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A Temperature Modulated DSC Study of Glass Transition in Poly(ethylene terephthalate)

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A dynamic heat capacity of poly(ethylene terephthalate) in the temperature range of glass transition has been examined by a new technique of temperature modulated differential scanning calorimetry. The shift of glass transition temperature caused by the desorption of water could be monitored by the change in the dynamic heat capacity. Under quasi-isothermal condition, the increase in the glass transition temperature causes the decrease in the magnitude of the dynamic heat capacity and a negative or positive change in the phase, depending on temperature.

§1. Introduction

Temperature modulated differential scanning calorimetry (TMDSC) applies a sinusoidal temperature modulation to a conventional DSC run and analyzes the response in heat flow.1)-3) The applicability of this technique has been mainly examined to the heat capacity determination during the glass transition (vitrification) of polymeric materials.4)-7) A dynamic heat capacity, $C(\omega) = C' + i\,C''$, has been introduced to describe the frequency response function of heat capacity against temperature modulation, and the following results have been obtained for the behavior on glass transition.6),7) The dynamic heat capacity shows a step like change of C' and a peak of C'' in a temperature range slightly higher than the vitrification temperature determined by the change in the heat flow of a conventional DSC run or in the mean (total) heat flow of TMDSC. The change in the dynamic heat capacity has been explained as a temperature dispersion of an α relaxation process. The technique has been proved to be equivalent to other techniques, e.g., dielectric relaxation, viscoelasticity and AC calorimetry, applicable to relaxation processes. However, TMDSC is not a suitable technique for relaxation processes because it has a limited range of frequency (< 0.05 Hz) owing to the difficulty of the temperature control of the furnace.

In this report, we will be mainly concerned with the time dependent behavior of the dynamic heat capacity in the temperature range of glass transition, instead of discussing the dispersion relation of the α relaxation. TMDSC has its advantage in the capability of heat capacity, $C(\omega)$, determination under quasi-isothermal condition of temperature modulation around a constant temperature. We have examined the dynamic heat capacity of poly(ethylene terephthalate), PET, which is known to absorb water in air at room temperature and desorb at higher temperature. Water is absorbed in PET up to 1% and decreases the glass transition temperature (~ 67°C) by several degrees.8) Therefore, the process of desorption can be monitored by the

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change in the dynamic heat capacity under quasi isothermal condition.

§2. Experimental

The DSC 2920 Module controlled with Thermal Analyst 2200 (TA Instruments) was used for all measurements. The raw data were transferred by a TA RMX Utility to calculate the phase of the dynamic heat capacity from the raw data of modulated sample temperature and of modulated heat flow. The magnitude of the dynamic heat capacity, $|C(\omega)|$, has been determined from the ratio of the amplitude of heat flow, $\widetilde{Q}$, to that of modulated temperature, $\widetilde{T_s}$; $|C(\omega)| \equiv \widetilde{Q}/(\omega\widetilde{T_s})$, after a correction of the absolute value. The sample was an amorphous poly(ethylene terephthalate) film supplied by TOYOBO Co., Ltd. The sample weight was in the range of 14 – 16 mg. It was confirmed that there was no qualitative change by the sample weight in this range. The sample was left for quite long time (> 1 year) in air at room temperature. For quasi-isothermal measurements, the sample temperature was raised from room temperature to 40 – 105°C covering the glass transition of PET. The modulation period of 32s was examined with the modulation amplitude fixed at ±0.2°K.

§3. Results and discussion

Figure 1 shows a typical result of the quasi-isothermal measurements of the change in the total heat flow F (Fig. 1(a)) and the magnitude of the dynamic heat capacity $|C(\omega)|$ (Fig. 1(b)). Near the glass transition temperature, endothermic heat flow always appeared, indicating the desorption of water from the sample (Fig. 1(a)).

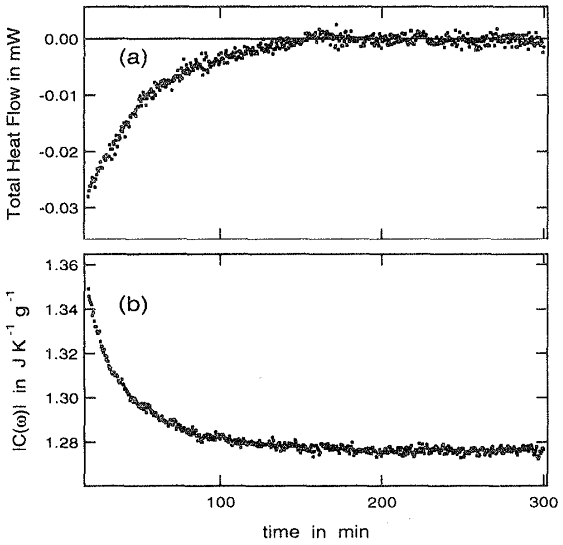

Fig. 1. A typical time sequence of quasi-isothermal measurement: (a) total heat flow F, (b) magnitude of the dynamic heat capacity $|C(\omega)|$. The mean temperature was kept at 70.0°C.

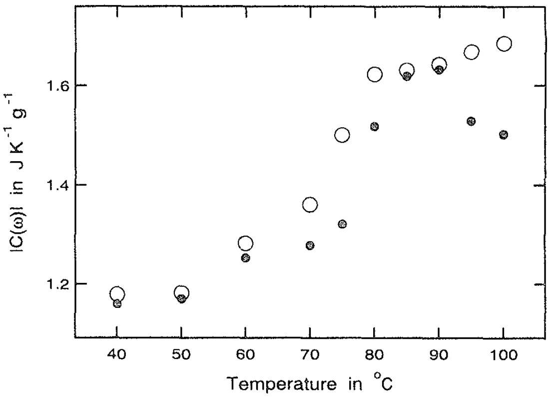

Fig. 2. Plots of the initial (○) and final (●) values of $|C(\omega)|$ obtained at each temperature under quasi-isothermal condition.

Following the change, the magnitude of the dynamic heat capacity showed a monotonous decrease to a constant value at each temperature (Fig. 1(b)). Figure 2 shows the initial and final values of the magnitude plotted against temperature. In this figure, the decrease seen at higher temperature (>90°C) is not due to the water desorption but due to the crystallization of amorphous PET. Finally, Fig. 3 shows the change in the phase of the dynamic heat capacity during the process. The change became negative or positive, depending on temperature.

Figure 4 shows a schematic illustration of the change in the dynamic heat capacity on increasing the glass transition temperature by the desorption of water. It is known that the imaginary part of the dynamic heat capacity, C'', is much less than the real part, C', ($C''/C' < 0.1$) and hence the change in the magnitude, $|C(\omega)|$, is mainly due to the change in the real part. As shown in Fig. 4(a), the decrease in $|C(\omega)|$ of Fig. 1(b) is therefore attributed to the shift of the glass transition to higher temperature. On the other hand, the change in the imaginary part, C'', is related to the change in the phase angle of $C(\omega)$; the negative change in the phase indicates the decrease in C'' and *vice versa.* The changes shown in Fig. 3 agree with the behavior of C'' in Fig. 4(b): negative and positive changes at lower and higher temperatures, respectively.

As a conclusion, the change in glass transition temperature caused by the desorption of water has been examined under quasi-isothermal condition by a new technique of TMDSC. The magnitude of dynamic heat capacity decreased, and the phase change became negative or positive, depending on temperature.

Those types of behavior have been successfully explained as the shift of glass

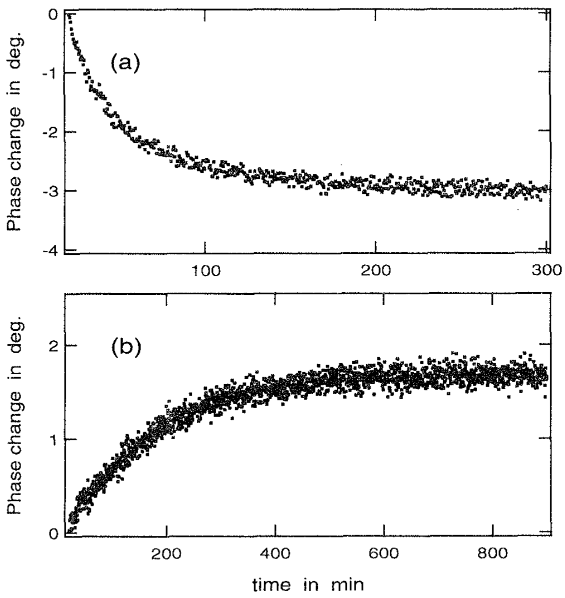

Fig. 3. Time sequences of quasi-isothermal measurements of the change in the phase of the dynamic heat capacity at (a) 70.0 and (b) 80.0°C.

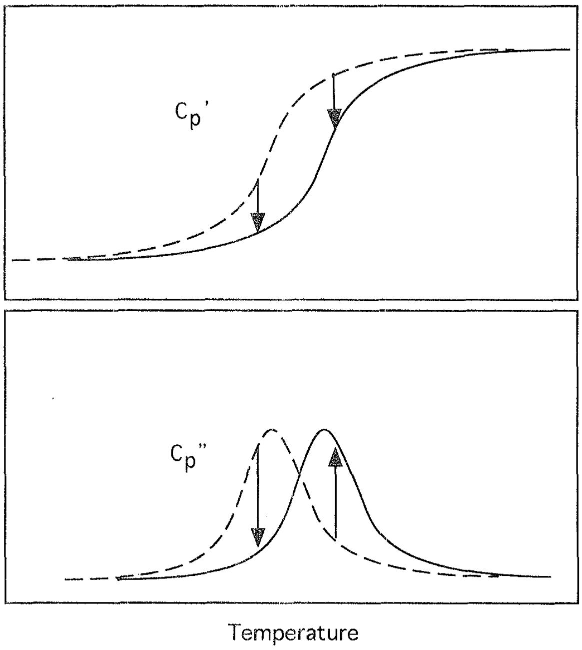

Fig. 4. A schematic illustration of the expected change in C' and C'' by the shift of glass transition to higher temperature: initial (broken) and final (solid) curves.

transition to higher temperature by about 5°C. The desorption of water is a process of diffusion and will be related to the molecular motion of PET, and hence this technique may be a useful tool to study the dynamics of glass transition.

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