Proceedings of Symposium on Ultrasonic Electronics, Vol. 31 (2010) pp. 297-298
6-8 December, 2010

Evaluation of Viscoelasticity of Polymer Films in High-Temperature Region by a QCM-D Method
QCM-D 法による高分子薄膜の高温領域での粘弾性評価

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1. Introduction

Evaluation of property of thin polymer film is very important to use for photoresist coating, surface reforming and protection of substrates, etc. Bulk polymers are examined by mechanical characteristic, viscoelasticity and thermal property of materials from dynamic viscoelastic measurement and thermal analysis, etc. Meanwhile, morphology and structure of thin polymer films have been well studied, but information of viscoelastic properties of thin polymer films is inadequate. In previous works[1,2], we indicated that the QCM-D (Quartz Crystal Microbalance with Dissipation) method is useful to investigate thin polymer films below their melting point. The method is available to estimate the viscoelastic properties of thin polymer films with thickness from several tens of nanometers to micrometer. In this work, we evaluated viscoelasticity of thin films of Polyvinyl chloride (PVC) and Polymethyl methacrylate (PMMA), and the composite in high-temperature region by the QCM-D, as the two polymers form compatible blend.

2. Experimental

QCM-D measurement: the experimental setup was shown in **Fig. 1**. A 5 MHz AT-cut quartz was driven by a signal generator (WF1943, NF ELECTRIC Instruments). The transducer was disconnected from a driving circuit by a relay (G6Z-1PE-A, Omron) controlled by a function generator (FG-272, KENWOOD). The decay curve of the QCM oscillation was recorded on an oscilloscope (DSO3062A, Agelent).

The frequency when the amplitude of decay curve becomes the maximum is defined as the resonant frequency f. the dissipation factor D is related to the decay time constant as

$$D = \frac{1}{\pi f \tau} \quad (1)$$

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For each samples, Δf ($\Delta f = f - f_0$) and ΔD ($\Delta D = D - D_0$) were measured. Δf is the change of resonant frequency. f and f_0 are the resonant frequency in measurement samples and the resonant frequency of the quartz oscillator, respectively. ΔD is the change of dissipation. D and D_0 are the dissipation in measurement and the dissipation of only quartz, respectively.

The temperature was regulated by a heater around the sample cell made of brass involving the quartz crystal. The measurements were carried out in the temperature range from 25 to 200 °C except for PVC films. They were measured from 25 to 170 °C because high-temperature, about 220 °C, induces dehydrochlorination[3].

Sample Preparation: PVC and PMMA with molecular weight of 40,000 and 75,000 were purchased from KANEKA CORPORATION and SCIENTIFIC POLYMER PRODUCTS, INC., and were used as received, respectively. These films were prepared by a casting method from PVC-cyclohexanone and PMMA-benzene solutions at ambient temperature under air atmosphere. Those concentrations were 0.1, 0.3, 0.5, 0.7 and 1.0 wt % (PVC) and 0.3, 0.5 and 0.7 wt% (PMMA).

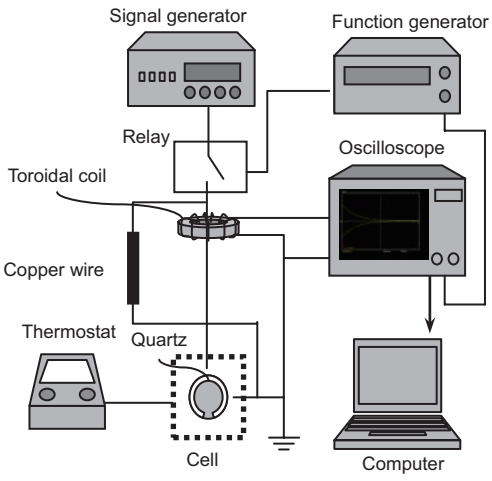

Fig.1 A schematic illustration of the experimental setup

3. Results and Discussion

The temperature dependence of Δf was investigated through three heating processes for the same sample at a temperature change rate of 1 °C /min and the results are shown in **Fig. 2**. When we compared the first process with other processes, we noticed a difference in Δf . It is reasonable to assume that this difference is caused by the evaporation of the residual solvent in the film after casting. Moreover, the quantity of the evaporated solvent measured counts for 17 % of the sample. It was also noticed that this difference is dramatically reduced with increasing the number of processes carried out for the same sample. This result clearly indicates that the residual solvent in the films after casting is almost entirely removed during the first process. Hereafter, we present the results of the second process.

Figures 3 and **4** show the temperature dependence of resonant frequency shifts and dissipation for PVC films. The magnitude of Δf depends on the concentration of PVC solutions. The glass transition temperature (T_g) and melting temperature (T_m) of polyvinyl chloride is around 80 °C and 220 °C, respectively. As the concentration of sample, that is mass of film, increased, the absolute value of Δf increased, because Δf reflects the mass on quartz crystal. The Δf is almost independent of temperature investigated here. The magnitude of ΔD increased with increasing the PVC concentration. In this work, the thicknesses of each PVC films prepared were roughly estimated as 25, 80, 175, 200, and 250 nm, respectively. In the low temperature region below T_g, ΔD was nearly constant, but in the high-temperature region above T_g, ΔD increased significantly. Moreover, the starting point of the change in ΔD decreases with increasing the film thickness and seems to approach to T_g. This is considered to be due to the increase in the thickness and in the fluidity.

About PMMA films, the results of PMMA films indicated similar trends as the PVC's.

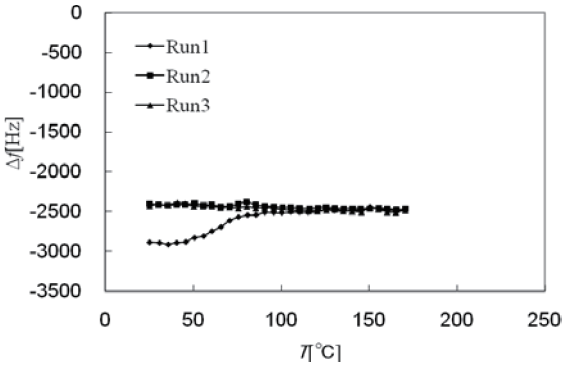

Fig.2 Temperature dependence of Δf of PVC film prepared with 0.5 wt% solution.

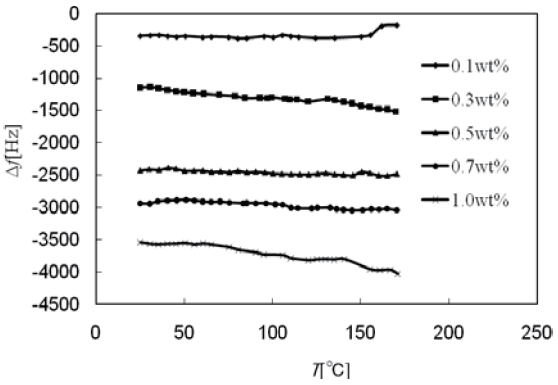

Fig.3 Temperature dependence of Δf of PVC films.

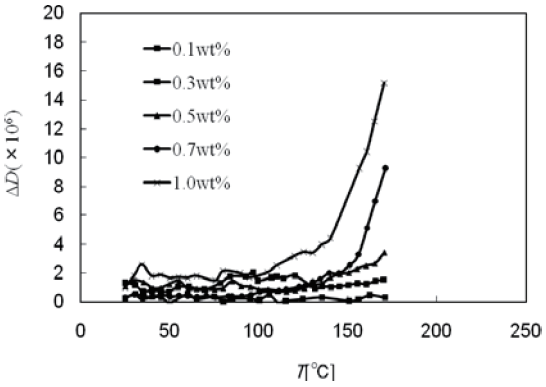

Fig.4 Temperature dependence of ΔD of PVC films.

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