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Diversity of Ion Path in Low Density Polyethylene Solid

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Summary: Electrical and Thermal properties of low density poly(ethylene) (LDPE) were observed by the measurement with the impedance analyzer and the differential scanning calorimetry (DSC) respectively. The frequency dispersion curves of the electric modulus were analyzed and investigated in comparison with the DSC data. The samples are annealed during various times. From the DSC data, it was found that the crystalline structure changes into more inhomogeneous structure on lamella thickness with increase in annealing time. On the other hand, the electrical experiment shows the plural process of ionic conduction on the frequency dispersion curves of the electric modulus. The number of processes is increased in the range from 1 to 3 with increase in the annealing time. In this manner, the correspondence between the result of the electrical experiment and the DSC strongly suggest that the ions included in LDPE move through the non-crystalline parts near the crystallite surface because the inhomogeneity in lamella thickness produces the inhomogeneity in the parts near the surface of the lamella.

Keywords: crystalline structure; DSC; electric modulus; ionic conduction; low density poly(ethylene)

Introduction

In crystalline polymer solid, lamellae are in variety of size in the melt-crystalline polymers and consequently it produces irregular packing of lamellae. Therefore, a non-crystalline region between lamellae has possibility to produce various ion paths. On the other hand, there are boundaries of the spherulites which could be an ion path as the melt-crystallized polymers are composed of various sized spherulites. Therefore, it is highly possible that the melt-crystallized polymer has hierarchical structure of ionic conduction which produces diversity of ion path.

In case of polyvinyl chloride-polybutadiene blends, plural kinds of long-range motion of ions were observed in frequency dispersion of electric modulus.[1] The ionic motion discussed in that study is caused by inhomogeneous microstructure of these samples. As there is also the density inhomogeneity in an amorphous region in crystalline polymers, it may well be that plural processes of ion motion could be detected by electrical observation in a low frequency region. Actually, plural processes were observed in low density polyethylene (LDPE) in a previous study.[2]

In order to confirm the diversity of ion path in crystalline polymers, LDPE was reexamined in this study. The electrical experiment was made to detect the ion paths dynamically and more precisely than the previous study.[2] An additional study of differential scanning calorimetry (DSC) was made to investigate the crystalline structure thermally.

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Experimental

Films of LDPE were obtained by vaporizing the solvent after pellets of LDPE had

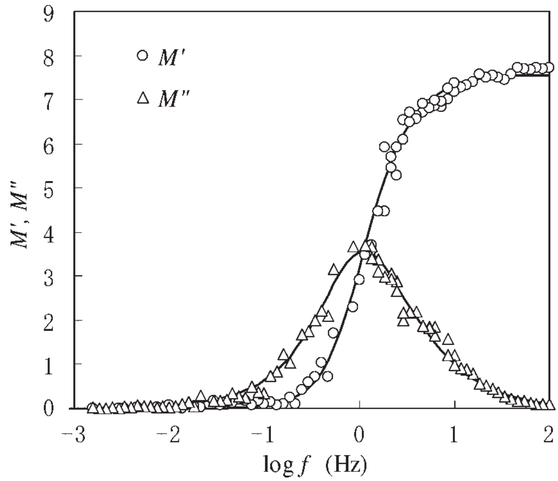

Figure 1.
Frequency dispersion of electric modulus for LDPE annealed at 100 °C for 2500 min.

been dissolved in toluene forcibly at about 120 C. After the vaporization, the films were cooled slowly to a room temperature. The films thus obtained were treated thermally to prepare quenched and annealed samples. The annealed samples were prepared for keeping at 100 °C during various times in the sample cells for both of the electrical and thermal experiments. As to the samples of electrical experiment, three samples were annealed for 2 min, 2500 min and 5700 min. Each sample is named here S2, S3, S4 respectively. As to the DSC measurement, the annealing time were 0, 10 min, 30 min, 60 min.

The electrical measurement was made by the apparatus of Schlumberger 1260 type Impedance Analyzer together with Keithley 428 Current Amplifier as a preamplifier. Tin films were attached to the films of sample as electrodes in a three-terminal configuration.[3] DSC was made by the apparatus of TA Instruments DSC2920 with reference sample of air. Heat flow was measured with heating rate of 5 min/s.

Results and Discussion

Figure 1 shows one of the experimental data of frequency dependence of the real and imaginary parts of electric modulus ($M^* = M' + iM''$) for the LDPE. Frequency dispersion of M', M'' are observed between 0.03 Hz and 100 Hz. Figure 2 shows logarithm of loss permittivity ε'' against logarithm of frequency. The loss permittivity shows monotonic decrease with increase in frequency. A slope of this plot is almost −1 in the same frequency range as the frequency dispersion of the electric modulus was observed. From the frequency dependence of loss permittivity, we recognize that d.c.conduction of ions occurs in this frequency range. Therefore, the frequency dispersion of electric modulus in

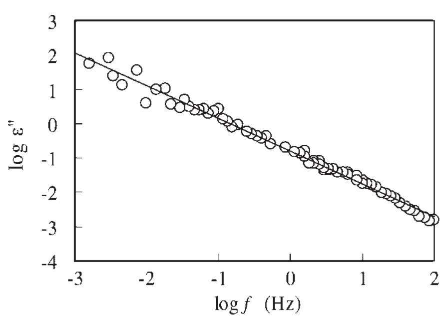

Figure 2.
Frequency dispersion of loss permittivity for LDPE annealed at 100 °C for 2500 min.

Figure 1 also reflects the d.c.conduction of ions.

The electric modulus versus frequency curves observed for sample S3 and S4 were broader than the Debye type dispersion curve. Accordingly, these curves were decomposed into plural processes on the assumption that an observed dispersion curve is composed by the plural Debye type dispersion curves. The data were analyzed with the following equation:

$$M^* = \sum_k \left\{ M_{s,k} \frac{(\omega\tau_k)^2}{1+(\omega\tau_k)^2} + iM_{s,k} \frac{(\omega\tau_k)^2}{1+(\omega\tau_k)^2} \right\}. \quad (1)$$

Here, $M_{s,k}$ is an asymptotic value of M' at the high frequency end of the k-th process. τ_k which is named the conductivity relaxation time in a literature[4] is a waiting time for ions to hop an energy barrier for the k-th process. ω is an angular frequency of measurement.

Results of the analysis are shown in Figure 3. The sample S2 was prepared by quenching but it took a time of 2 min for measurement. We cannot avoid taking a little of time in this experiment. Samples S3 and S4 were annealed and the annealing time is longer in this order. The frequency dispersion of M' and M'' for the sample S2 shows one stepwise increase and one peak around 4 Hz while those for the sample S3 and S4 show two processes as shown in Figure 3. These processes seem to be classified into three processes located around 0.2 Hz, 1 Hz and 8 Hz, which are named the low, the middle and the high processes in this paper. Intensity of these processes depends on the annealing time.

In order to clarify the difference in the intensity of each process, annealing time dependence of the intensity for each process was plotted as shown in Figure 4. From Figure 4, the intensity of the high process remarkably decreases at the annealing time of 2500 min while the large peak of the middle process appears simultaneously. When the annealing time is increased further, the intensity of the middle process decreases and the low process appears instead.

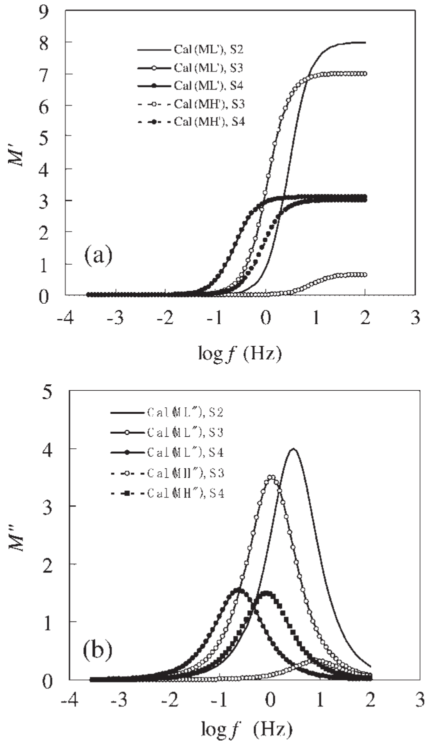

Figure 3.
Ionic conduction processes observed in the frequency dispersion of electric modulus for LDPE annealed at 100 C. The sample S2, S3 and S4 were annealed for 2, 2500 and 5700 min respectively. (a) and (b) are for the real and the imaginary parts of electric modulus respectively.

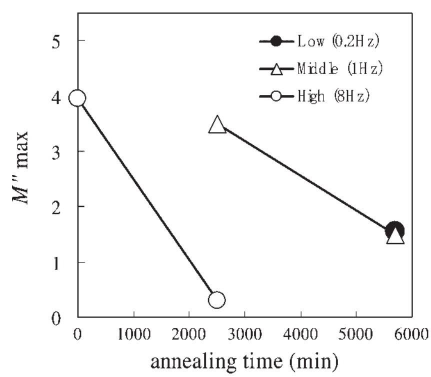

Figure 4.
Maximum value of M″ for each process plotted against the annealing time for the LDPE. Annealing temperature is 100 °C.

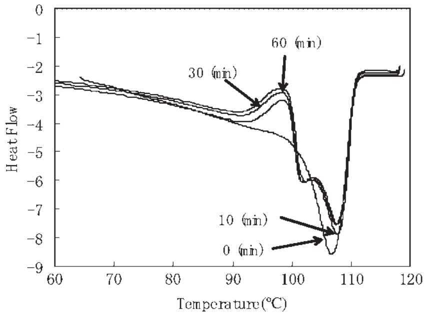

Figure 5.
DSC curves for the LDPE samples treated thermally at several temperatures indicated in the figure.

The conductivity relaxation time τ_k is given by a follwoing equation:[4]

$$\tau_k = \frac{\varepsilon_0}{\sigma_{dc,k} M_{s,k}}. \qquad (2)$$

Here, ε_0 is the permittivity of free space and σ_{dc} is d.c.conductivity for the k-th process. If we assume τ_k is inversely proportional to the peak frequency of M'', the peak frequency of M'' is proportional to the d.c.conductivity.[1] Therefore, the result of this analysis suggests that the lower d.c.conductivity processes appear one after another instead of disappearance of the higher d.c.conductivity processes with increase in the annealing time.

We consider about the structural back ground of the electrical phenomena described above. There are two possibilities of the ways for the annealing to affect the ion path; (1) density of non-crystalline part between the crystallites decreases as the crystallites grow; (2) The boundaries of spherulites decrease as the spherulite grows. In order to investigate the change of the ion path from these points of view, DSC experiment was made. Figure 5 shows DSC curves obtained by the experiment. In the samples annealed longer, three absorption peaks appear while only one peak appears in the quenched sample. This result means that the annealing causes recrystallization with inhomogeneous crystallite thickness. Therefore, it is considered that the recrystallization makes the ion path narrower and more inhomogeneous. If we made speculation like this, the experimental results of the DSC corresponds with the results of the electrical experiment. Therefore, ions seem to pass through the inhomogeneous non-crystalline part. Consequently, first possibility for the ion path seems like truth. However, it is not a proof to deny the second possibility. It is a future problem weather the second possibility is comatible wjth the first or not, although the first possibility was supported by the present research.

Conclusion

From the experimental study about the ion path in semicrystalline polymer solid, it is considered that the ions in LDPE pass through the inter lamellae non-crystalline parts, although the confirmation of the possibility of passing through the boundaries of spherulites is necessary to make sure. This study also suggest the possibility that the microstructure change in the semicrystalline polymer solid could be detected by the investigation of the motion of the impurity ions.

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