1. Introduction

The properties of plastic products depend on their processing and thermal history. Thermal analysis is the most widely used method to evaluate plastic products\(^1\), but the dynamic viscoelasticity method is also an effective evaluation method.

PET (Polyethylene Terephthalate) is a general-purpose resin used in a wide variety of fields. As with other polymer materials, how PET products are to be used determines how they are made. For example, melt spinning is used for the fibers (polyester fibers) used in raw materials for clothing, biaxial drawing is used for film used in electronic parts and magnetic tape and injection or blow molding is used for products like plastic bottles.

In this brief, three PET products created using different molding methods are analyzed to determine their viscoelasticity differences.

2. Experiment

Three PET products from the same maker were used as samples for the experiment: fibers made using melt-spinning process, 10μm-thick film made using biaxial drawing\(^2\), and a 500μm-thick sheet formed using extrusion.

DMS200 Dynamic Mechanical Spectrometer (Tension Module) connected to a SDM5600H Rheol. Station was used for the measurements. Measurement conditions included 5 measurement frequencies of 0.5, 1, 2, 5, and 10Hz. The measurement temperature range was -150ºC to 220ºC and the heating rate was 1ºC/min.

3. Measurement results

Figures 1 to 3 show the dynamic viscoelasticity spectrums for the melt spun PET fiber, the drawn PET film, and extruded PET sheet. The results are simultaneous measurement of temperature and frequency dispersions and show the $E'$, $E''$, and tanδ curves for 5 frequencies from 0.5Hz to 10Hz. The results for the PET fiber in Figure 1 and the drawn PET film in Figure 2 show $\alpha$- and $\beta$-dispersions from the high temperature side. The $\alpha$-dispersion is attributed to main dispersion (glass transition) and the $\beta$-dispersion is attributed to local mode relaxation\(^3\). The measurement results of the extruded PET sheet in Figure 3 also show the $\alpha$- and $\beta$-dispersions. Furthermore, there are peaks on the $E''$ and tanδ curves along with an increase in $E'$ between 120ºC to 140ºC. The extruded PET sheet was nearly quenched from a melted state so it was largely amorphous. The crystallization of the amorphous material, in other words, cold crystallization, likely occurred in the vicinity of 120ºC to 140ºC in Figure 3.
Figure 1  Dynamic viscoelasticity spectrum of PET Fiber

Figure 2  Dynamic viscoelasticity spectrum of Drawn PET Film

Figure 3  Dynamic viscoelasticity spectrum of Extruded PET Sheet
Figure 4 shows the $E'$ curves for the 1Hz results in Figures 1 to 3. The data indicates that the elastic modulus for the samples took the following order from highest to lowest: PET fiber, drawn PET film and extruded PET sheet. It is known that the storage modulus ($E'$) of oriented polymers is generally higher than that of non-oriented polymers\textsuperscript{4,5}. Different PET formation methods cause different molecular orientation and this difference likely caused the elastic modulus difference seen in Figure 4. PET fibers, which are considered to have a high drawing ratio, also have a high degree of molecular orientation and thus the highest $E'$. Extruded PET sheets are not drawn and are close to amorphous so its $E'$ value is the lowest.

Figure 4  Comparison of $E'$ curves for PET Fiber, Drawn PET Film and Extruded PET Sheet
Frequency : 1Hz
- - - - - : PET Fiber
- - - - - : Drawn PET Film
- - - - - : Extruded PET Sheet

Figure 4  Comparison of $E''$ curves for PET Fiber, Drawn PET Film and Extruded PET Sheet
Frequency : 1Hz
- - - - - : PET Fiber
- - - - - : Drawn PET Film
- - - - - : Extruded PET Sheet
Figure 6  Apparent Activation Energy for $\alpha$- and $\beta$-dispersion of PET Fiber

Figure 7  Apparent Activation Energy for $\alpha$- and $\beta$-dispersion of Drawn PET Film

Figure 8  Apparent Activation Energy for $\alpha$- and $\beta$-dispersion of Extruded PET Sheet
Figure 5 shows the $E''$ curves for the 1Hz results in Figures 1 to 3. Similar to the absorption spectrum acquired from spectrometry measurements, the $E''$ curve of the dynamic viscoelastic spectrum also shows energy absorbed by activity. The area of the $E''$ peak is called the relaxation intensity and is proportional to the number of moving molecular units, which cause the energy absorption \(^3\). The relaxation intensity of the $\beta$-dispersion of the extruded PET sheet was higher than that of the PET fiber and drawn PET film. The $\beta$-dispersion is attributed to the local mode relaxation of the amorphous region so this relaxation intensity is proportional to the degree of amorphousness.

The relaxation intensity of the $\alpha$-dispersion is also proportional to the degree of amorphousness but the $\alpha$-dispersion of the extruded PET sheet is affected by the cold crystallization that occurs directly after, which changes the form of the peak. When the different molecular movements such as glass transition and crystallization coexist like this, it is difficult to simply acquire the relaxation intensity and activation energy. A comparison of relaxation intensity shows that the intensity of the drawn PET film is slightly lower of that of the PET fiber. Because the fiber was drawn along a single axis and the film was drawn along dual axes, these samples show the effects of the drawing method on the degree of crystallization. Comparing the $E''$ curves shows that the degree of amorphousness of the three PET products takes the following order from highest to lowest: extruded PET sheet, PET fiber, and drawn PET film.

The apparent activation energy of each dispersion was obtained from the dispersion peaks of the $E''$ curves in Figures 1 to 3. Figures 6 to 8 show the results of the analysis of the apparent activation energy. Comparing the activation energy from the $\beta$-dispersion of each sample shows that the activation energy descended in the following order: drawn PET film, PET fiber, and extruded PET sheet. This indicates that the larger the degree of amorphousness, the easier it is for local mode relaxation to occur. The activation energy for the extruded PET sheet from the $\alpha$-dispersion is overlapped by the aforementioned crystallization and therefore is not a precise value. However, the drawn PET film and the PET fiber definitely react well to the degree of amorphousness and the higher the degree of amorphousness, the more easily $\alpha$-dispersion occurs.

### 4. Conclusion

In this brief, an analysis of PET fibers, drawn PET films and extruded PET sheets found differences in viscoelastic properties. From comparison of the relaxation intensities and the analysis of apparent activation energies, it is surmised that different thermal histories during processing and different molecular chain orientations result in different crystallization states in PET, which in turn produce different viscoelastic properties.

**References**

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2) Application Brief DMS No.9, Hitachi High-Tech Science Corporation (1991)
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