonate disappears and the diameter of spherulites becomes larger. Characteristic (g) in Fig. 19 (2) relates to PE with only a silica additive in the amount of 1% by weight. Treatment for more than 20 minutes resulted in the reduction of spherulite diameter to $14\text{ }\mu\text{m}$ due to the effect of the nucleation material, but no complete elimination of spherulites was observed. It was also established that no formation of ribbon-shaped crystals due to the destruction of spherulites observed in samples treated with lithium carbonate takes place.

We also found that in samples with aluminum silicate as the additive, similarly to samples with silica additive, the diameter of spherulites cannot be reduced to below $20\text{ }\mu\text{m}$.

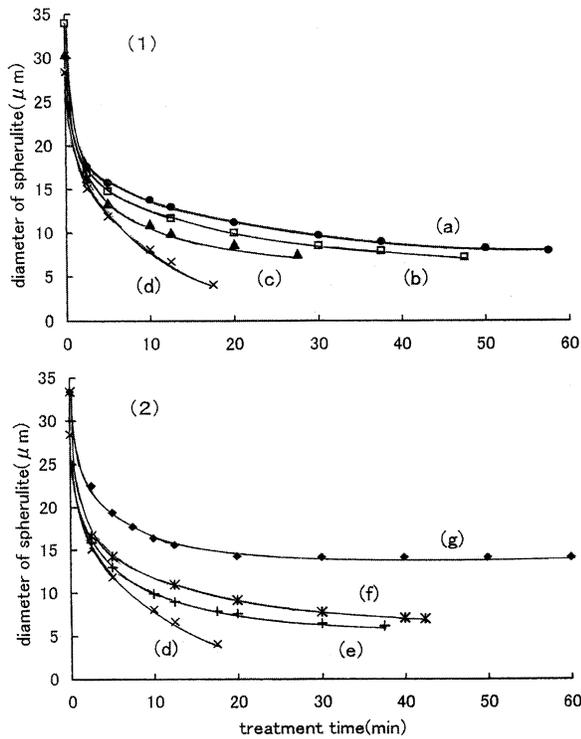


Fig. 19. Characteristics of spherulite diameter of PE with silica as the compounding agent.

Figure 20 demonstrates the effect of such compounding agents as lithium carbonate, aluminum silicate, and silica on the elimination of spherulites.

Curve (a) in Fig. 20 presents the diameter of spherulites in noncompounded PE containing 1% by weight of lithium carbonate as a function of the treatment time. Curves (b), (c), and (d) are characteristics of spherulite diameter in PE containing respectively lithium carbonate, aluminum silicate, and silica in the amount of 0.5% by weight as compounding agents in PE represented by curve (a). These characteristics suggest that silica (d) is the most efficient compounding agent from the standpoint of the time required for the reduction of spherulite diameter and their eventual elimination by promoting the formation of gauche chains in PE. Figure 21 shows characteristics of absorbance of gauche chains, D_g , for the 1078 cm^{-1} band in 0.1-mm-thick films prepared from the same samples as in Fig. 20. Compared to absorbance of the untreated sample (treatment time 0 min), absorbance of samples with lithium carbonate (b) is slightly higher, absorbance of samples with aluminum silicate (c) is higher, and absorbance of samples with silica (d) is much higher. In other words, the use of silica as the compounding agent results in a greater efficiency regarding the formation of gauche chains.

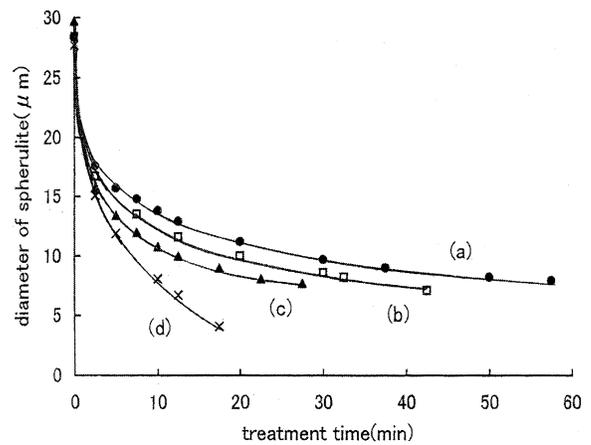


Fig. 20. Characteristics of spherulite diameter of PE with various compounding agents.

However, the infrared bands selected as the baseline for measurements of lithium carbonate, Dg, were 1120 and 1000 cm^{-1} , while those for aluminum silicate and silica were 1160 and 1000 cm^{-1} . The reason was that since the maximum silica absorption is at 1110 cm^{-1} , this band spectrum (see curve *d* in Fig. 18) is expanded in the direction of a higher wave number and the left-side boundary of the band is assumed to be 1160 cm^{-1} . Baseline of the aluminum silicate spectrum was aligned with that of silica.

From the above, it is seen that the thermal excitation strongly depends on the absorption by these additives and compounding agents for the 1078 cm^{-1} band, which is the premise of Condition 1 of the infrared absorption by PE gauche chains mentioned in Section 2.

In addition, by melting these compounding agents with lithium carbonate, which is of alkaline nature, it is possible to produce a glaze, which can be converted to

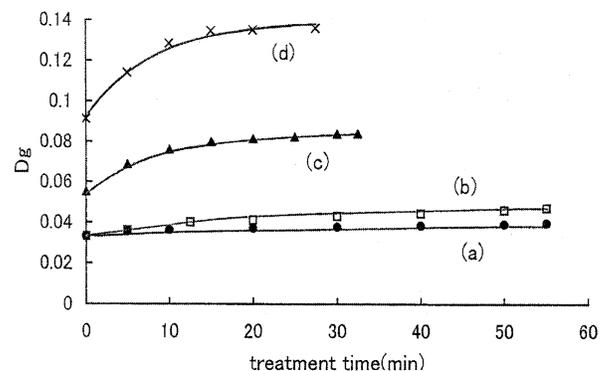


Fig. 21. Characteristics of absorbance by gauche chains in PE with various compounding agents.

fusion balls to be used in the contact method without additive agents.

Moreover, U.S. and Japanese patents were received on the process for the PE quality improvement based on the treatment with lithium carbonate described above [26, 27].

6. Conclusions

Various tests were performed to check the improvement of electrical, mechanical, and thermal properties due to the spherulite extinction treatment by lithium carbonate intended to eliminate nonhomogeneous parts of the amorphous phase, which are a weak point of PE. Below, we summarize the results of these tests.

(1) Because of the kneading treatment of PE with lithium carbonate, trans chains connecting PE lamellae are destroyed and converted into gauche chains, which leads to the extinction of PE spherulites. Therefore, amorphous parts, which are the weak point of PE, become homogeneous, resulting in improved electrical, mechanical, and thermal properties of PE.

(2) At present, the extinction of PE spherulites is limited only to lithium carbonate. Gauche chains of PE show infrared absorption for the 1078 cm^{-1} band and the only substance having absorption at this band is lithium carbonate.

(3) PE homogenization can be carried out by contact treatment with lithium carbonate, but we developed a contact treatment method not requiring the use of lithium carbonate.

(4) We believe that carbonyl radicals formed in the molecular chains of samples subjected to the contact treatment contribute to the formation of gel, thus accelerating the conversion to gauche chains.

(5) Treeing growth in LDPE and XLPE samples improved by the contact treatment is reduced compared to that in the original samples by almost 40%.

(6) The impact destruction strength of the improved samples determined by tearing tests is higher than that of the original samples by 9% for LDPE and by 13% for XLPE. The proposed treatment makes it possible to increase the impact destruction strength of XLPE (which is low due to the cross-linking, only 95% of that of LDPE), by improving the homogeneity of polyethylene. The strength of treated XLPE is 107% of the impact destruction strength of LDPE.

(7) Measurements of corona pulses on samples with multiple depressions prepared for the tests on mechanical impact strength indicate that homogenization of improved samples results in substantial suppression of crevices and microcracks.

(8) Vicat softening temperature of improved XLPE samples was $95.9\text{ }^{\circ}\text{C}$, which is $3.5\text{ }^{\circ}\text{C}$ higher than that of

the original samples, confirming the positive effect of homogenization on thermal properties of polyethylene.

(9) Reduction of the diameter of PE spherulites and their eventual extinction due to the treatment with lithium carbonate can be accelerated by blending with silicates. Using silica as the blending agent made it possible to reduce the treatment time by 30% compared to the treatment with lithium carbonate alone.

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