

Evaluation of Viscoelasticity of Polymer Blend Thin Films in High-Temperature Region by a QCM-D Method

QCM-D 法を用いた 2 成分混合系高分子薄膜の高温領域での粘弾性評価

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1. Introduction

In previous works, we indicated that the QCM-D (Quartz Crystal Microbalance with Dissipation) method is useful to investigate polymer thin films below their melting points.^{1,2} The method is available to estimate the viscoelastic properties of polymer thin films with thickness from several tens of nanometers to micrometer. The compatibility of polymer blends strongly influences the mechanical properties of bulk polymers and the films. But there is little information about the compatibility of polymer blend thin film from the viewpoint of nano-rheology. In this work, we evaluated viscoelasticity of thin films of Polyvinyl chloride (PVC), Polymethyl methacrylate (PMMA) and their composites in high-temperature region by the QCM-D, as the two polymers form compatible blend, and then compared their results to viscoelasticity of bulk materials.

2. Experimental

The QCM-D measurement method was mentioned in our previous paper. The square pulses were bifurcated and then used as trigger signals of a digital oscilloscope (Agilent, DSO3062A). The reverberation signals of the quartz crystals driven at resonance (15MHz) were probed by a ferrite toroidal coil used as a current transformer and the signals were recorded on an oscilloscope as digital data. The change in the resonance frequency (Δf) and the dissipation (ΔD) were obtained through analysis of the decay oscillation curve.² $\Delta f (= f - f_0)$ and $\Delta D (= D - D_0)$ were obtained as a function of temperature. f and f_0 are the resonant frequencies of the casting quartz oscillator and the quartz oscillator itself, respectively. D and D_0 are the dissipations of the casting quartz oscillator and dissipation of the quartz only, 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 170 °C because high-temperature, about 220 °C, induces dehydrochlorination of PVC.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., respectively. They were used as received. The blend polymer samples with different volume fractions were prepared. These films were prepared by a spin-coating method (600 rpm) from PVC-cyclohexanone, PMMA-toluene, and PVC/PMMA-tetrahydrofuran solutions at ambient temperature under air atmosphere. Film thicknesses were measured by ellipsometer (PLASMOS SD 2300, Philips Analytical Technology GmbH). The thicknesses for all samples were roughly in accordance with the values estimated from film area and the weight of polymer on the crystal.

3. Results and Discussion

In this research, we measured at least three times for each film and obtained reproducible results. The temperature dependence of Δf and ΔD was investigated through a heating process at a temperature change rate of 1 °C/min.

Figures 1 and 2 show the temperature dependence of resonant frequency and dissipation shifts for PVC, PMMA and PVC/PMMA blend thin films. The thicknesses of these films were 280 nm-PVC/PMMA (100/0), 300 nm-PVC/PMMA (80/20), 280 nm-PVC/PMMA (60/40), 300 nm-PVC/PMMA (40/60), 310 nm-PVC/PMMA (20/80) and 280 nm-PVC/PMMA (0/100), respectively. The value of Δf reflects the mass of films. The Δf of all films were almost independent of temperature investigated here. The magnitude of ΔD increased with increasing the volume fraction of PVC. The value of ΔD was nearly constant in the low temperature region below PVC's and PMMA's T_g , about 80 and 100 °C, respectively. The slightly

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larger value of ΔD with the content of PVC is caused by the low modulus of PVC in comparison with PMMA.⁴ The increase of ΔD started above their T_g in the high temperature region. Moreover, the starting point of the change in ΔD was around 130 °C. This is considered to be due to the increase in the fluidity, since in the high temperature region, the increase in ΔD comes from both the decrease in viscosity and the increase in shear modulus.

Figure 3 shows the temperature dependence of $\tan\delta$ which is called loss tangent. It is also defined as

$$\tan\delta = \frac{G''}{G'}, \quad (1)$$

where G' is storage elastic modulus and G'' is loss elastic modulus; they are real and image part of complex elastic modulus G . The value of $\tan\delta$ of films was calculated using Δf , ΔD and film thickness from the equation of V. Voinova et al.⁵ As well as ΔD , $\tan\delta$ is dependent on temperature and increases significantly with increasing the fraction of PVC. These results are useful to understand the viscoelastic properties of the compatible blend thin films.

4. Summary

The Δf , ΔD , and $\tan\delta$ of PVC/PMMA blend thin films were measured in the temperature range from room temperature to ca. 200 °C by the QCM-D method. This method gives useful information about the viscoelastic properties of polymer blend thin film above glass transition temperature.

References

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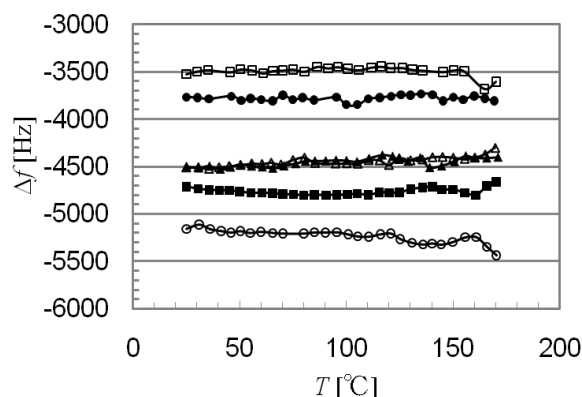


Fig.1 Plots of Δf for PVC, PMMA and PVC/PMMA blend thin films against temperature.

●: PVC/PMMA (100/0), ▲: PVC/PMMA (80/20), ■: PVC/PMMA (60/40), ○: PVC/PMMA (40/60), △: PVC/PMMA (20/80), □: PVC/PMMA (0/100)

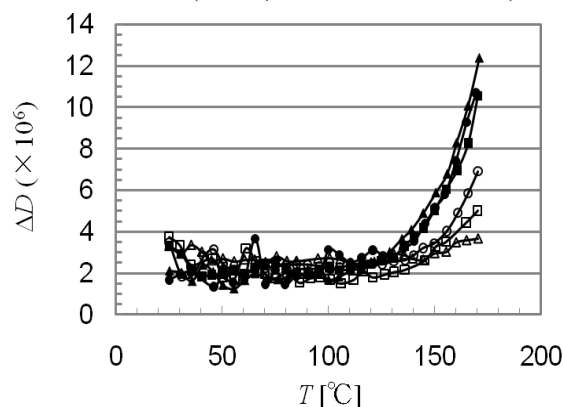


Fig.2 Temperature dependence of ΔD for PVC, PMMA and PVC/PMMA blend thin films.

The symbols are the same as those in Fig. 1.

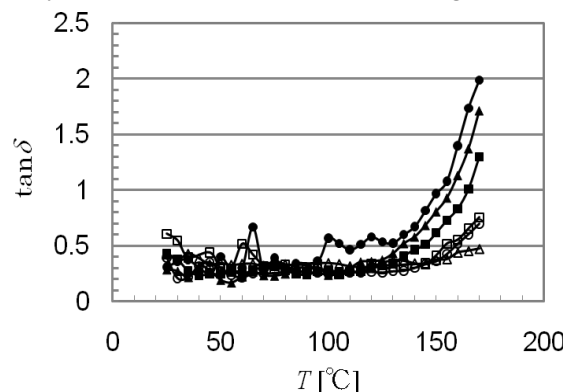


Fig.3 Temperature dependence of $\tan\delta$ for PVC, PMMA and PVC/PMMA blend thin films.

The symbols are the same as those in Fig. 1.