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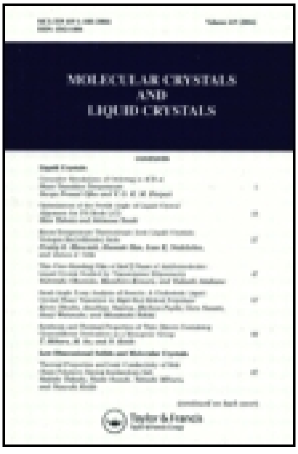

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Analysis of the Phase Change Phenomena of PMMA and PVAC Blends Using Quartz Crystal Analyzer(Q.C.A.)

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ANALYSIS OF THE PHASE CHANGE PHENOMENA OF PMMA AND PVAC BLENDS USING QUARTZ CRYSTAL ANALYZER(Q.C.A.).

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Abstract This paper shows that an AT-cut quartz crystal analyzer can be applied to the phase change study of polymer blend thin films. The phase trasition and phase separation phenomena of blend films of poly (methyl methacrylate) (PMMA) and poly (vinyl acetate) (PVAc) cast from ethyl acetate have been investigated by quartz crystal analyzer(Q.C.A.). The resonant frequency and resonant admittance are measured simultaneously and the mass change and viscoelastic change of the polymer blend thin films are analyzed.

INTRODUCTION

The quartz crystal 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]. A large number of analytical applications in the area of gas sensing, trace ion determination, immunoassay, gelation monitoring, and electro-chemical examinations have been published. 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[8-9].

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 the admittance) of the quartz crystal with polymer thin films.

The purpose of this paper is to 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 solevent evaporation by in situ measuring the resonant frequency and the resonant admittance of PMMA/PVAc blends coated AT-cut quartz crystal.

EXPERIMENTAL

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

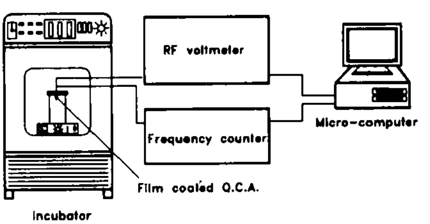

Fig 1. Schematic diagram of measurement system for PMMA/PVAc blend analysis.

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

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(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 (admittance) change of the quartz crystal in the blend solutions during the evaporation of solvents were measured at 20 °C. 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 °C/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 °C/min, quenched at the same cooling rate, and heated again at the same heating rate. The transition temperature was taken at the inflection point on the resonant admittance as a function of temperature on the second heating runs.

RESULTS AND DISSCUSSION

Figure 2 shows the normalized resonant frequency and resonant admittance changes of blend solutions during evaporation . Two homopolymers and 50 % blend are shown for comparison. The normalized resonant frequency reduces rapidly after about 60 seconds for both homopolymers and polymer mixture, which means that the mass of the coated film and the viscosity of the coated film increase first and decreases with time during evapoation of ethyl acetate. The normalized resonant resistance in terms of the admittance inductance initially decreases but increases with solvent evaporation time lapse. Of interesting is that the rate of the decrease of the normalized resonant admittance is decreased in the order PMMA, 50 % blend, PVAc. The result implies that the resonant admittance is closely related to the relaxation or the mobility of polymer chains. The higher normalized resonant admittance of PMMA as compared to PVAc is attributed to the lower mobility of the former homopolymer in the solution state because of its higher glass transition temperature(about 100 °C) than that of PVAc(37 °C). The result means that there is some molecular interaction between each homopolymer at the initial stage of the evaporation process, since PVAc chain having lower glass transition temperature can inter-mix with PMMA chain at lower polymer concentration in the solution state, resulting in the increase in the viscosity and thus increase in the resonant admittance.

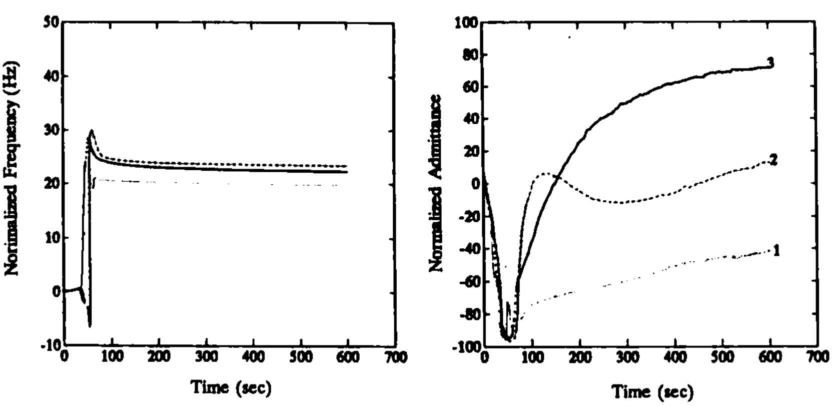

Fig 2. Normalized frequency and admittance shift of PMMA/PVAc blends coated Q.C.A. durig ethyl acetate evaporation.(1. PMMA, 2. PVAc 50%, 3. PVAc).

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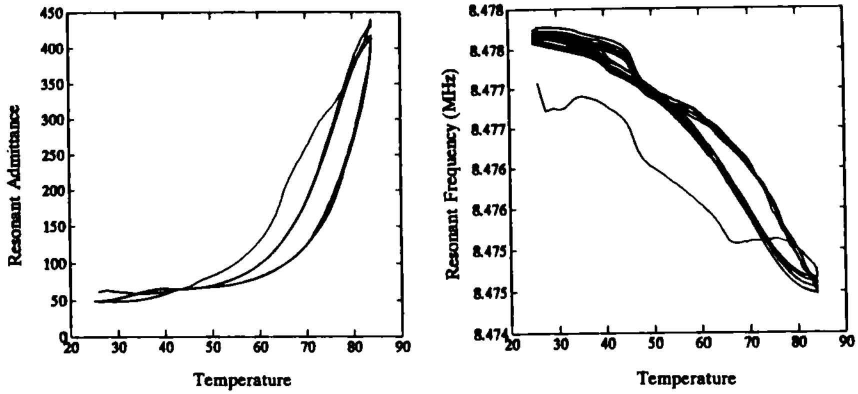

Fig 3.Characteristics change of 50% PVAc coated Q.C.A. with temperature (°C).

Figure 3 of resonant admittance and resonant frequency changes of dried film with temperature swing. Figure 3 showes always identical hystersis within the experiment error after second thermal swing. Thus, we took the inflection point on the second heating cycle as phase transition temperatures. Similar data on the second heating cycle are taken for the other blend films, respectively. It should be noted that there is some correspondance between the glass transition temperatures on DSC and the transition temperatures on Q.C.A., although certain extent differences between values.

CONCLUSIONS

This paper shows that an AT-cut quartz crystal analyzer can be applied to the micro-rheological study of polymer blend thin films. The phase trasition and phase separation

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phenomena of blend films of PMMA and PVAc cast from ethyl acetate have been investigated by (Q.C.A.). 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 evaporational and near the Tg point.

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