수정진동자를 이용한 PMMA/PVAc 블랜드의 상전이와 상분리현상 해석

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Analysis the Phase Transition and Separation phenomena of PMMA and PVAc Blends by Q.C.A.

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Introduction

The quartz crystal analyzer(Q.C.A) has been known as a sensitive mass detecting device and liquid viscosity monitoring device[1-3]. The equations for the resonant frequency change and the resonant resistance for the quartz crystal with a coating film and the quartz crystal in contact with liquid have been derived from theoretical models[4-6] .

Phase-transition phenomena of liquid crystals, lipid multibilayer films, and Langmuir-Blodgett (LB) films have been studied using the quartz crystal and the surface acoustic wave device. However in the above studies, only the resonant frequency change was measured, but it is not enough to examine the detail of the viscoelastic phenomena.

The importance of studying the viscoelastic phenomena on the coating films has been recommended, especially in the field of the electrochemical analysis to clarify the causes of the resonant frequency change in viscoelastic films. This can be done by measuring the resonant resistance (or admittance intensity) of the quartz crystal with polymer thin films.

In this work, viscoelastic changes on the phase transition and phase separation of the blends of PMMA and PVAc films were studied with the quartz crystal by the in situ measurement of the resonant frequency and the resonant resistance.

The purpose of this paper is , present the applicability of the Q.C.A. for analysis of phase separation and phase transition of PMMA/PVAc blends at its initial state during the solvent (ethyl acetate) evaporation by in situ measuring the resonant frequency and the resonant admittance of PMMA/PVAc blends coated AT-cut quartz crystal and analyzing the viscoelastic characteristics of PMMA/PVAc blend thin films.

Experiment

The brief schematic of experimental setup is shown in Figure 1.

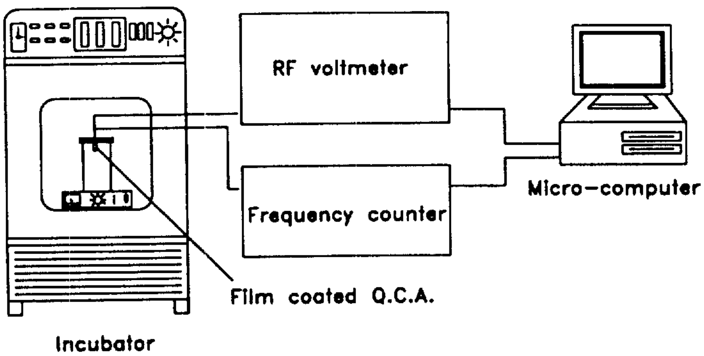

Figure 1. Schematic setup for experiment.

The polymers used in this study were PMMA(Mn= 78,000, Mw= 90,000) and PVAc(Mn=81,000, Mw=110,000). PMMA and PVAc were purchased from Aldrich Chem. Co. Both polymers were characterized by gel permeation chromatography (GPC) and differential scanning calorimeter(DSC) measurements. PMMA/PVAc blend solutions with various blend ratios were prepared by dissolving 3 wt % of total polymers in ethyl acetate. The blend samples are designated as A% blend by weight %. The 30% blend, for instance, denotes that the blend contains 70 wt% of PMMA and 30 wt% of PVAc.

The resonant frequency and resonant resistance (as admittance intensity) change of the quartz crystal in the blend solutions during the evaporation of solvents were measured at 20 ℃. Meanwhile, the solid blend films were prepared by casting the solutions on AT-cut quartz crystal and dried them until to reach constant weight. Glass transition temperature of films were measured by Perkin-Elmer DSC 7 at a heating rate of 10 ℃/min on the second run. In order to investigate the dynamic properties of the final solid films, the resonant admittance of the quartz crystal was measured. The films were heated at a heating rate of 10 ℃/min, quenched at the same cooling rate, and heated again at the same heating rate.

Results and Discussion

The changes of resonant frequency and resonant admittance are different from one another, but cannot be compared directly with each other because of different scales. Normalization is necessary for comparison. Therefore, we normalize the response as A/A_0 and F/F_0.

Figure 2 shows the normalized resonant frequency changes and normalized resonant admittance changes of blend solutions during evaporation . The normalized resonant frequency reduces rapidly after 60 seconds both homopolymers and blends, which means that the mass of the coated film and the viscosity(as admittance intensity) of the coated film increase first and decrease with time during evaporation of ethyl acetate.

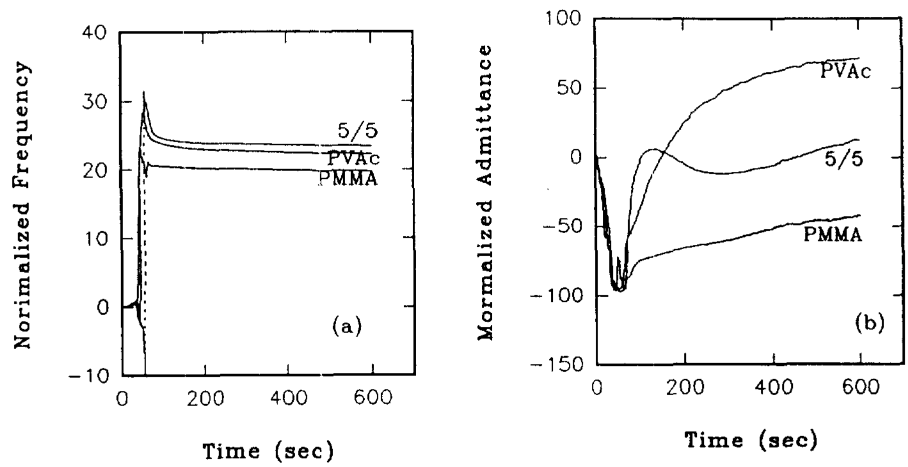

Figure 2. Normalized frequency and admittance with ethyl acetate evaporation.

Figure 3 of resonant frequency(a) and resonant admittance(b) of dried film with temperature swing shows always identical hystersis within the experiment error after second thermal swing. The transition temperature was taken at the inflection point on the resonant admittance as a function of temperature on the second heating runs. The resonant frequency and resonant admittance are measured simultaneously and the mass change and viscoelastic change of the polymer blend thin films are analyzed. The PMMA/PVAc blend cast from ethyl acetate exhibited critical changes of resonant frequency and resonant admittance at during ethyl acetate evaporation and near the Tg point.

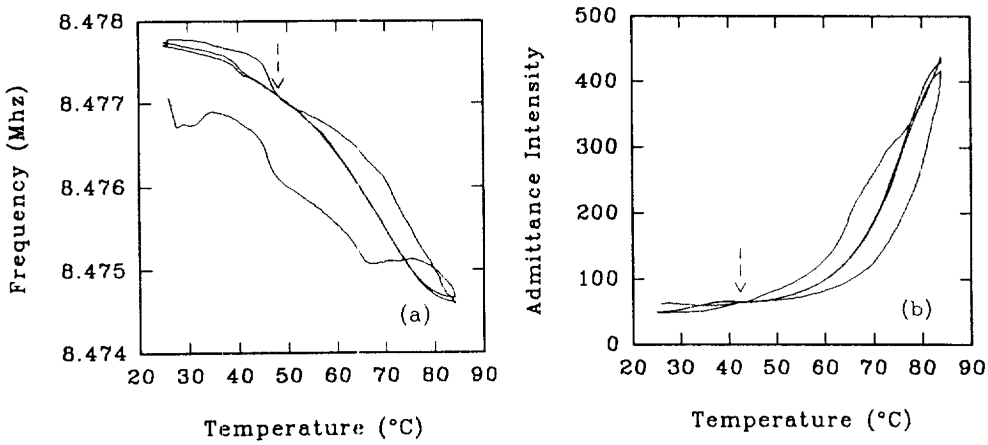

Figure 3. Resonant frequency and admittance by thermal hysterisis.

References

(1) Chang, S.M., Iwasaki, Y., Suzuki, M., Tamiya, E., Karube, I.: *Anal.Chim.Acta*, 249, 323(1991).

(2) Muramatsu, H., Kimura, K.: *Anal.Chem*, 64, 2502(1992)

(3) King, W.H.:*Jr.Anal.Chem*, 36, 1735(1964)

(4) Sauerbrey. G. Z.: *Phyzik* 155, 206(1959).

(5) Muramatsu, H., Tamiya, E., Karube, I.: *Anal.Chem*, 60, 2142(1988).

(6) Kanazawa, K.K,Gordon, J.G.: Anal.Chim.Acta, 175, 99(1985).