Paper

Effects of Blend of Polypropylene Copolymer on Electrical Breakdown of Low Density Polyethylene

Student-Member Zhang Chao (Nagoya University)
Member Tatsuo Mori (Nagoya University)
Member Teruyoshi Mizutani (Nagoya University)
Member Mitsugu Ishioka (Japan Polychem Co.)

In order to improve the breakdown properties of low density polyethylene (LDPE), the electrical properties of blend polymers of LDPE and random copolymer of ethylene and propylene (EP) have been investigated at 30℃, 60℃ and 90℃. The specimen with a higher EP content had a higher impulse breakdown strength at 90℃ than the specimen with a lower EP content, but there was no obvious difference at 30℃ and 60℃. However, in the case of DC breakdown, any improvement was not recognized for blend polymers throughout the temperature range from 30℃ to 90℃. The morphology of blends was studied by a polarizing microscope and X-ray diffraction. The influences of morphology on breakdown properties were discussed. The morphological change by introduction of EP into LDPE was demonstrated by the decrease in the size of a spherulite, the existence of EP in the inter-spherulitic boundary region and the enhancement of orientation. The improvement of impulse breakdown strength at 90℃ was explained on the basis of morphological change.

Keywords: Low Density Polyethylene, Polypropylene, Blend Polymer, Breakdown, Morphology

1. Introduction

Low density polyethylene (LDPE) has been widely used as power cable material because of many advantages in both electrical and mechanical properties. Further improvement of breakdown strength of LDPE especially in a high temperature region is required in developing a high performance power cable. Blending a high melting point polymer with LDPE is one of the effective methods [1-3]. However, the mechanism of improving breakdown strength by blending has not been fully understood.

In this paper, a blend polymer was made by the random copolymer of ethylene and propylene (EP) and LDPE, and the weight content of EP was 5 or 10 %. The reason of selecting EP is due to its better compatibility with LDPE in blending and its easy processability during the manufacturing process. We investigated the breakdown and DC current of the blend polymer at 30℃, 60℃, and 90℃.

Generally speaking, the electrical breakdown properties are influenced by the morphology and/or chemical structure of the materials. In this study, the morphology and chemical composition were changed by the introduction of EP into LDPE, and these changes would possibly affect the electrical properties of blend polymers. To understand the experiment results of electrical breakdown, it is necessary to investigate the influences of blend on the morphology of a specimen. In this paper, X-ray diffraction (XRD) and polarizing microscope were used to characterize the morphology of the specimen, and the relationship between electrical breakdown and morphology was discussed.

2. Experimental

2.1 Specimens

Table 1 shows the properties of three kinds of film specimens used in this study. All specimens were made by the film blowing process in which molten polymer was extruded through an annular die and then was drawn upwards by a take-off device. The blowing condition was the same for all the specimens. The original LDPE was made by the high-pressure process. The specimens, B5 and B10, were blend polymers of LDPE and EP with the EP content of 5 and 10 wt %, respectively. The thickness of film was about 20 μm. Table 1 also shows the density, melting point and MFR (melt flow rate).

2.2 Experimental procedures

Specimens used for electrical measurements were vacuum-evaporated with gold as electrodes on both sides. The upper electrode (diameter: 6 mm) had a diffused edge to moderate the electrical field near the electrode edge. The diameter of the lower electrode was 20 mm for the breakdown test and 12mm for the current test. The specimen was placed between a brass spherical electrode (upper) and a brass plate electrode

Table 1. Specimens

Specimens	Composition	Density (g/cm^3)	Melting Point (℃)	MFR* (g/10min)
PE	LDPE	0.9174	109.4	1.40
B5	95wt%LDPE+5wt%EP	0.9156	109.4	1.68
B10	90wt%LDPE+10wt%EP	0.9141	109.4	1.73

*MFR: melt flow rate

(lower) in silicone oil. The rise rate of applied voltage was 2.6 GV/s for the impulse breakdown test, and 500 V/s for the DC breakdown test, and 30V/s for the current test. The breakdown strength was measured 16-20 times for each point, and the average value and the standard deviation were given as the breakdown strength. All electrical measurements were conducted at 30℃, 60℃, and 90℃.

X-ray diffractometer (RINT 2100 Ultima, Rigaku Co.) was used to investigate the crystal structure of a specimen. X-ray diffraction pattern was measured by CuK α radiation in the 2θ range of 10° to 40°. The crystal size which was calculated by the Scherrer equation [4, 5] and the values of 2θ of diffraction peaks were employed to express the crystal structure of the specimen. Six samples taken from different places of each specimen were measured. The result was given by the average value and the standard deviation [4].

The melting point was measured by Differential Scanning Calorimetry (DSC). The heating rate was 10 K/min. The melting point was defined as the temperature at which melting ends in DSC curve of melting.

Nikon OPTIPHOT-2 polarizing microscope was used to observe the morphological structure of a specimen. Two methods, one Nicol and crossed Nicols (one polaroid and crossed polaroids) were used to get the different views of the specimen.

The blown film has an oriented structure due to the blowing process. To examine the orientation ratio of the specimen, the thermal shrinkage was measured with the standard method of ASTM: D 1204-84 on both the machine direction (or the draw direction) and transverse direction (which is normal to the machine direction) of the specimen. The thermal shrinkage is expressed by a parameter of $(L_0-L)/L_0*100\%$, where L_0 is the original length of the specimen at room temperature and L is the length at an elevated temperature (90℃, 95℃ or 100℃).

The density of film was measured with the density gradient method based on JIS K 6760-1981.

3. RESULTS AND DISCUSSION

3.1 Influence of blend on morphology

X-ray diffraction method was used to study the crystal structure of the specimen. Figure 1 shows the crystal size and the value of 2θ of crystalline peak as the function of the content of EP. Two crystalline peaks (with indices of 110 and 020) due to LDPE were analyzed. No changes in the 2θ and crystal size could be observed among specimens. Therefore, it could be concluded that blending with EP does not change the crystal structure of LDPE so much.

No influence on XRD 2θ peak or melting point (shown in Table 1) of LDPE by blending suggests that the crystalline parts of both LDPE and EP exist independently, and that the blend polymer of LDPE and EP has 'sea-island morphology'.

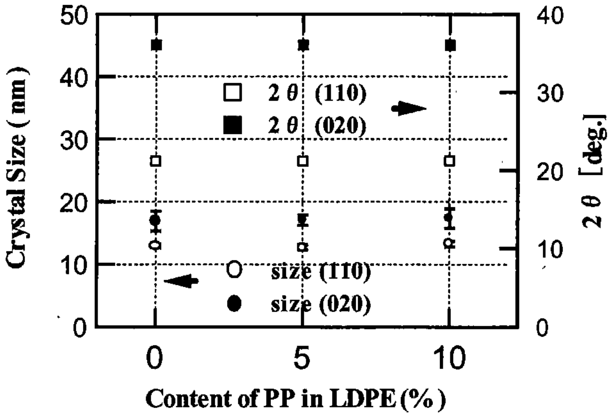
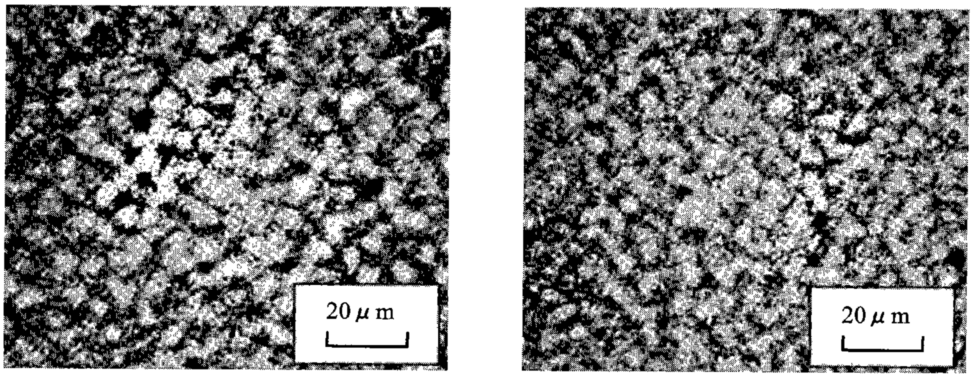


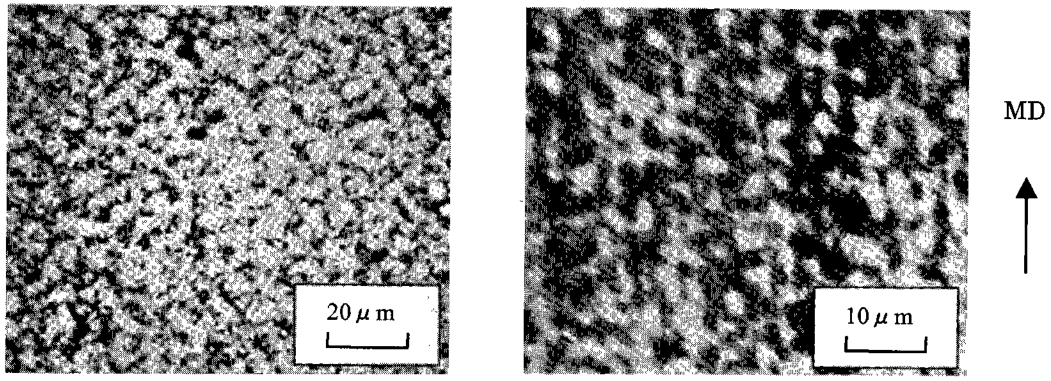
Figure 1. Peak values of 2θ and crystal size as a function of the EP content.

We also estimated the degree of crystallinity of all specimens based on their densities [3]. There was almost no obvious difference among the specimens.

Figure 2 shows the micrographs of all specimens under polarized light. Figures 2(a), (b) and (c) were taken under one Nicol in which the spherulites were distinguishable. Because the specimens did not have homogeneous structure, different



(a) PE (b) B5



(c) B10 (d) B10

Fig.2. Polarized light micrographs of specimens: (a), (b), and (c) were taken under one Nicol; (d) was taken under crossed Nicols

images could be observed by adjusting the focus. Figures 2(a), (b) and (c) were focused on the position at which the biggest spherulites could be observed. The specimen, PE, which is free of EP, shows spherulitic texture with ca. 8 μm in diameter of spherulite as shown in Fig. 2(a). This value of the spherulite diameter is close to the reported one for LDPE annealed from melting at a cooling rate of 50℃/s. [6]. The micrographs of B5 and B10 are shown in Figures 2(b) and (c). The diameter of spherulite decreases with the increase of the content of EP in blends. The size of the inter-spherulitic boundary region is also smaller. But the ratio of spherulites and inter-spherulitic boundary regions was difficult to be estimated.

We also observed all the specimens under crossed Nicols. The specimens, PE and B5, still showed spherulitic texture like Figures 2(a) and (b) (not shown here). Although any image could not be observed for B10 with the focus on the same position as in Fig. 2(c), B10 showed the image in which many grains align along the machine direction by adjusting focus as shown in Fig. 2(d).

This kind of image didn't appear in PE and B5. B10 also didn't show this kind of image clearly under one Nicol. This image is attributed to the elongation effect [7, 8]. It indicates that B10 has a stronger orientation structure than PE and B5 along the machine direction.

The different images of Figures 2(c) and (d) taken from the same B10 show that the film has the different morphology along the direction through-thickness. This is consistent with the results reported by W. F. Maddams et al. [9]. In general, the film made by the blowing process does not have homogeneous layer structure and it consists of some layers with different structure determined by manufacturing conditions. The disappearance of the image of B10 under crossed Nicols is also thought to be attributed to the different structures of the film [5]. The image shown in Fig. 2(c) was not located in the same layer with the image of Fig. 2(d).

The size of a spherulite getting smaller by blending LDPE with HDPE was reported by T. Yamakita et al. [10]. It suggests that the blending can suppress the growth of a spherulite. The size of spherulite is in the order of B10 < B5 < PE.

Figure 3 shows thermal shrinkage in the machine direction as a function of temperature for all specimens. The thermal shrinkage for the specimen with a high content of EP was larger than that with a low content of EP in this direction. However, in the transverse direction, no obvious thermal shrinkage was observed.

The film blowing process can introduce an orientation structure into the film [9]. When the temperature increases, the orientation introduced during the process of blowing gradually relaxes and the film shrinks in the elongation direction.

Therefore the orientation of the film can be evaluated by the measurement of thermal shrinkage. The result of thermal shrinkage indicates the differences in the orientation among the specimens in the machine direction. B10 has the highest orientation ratio, and PE has the smallest orientation ratio. This result is consistent with the fact that B10 shows the image of grains aligning along the machine direction shown in Fig. 2(d).

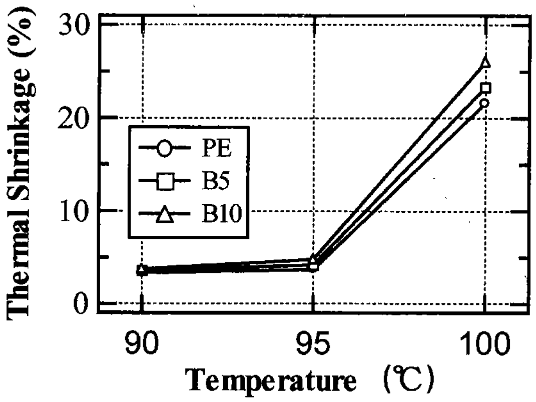


Figure 3. Temperature dependence of thermal shrinkage

The reason for the difference in orientation between PE and B10 is not clear now. But the smaller size of spherulite being easier to get a morphological metamorphosis may be one of the possible reasons [11]. The difference in rheologic properties (such as MFR shown in Table 1) may be also related to this phenomenon.

As LDPE has the spherulite structure, EP and impurities exist in the inter-spherulitic boundary regions due to the exclusion effect of spherulite [12, 13].

To summary the above discussion, the effect of blending EP with LDPE on morphology was not found under the lamella level, but was found in the level of spherulite. In the blends, the sizes of spherulites and the inter-spherulitic boundary regions were smaller than those of the virgin LDPE. The morphological changes in orientation were found among the specimens along the machine direction. B10 has the highest oriented structure, and PE has the lowest.

3.2 Influences of blend on the electrical properties

Figure 4 shows the temperature dependence of impulse breakdown strength (F_{BImp}) for PE, B5 and B10. There is almost no difference in F_{BImp} among the three kinds of specimens at 30℃ and 60℃, but B10 has the highest F_{BImp} and PE has the lowest F_{BImp} at 90℃. F_{BImp} at 90℃ increases with increasing the content of EP.

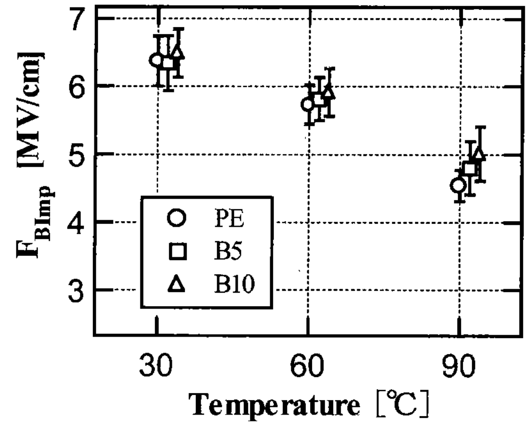


Figure 4. Temperature dependence of impulse breakdown strength (F_{BImp})

Figure 5 shows the temperature dependence of DC breakdown strength (F_{Bdc}) for PE, B5 and B10. No obvious difference could be observed throughout the temperature range from 30℃ to 90℃.

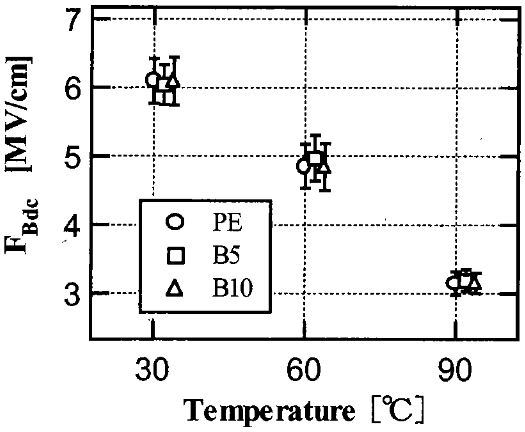


Figure 5. Temperature dependence of DC breakdown strength (F_{Bdc})

The relationship between the current density and the applied field for PE, B5 and B10 is shown in Figure 6 (at 30℃ and 90℃). At 30℃, all specimens have about the same value in the low field region below 3 MV/cm, but B10 has a higher current density than B5 and PE when the field is above 3 MV/cm, and PE demonstrated the most limited current growth. At 90℃, no difference is found in current density among the specimens in the low field region. The current density of PE increases a little faster than the others in the high field region, while it is difficult to distinguish the current densities between B5 and B10. In other words, the current in the high field region at 90℃ is suppressed by blending EP.

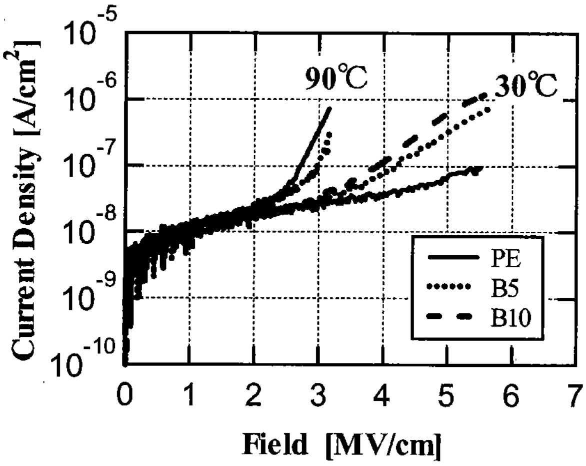


Figure 6. Current density-field characteristics of all the specimens at 30℃ and 90℃

3.3 Relationship between morphology and electrical properties

3.3.1. High temperature region (at 90℃)

In Figures 4 and 5, all specimens exhibit a clear negative temperature dependence. Therefore the breakdown at 90℃ may be caused by the thermal breakdown process.

EP has a higher melting point (155℃) than LDPE (110℃), therefore, blending with EP can improve the high temperature properties. This is helpful to improve electrical breakdown properties in the high temperature region.

The morphology of the inter-spherulitic boundary region could be changed by introduction of EP into LDPE and, as a result, the F_{BImp} at 90℃ increases with increasing the blend ratio of EP. First, the sizes of spherulities and the inter-spherulitic boundary regions became smaller by blending EP with LDPE, and this would reduce the internal stress and mitigate the irregularity in the inter-spherulitic boundary regions which are supposed to influence the electrical strength [9, 12, 14]. Secondly, the existence of EP in the inter-spherulitic boundary region can make this region more thermally stable due to its relatively high melting point, and the electrical strength of this region can be reinforced. Thirdly, the enhancement of orientation of the film may promote the molecular packing in the amorphous region and it would result in the increase in breakdown strength of B5 and B10 [7, 15].

No obvious improvement on DC breakdown strength could be found. The difference between F_{BImp} and F_{Bdc} is due to the different voltage duration. The time from applied voltage to breakdown was 3-4 μs for impulse breakdown, and about 12 sec for DC breakdown at 90℃ in this study. The temperature increases rapidly during the DC voltage application by the positive feedback of current increase and temperature rise [16], while it stops in a very short period. Therefore, the blend effect on breakdown strength at 90℃ is not clear for DC breakdown compared with impulse breakdown. Figure 5 may also suggest a possibility that DC current flows preferentially in the LDPE part whose fraction is 90% in weight and that DC breakdown occurs there.

3.3.2. Low Temperature region

The impulse breakdown process has been reported to be electronic at 30℃ and to be triggered in the crystalline region [4]. This is consistent with our experimental result that there was no difference in breakdown strength at 30℃ shown in Fig. 5. As mentioned in section 3.1, the blending EP in LDPE couldn't affect crystalline structure under the lamella level. There was also no apparent difference in crystallinity among the specimens in room temperature.

The breakdown at 60℃ is an intermediate stage between electronic breakdown and thermal breakdown and no distinct change in F_{BImp} was observed.

4. Conclusion

We have studied the electrical breakdown properties and morphology of blend polymers of LDPE and EP. It was found that the F_{BImp} at 90℃ increases with increasing the content of EP. The improvement of the high temperature property by blending with EP is supposed to be main reason. But F_{BImp} at 30℃ and 60℃ didn't show such a tendency. We did not found obvious improvement of DC breakdown strength by blending throughout the temperature range from 30℃ to 90℃.

The relationship between morphological changes by blending and electrical properties has been discussed. The possible effects of morphology on F_{BImp} at 90℃ are as follows:

(1) The small size of spherulities can reduce the internal stress in the inter-spherulitic boundary region and, as a result, F_{BImp} increases.

(2) The existence of EP in inter-spherulitic boundary region will enhance the thermal stability of this region at 90℃, hence F_{BImp} can be improved in this case.

(3) The enhancement of orientation by blending will be useful for improvement of F_{BImp}.

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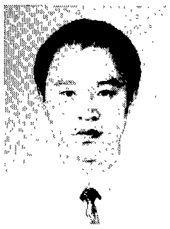

Zhang Chao (student member) received the B.S. and M.S.degrees from Xi'an Jiaotong University (China) in 1984 and 1987, respectively. Presently is a doctor course student at the Department of Electrical Engineering of Nagoya University.

Tatsuo Mori (member) received the B.S., M.S. and Ph. D. degree from Nagoya University. He is now Assistant Prof. at Dept. of Electrical Eng., Nagoya Univ.. He was Visiting researcher at Paul Sabatier University, France (2000). He is mainly engaged in development and characterization of thin films, as well as improvement of capabilities of polymer insulation materials for power applications. He is member of Jpn. Soc. Appl. Phys. and Jpn. Soc. Polym. Sci..

Teruyoshi Mizutani (member) received the B.S., M.S. and Ph. D. degree from Nagoya University. He is now Professor at Dept. of Electrical Eng., Nagoya Uni.. He was Visiting researcher at Laval University, Canada (1973/4) and Visiting professor at TU Braunschweig, Germany (1994). His research interests include electrical insulation, semiconductors and thin film devices. He is IEEE Fellow and member of Jpn. Soc. Appl. Phys..

Mitugu Ishioka (member) graduated from the Hachinohe National College of Technology, 1975. He then joined Mitsubishi Petrochemical Co. Ltd.. He currently works in the Film & Sheet Laboratory, Products R&D Center of Japan Polychem Co.. His research interests include novel low-density polyethylene and copolymerization materials.