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Author(s)	Yamaguchi, Masayuki; Masuzawa, Kenji
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Description	

**Birefringence Control for Binary Blends of
Cellulose Acetate Propionate and Poly(Vinyl Acetate)**

Masayuki Yamaguchi and Kenji Masuzawa

**School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN**

Corresponding to

Masayuki Yamaguchi
Japan Advanced Institute of Science and Technology
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN
Phone +81-761-51-1621, Fax +81-761-51-1625
e-mail m_yama@jaist.ac.jp

ABSTRACT:

Structure and optical properties for binary blends composed of biomass-based cellulose acetate propionate (CAP) and poly(vinyl acetate) (PVAc) have been studied. It is found that the blends exhibit high level of transparency, although the dynamic mechanical analysis in the solid state suggests that phase separation occurs in the blend. Furthermore, the birefringence resulting from molecular orientation decreases with increasing the content of PVAc. In particular, the blend with approximately 50 wt% of PVAc exhibits no birefringence even after stretching.

Key words: biomass-based polymer; rheological properties; optical properties

INTRODUCTION

Biomass-based plastics have attracted great attention of a lot of scientists because of the growing interest in global environment [1]. The current research target of the biomass-based plastics is not only for the replacement from conventional plastics produced from fossil resources but also for the development of new functional materials. For example, an artificial bone has been developed utilizing good biocompatibility and piezoelectricity of poly(lactic acid) [2,3]. Further, the application to biological nitrogen removal at water-purification process is currently studied employing poly(3-hydroxybutyrate) because of the excellent biodegradability, which occurs even in an anaerobic condition [4-7].

Another famous functional material from biomass-based plastics is the protect film for a polarizer, which has to be free from birefringence and is employed for liquid crystal displays. Currently, triacetyl cellulose (TAC) is mainly employed in this application because of the appropriate hygroscopic property and excellent heat resistance. The protect film is produced by the solvent-casting method in the industry, because (1) the birefringence resulting from molecular orientation has to be avoided, and (2) the melting point of TAC is higher than the decomposition temperature, which prohibits the conventional processing techniques, such as extrusion and injection-molding. From the viewpoints of the cost-performance, however, it is desired to produce the protect film by a T-die extrusion technique. For the purpose, various material-designs have been proposed to diminish the orientation birefringence. Hahn and Wendorff found that a miscible blend composed of poly(methyl methacrylate) PMMA and poly(vinylidene fluoride) PVDF with a specific blend ratio exhibits no birefringence even though the molecular orientation occurs, because the sign of intrinsic birefringence of PMMA is opposite to that of PVDF [8]. Further, Saito and Inoue demonstrated 10 miscible polymer pairs having no birefringence [9]. Furthermore, Iwata et al. have developed the random copolymerization method, in which one monomer has the opposite polarizability anisotropy to the other and obtained the “zero-birefringence” polymer [10,11]. Moreover, Tagaya et al. established another method to prepare the

“zero-birefringence” polymer by adding rod-like molecules having opposite polarizability anisotropy to that of a host polymer in order to compensate the orientation birefringence, which is called as “anisotropic molecule dopant method” [12,13].

In spite of the numerous efforts, almost all of the protect film in the industry is still produced by the solvent casting method employing TAC, because TAC film has a lot of attractive properties besides “zero-birefringence”. Considering the industrial application, another cellulose-derivative, *i.e.*, cellulose acetate propionate CAP, is employed in this study, because various properties of CAP, such as transparency, refractive index and the dispersion, hygroscopic property, and heat resistance, are quite similar to those of TAC. Further, the extrusion technique is available for CAP, which is different from TAC. Moreover, poly(vinyl acetate) (PVAc) is employed as the blend polymer in this study, because the sign of the intrinsic birefringence is negative while that for CAP is positive. Furthermore, it has been known that PVAc has a similar solubility parameter to CAP, because both CAP and PVAc are miscible with poly(3-hydroxybutyrate) [7,14-19].

EXPERIMENTAL

Materials

Raw materials employed in this study are cellulose acetate propionate (CAP) (Eastman Chemical, CAP-482-20; 2.5% of acetyl, 46.0% of propionyl, and 1.8% of hydroxyl) and two types of poly(vinyl acetate) (PVAc) (Aldrich) with different molecular weights, *i.e.*, PVAc-H for high molecular weight PVAc and PVAc-L for low molecular weight one. The molecular weights of the samples were evaluated by a gel permeation chromatograph, GPC, (Tosoh, HLC-8020) with TSK-GEL® GMHXL, in which chloroform was employed as eluant at 40 °C at a flow rate of 1.0 ml/min. The sample concentration was 1.0 mg/ml. The number- and weight-average molecular weights as a polystyrene standard are as follows: $M_n = 7.7 \times 10^4$ and $M_w = 2.0 \times 10^5$ for CAP; and $M_n = 5.4 \times 10^4$ and $M_w = 1.7 \times 10^5$ for PVAc-L; and $M_n = 7.8 \times 10^4$ and $M_w = 3.4 \times 10^5$ for PVAc-H.

In order to avoid hydrolytic degradation and transesterification reaction, CAP pellets were dried in *vacuo* at 120 °C for 24 h and PVAc pellets at 40 °C for 24 h, prior to melt mixing. Then, CAP and PVAc were blended by a 60 cc internal batch mixer (Toyoseiki, Labo-Plastomill) with various blend ratios at 200 °C. The blade rotation speed was 30 rpm and the mixing time was 5 min. In this study, the effect of mixing time was investigated at first. It was found that the sample obtained by prolonged mixing, *i.e.*, 15 min-mixing, has the same characteristics as that by 5 min-mixing, which were confirmed by GPC, dynamic mechanical analysis, and Fourier-transfer infrared spectroscopy. This result suggests that neither hydrolytic degradation nor transesterification reaction takes place dominantly.

The samples obtained by 5 min-mixing were compressed into a flat sheet with 1.0 mm thickness by a compression-molding machine (Tester sangyo, table-type-test press SA-303-I-S) for 5 min at 200 °C under 10 MPa and subsequently plunged into an ice-water bath.

Measurements

The frequency dependence of oscillatory shear moduli in the molten state, such as storage modulus G' and loss modulus G'' , was measured by a strain-controlled cone-and-plate rheometer (UBM, MR-500) at 200, 220, and 240 °C under a nitrogen atmosphere.

The temperature dependence of oscillatory tensile moduli in the solid state, such as storage modulus E' and loss modulus E'' , was measured from -100 to 170 °C using a dynamic mechanical analyzer (UBM, E-4000). The frequency and heating rate used were 10 Hz and 2 °C/min, respectively. The rectangular specimen, in which the width is 3.0 mm, the thickness is 1.0 mm, and the length is 15 mm, was employed.

The refractive index of CAP and PVAc was evaluated by Abbe refractometer (Atago, NRA 1T) employing a thin film at room temperature.

The optical transparency of the plaque with 1.0 mm thickness was evaluated at room temperature by a haze machine (Toyoseiki, Direct Reading Haze Meter). Haze is

defined as the percentage of total transmitted light passing through the specimen that is scattered from the incident beam by more than 2.5 degree.

The birefringence of the oriented film was evaluated by an optical microscope with a tilting compensator (Leica, Tilting Compensator B). The oriented films were prepared by stretching the rectangular sample at a stretching rate of 1.0 mm/min in the dynamic mechanical analyzer. The initial distance between the clumps is 10 mm. The hot-drawing was carried out at the temperature when the tensile storage modulus is 100 MPa at 10 Hz. The stretched sample was quenched immediately by blowing cold air in order to avoid relaxation of molecular orientation.

RESULTS AND DISCUSSION

Viscoelastic Properties

Figure 1 exemplifies the frequency dependence of oscillatory shear moduli in the molten state for CAP, PVAc-H, and CAP/PVAc-H (70/30) blend at 200 °C. Both G' and G'' for the blend are found to be intermediate between those of the individual pure components. Further, there seems to be no shoulder peak in the G' curve, suggesting that entanglement slippage is the longest relaxation mechanism. Moreover, G'' is proportional to the frequency in the lower frequency region for all samples. Therefore, the zero-shear viscosities at 200 °C are evaluated as follows; 1.3×10^4 (Pa s) for CAP, 8.7×10^3 (Pa s) for CAP/PVAc-H (70/30), and 1.4×10^3 (Pa s) for PVAc-H.

Furthermore, it is found that the principle of time-temperature superposition is applicable for CAP/PVAc-H (70/30) blend in the temperature range between 200 and 240 °C as shown in Figure 2. This result suggests that molecular aggregation state is unchanged in this temperature range.

[Figure 1] [Figure 2]

Figure 3 shows the temperature dependence of oscillatory tensile moduli in the solid state for CAP, PVAc, and the blends. Since both CAP and PVAc are amorphous

materials with different glass transition temperatures, E' drops off sharply at the glass transition temperatures; 145 °C for CAP and 40 °C for PVAc.

[Figure 3]

It is obvious from the figure that CAP shows lower E' than PVAc in the low temperature region, *i.e.*, in the glassy region. Above the glass transition temperature of PVAc, CAP exhibits higher modulus due to high T_g .

As for the blends, E' decreases around at T_g of PVAc and falls off sharply at T_g of CAP. Correspondingly, there appear apparent double peaks in the E'' curve in the temperature region between the glass transition temperatures of the individual pure components. These dynamic mechanical spectra indicate that phase separation occurs in the blends, which is contrary to the rheological properties in the molten state. This result suggests that phase separation will take place during cooling or the size of phase separation in the molten state is too small to be detected by the rheological analysis. A similar result has been reported for binary blends of CAP and poly(epichlorohydrin) recently [20,21]. Further, it is found that the molecular weight of PVAc has no effect on the morphology as seen in Figures 2(b) and 2(c). Moreover, the peak temperature of E'' located at the higher temperature is found to be lower than that for the pure CAP, and vice versa. The phenomena demonstrate that both materials are dissolved into each other to some degree. Furthermore, considerable effort has been paid to observe phase-separated structure by means of a scanning electron microscope, a transmission electron microscope, and an atomic force microscope for the better understanding of the morphology in the solid state in detail. However, phase separation has not been detected by the microscopic methods until now.

Optical Properties

Transparency is considerably important for optical applications including the protect film. Figure 4 shows the haze value of the plaques with 1 mm thickness. As seen in the figure, the haze of the blends is as low as that of the pure CAP, demonstrating that

the blends exhibit excellent transparency although dynamic mechanical properties indicate phase separation. Further, the transparency is independent of the molecular weight of PVAc.

[Figure 4]

The refractive indexes of the polymers employed are measured by an Abbe refractometer. The results are as follows; 1.4738 for CAP and 1.4651 for PVAc at room temperature. The small difference in the refractive index and the small size of phase separation with some degree of mutual dissolution will be responsible for the transparency of the blends.

Birefringence

Figure 5 shows the orientation birefringence as a function of draw ratio. As increasing the stretching ratio, the absolute value of birefringence increases monotonically and the slope of the birefringence decreases with the stretching ratio for CAP and PVAc-H. The decrease in the slope is attributed to the relaxation of molecular orientation during stretching. Furthermore, the absolute value of birefringence for CAP is found to be almost the same as that for PVAc-H.

[Figure 5]

It should be noted that the birefringence of the blends is between those of the pure components. In particular, the drawn film containing 50 wt% of PVAc-H exhibits no birefringence irrespective of the draw ratio.

Figure 6 shows the orientation birefringence at a stretching ratio of 2.0. The figure demonstrates that the blends with PVAc-L exhibit larger birefringence than those with PVAc-H. This would be attributed to the difference in relaxation of molecular orientation. Since PVAc-L chains relax the orientation faster than PVAc-H, CAP chains in the CAP/PVAc-L blends have more dominant effect on the birefringence resulting

from the molecular orientation. Consequently, molecular weight of each component as well as the volume fraction determines the orientation birefringence. Of course, the birefringence depends on the draw ratio except for the “zero-birefringence” polymer. This will be important information on the material design of “zero-birefringence” polymer.

[Figure 6]

CONCLUSION

Structure and optical properties, especially birefringence resulting from molecular orientation, have been studied for binary blends of CAP and PVAc. Although dynamic mechanical analysis suggests phase separation, the blends show high level of transparency, which is as good as the pure CAP. Further, the blends show low level of birefringence even after stretching. In particular, the blend with a specific CAP/PVAc ratio exhibits no orientation birefringence. Moreover, the effect of molecular weight of PVAc is also investigated in this study. It is found that the blends with low molecular weight PVAc show larger birefringence than those with high molecular weight one. This would be attributed to the difference in the relaxation of molecular orientation.

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Figure Captions

- Figure 1 Frequency dependence of (a) shear storage modulus and (b) loss modulus for CAP, PVAc-H, and CAP/PVAc-H (70/30) at 200 °C.
- Figure 2 Master curves of frequency dependence of oscillatory shear moduli for CAP/PVAc-H (70/30) measured at (circle) 200 °C, (diamond) 220 °C, and (triangle) 240 °C. The reference temperature is 200 °C.
- Figure 3 Temperature dependence of oscillatory tensile modulus for CAP, PVAc, and the blends at 10 Hz; (a) storage modulus E' for CAP/PVAc-H, (b) loss modulus E'' for CAP/PVAc-H, and (c) loss modulus E'' for CAP/PVAc-L; (open circle) CAP, (closed circle) CAP/PVAc (70/30), (open triangle) CAP/PVAc (50/50), (closed triangle) CAP/PVAc (30/70), and (open square) PVAc.
- Figure 4 Haze values of CAP/PVAc blend; (open circle) CAP/PVAc-L and (closed circle) CAP/PVAc-H.
- Figure 5 Birefringence of the drawn film plotted against draw ratio; (open circle) CAP, (closed circle) CAP/PVAc-H (70/30), (open triangle) CAP/PVAc-H (50/50), (closed triangle) CAP/PVAc-H (30/70), and (open square) PVAc-H.
- Figure 6 Birefringence of the film drawn at a draw ratio of 2 as a function of the PVAc content in the blend; (open circle) CAP/PVAc-L and (closed circle) CAP/PVAc-H.

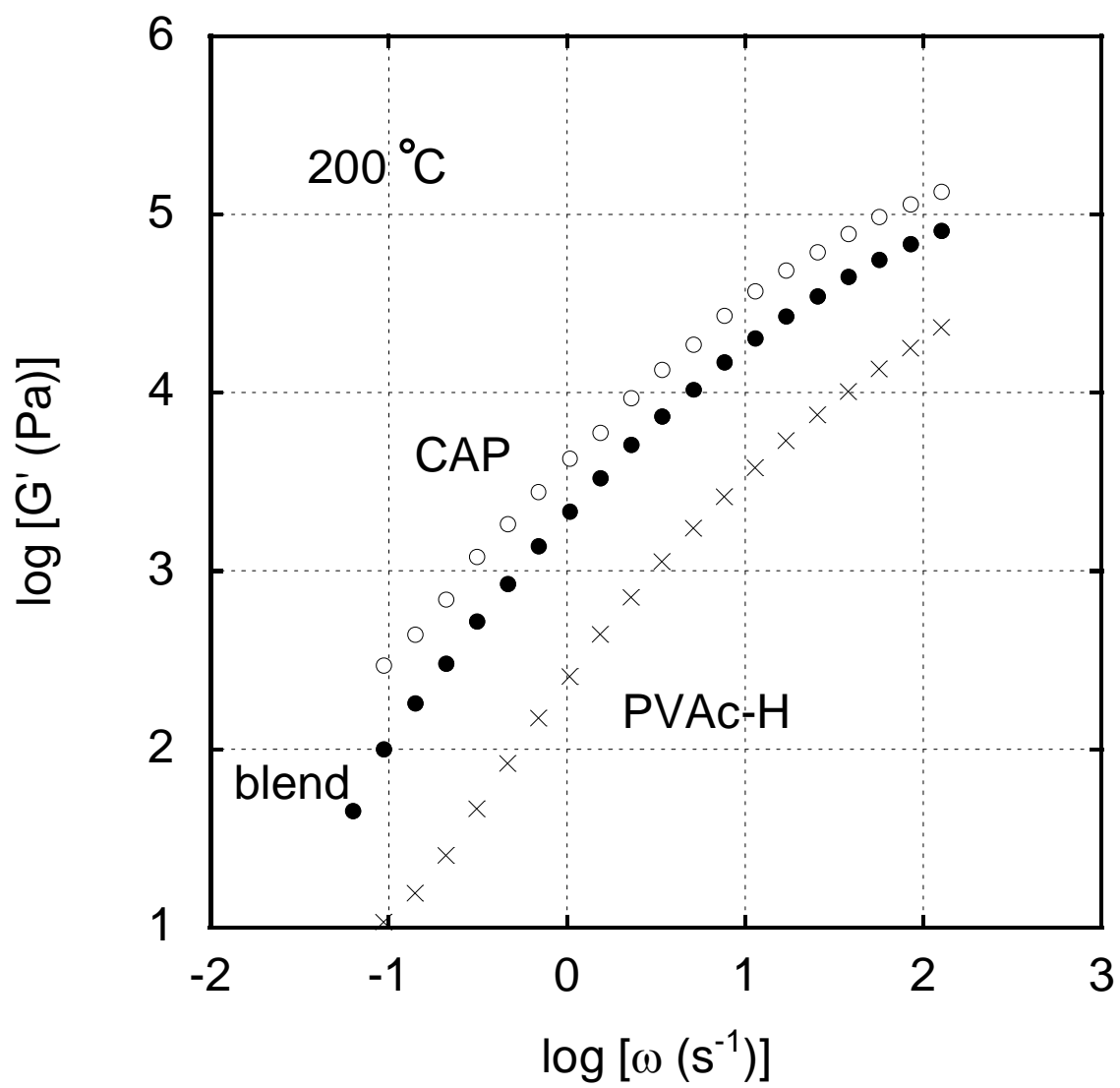


Figure 1(a)

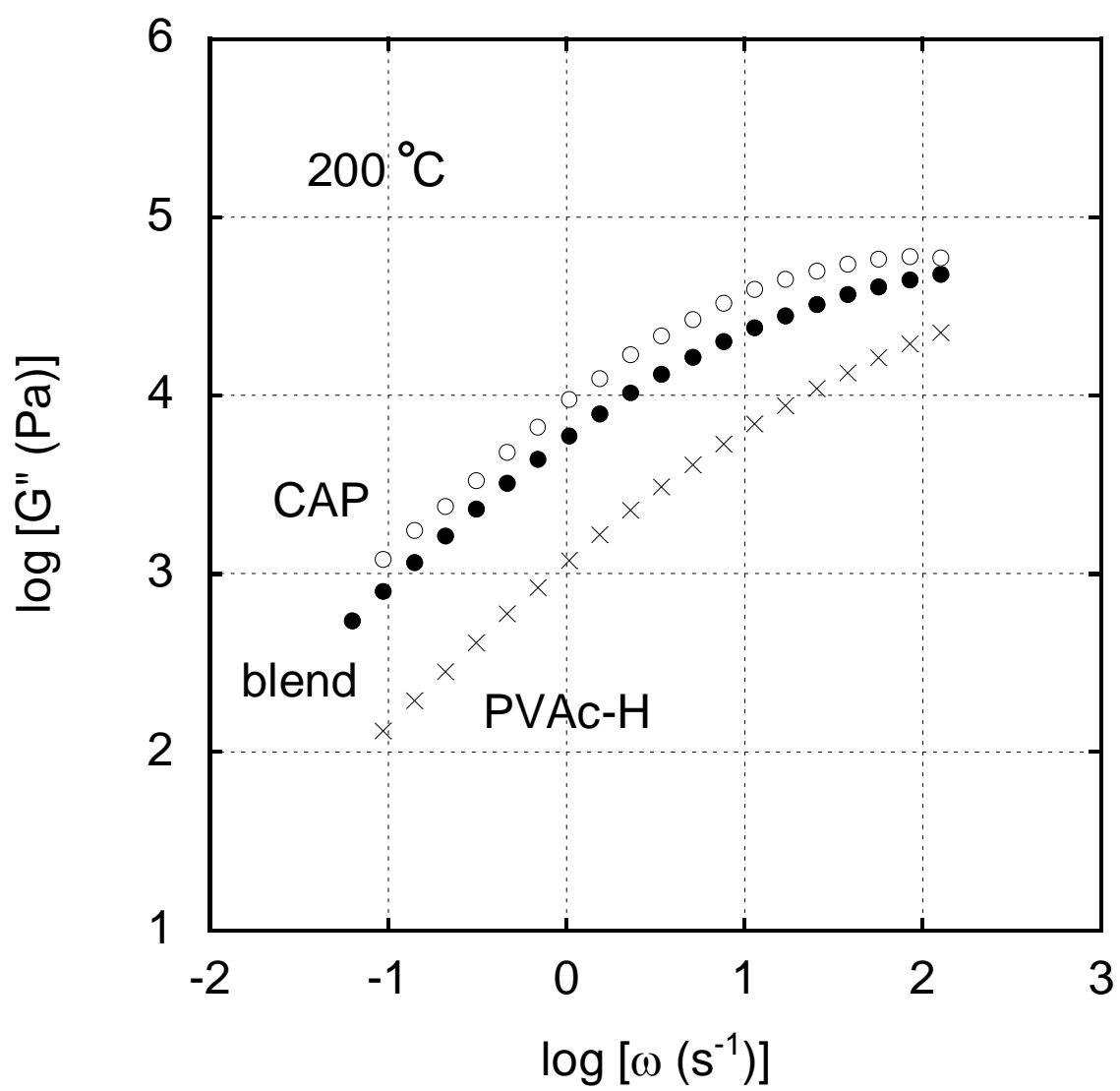


Figure 1(b)

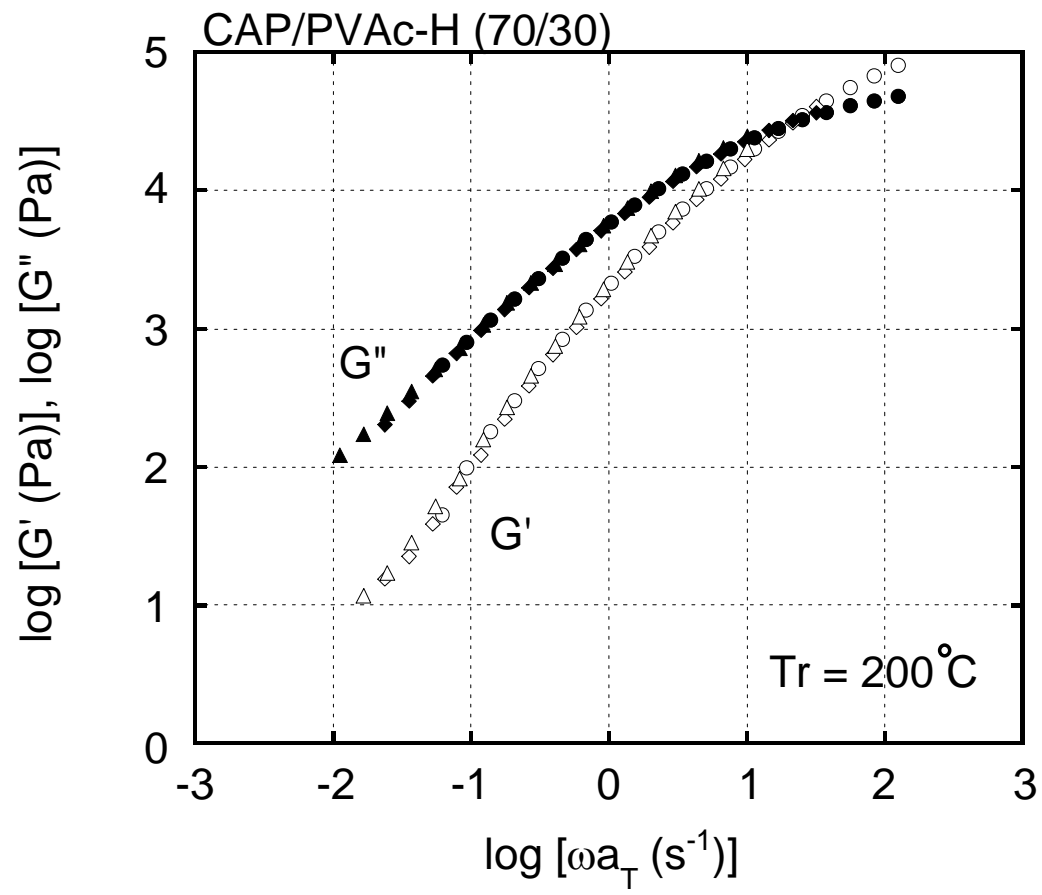


Figure 2

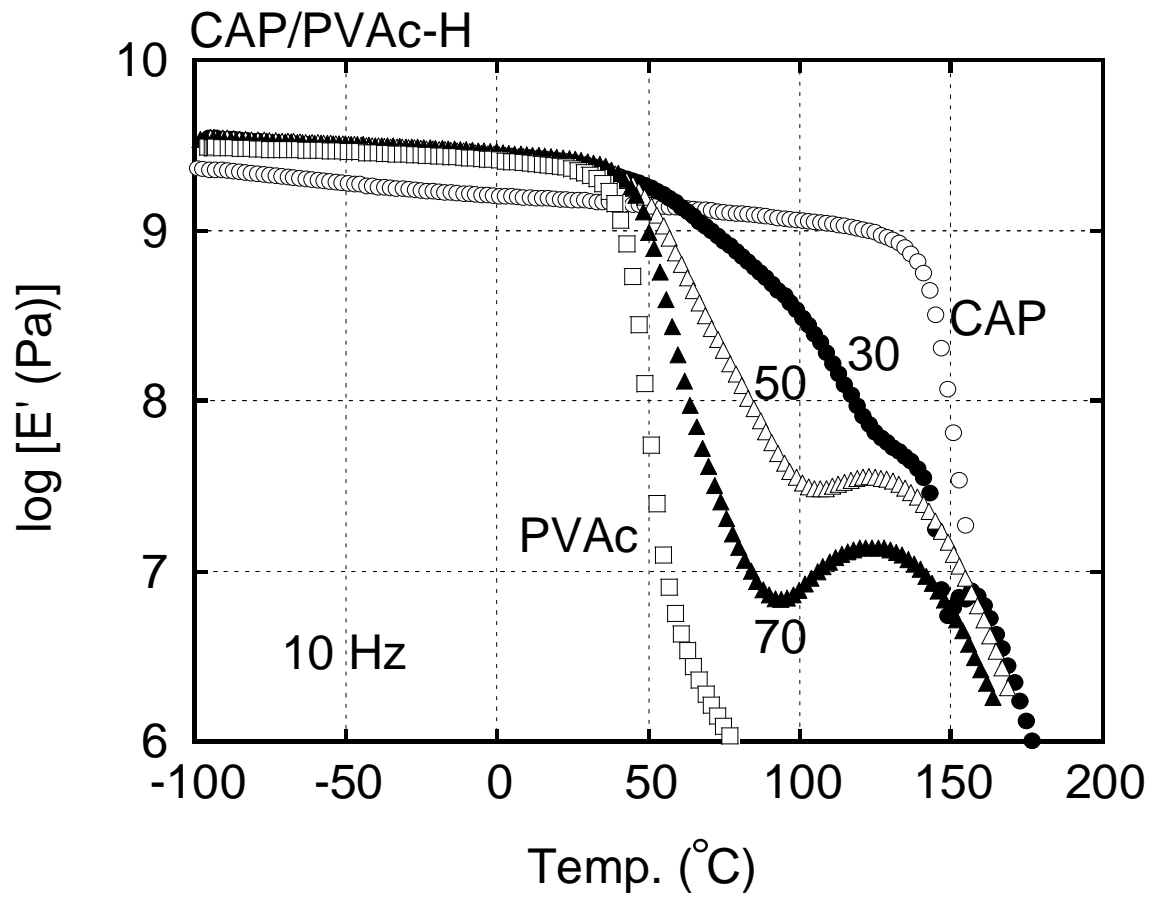


Figure 3(a)

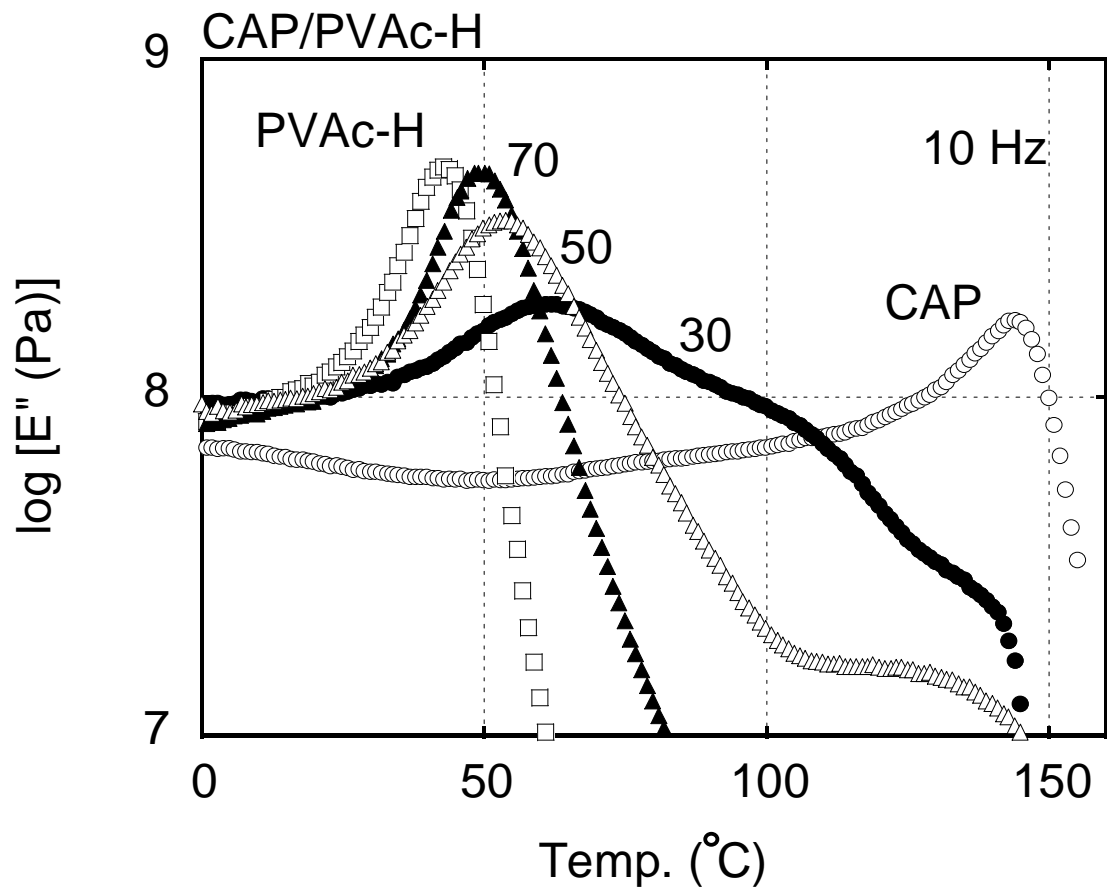


Figure 3(b)

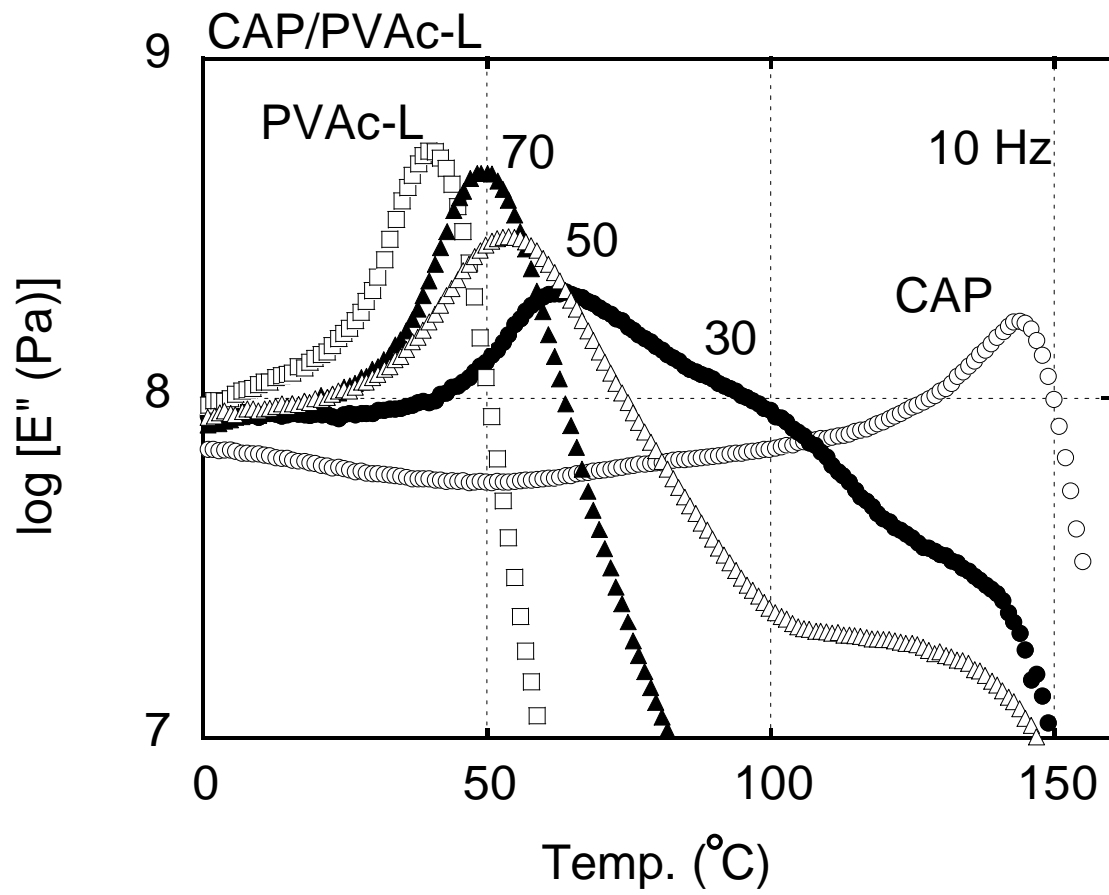


Figure 3(c)

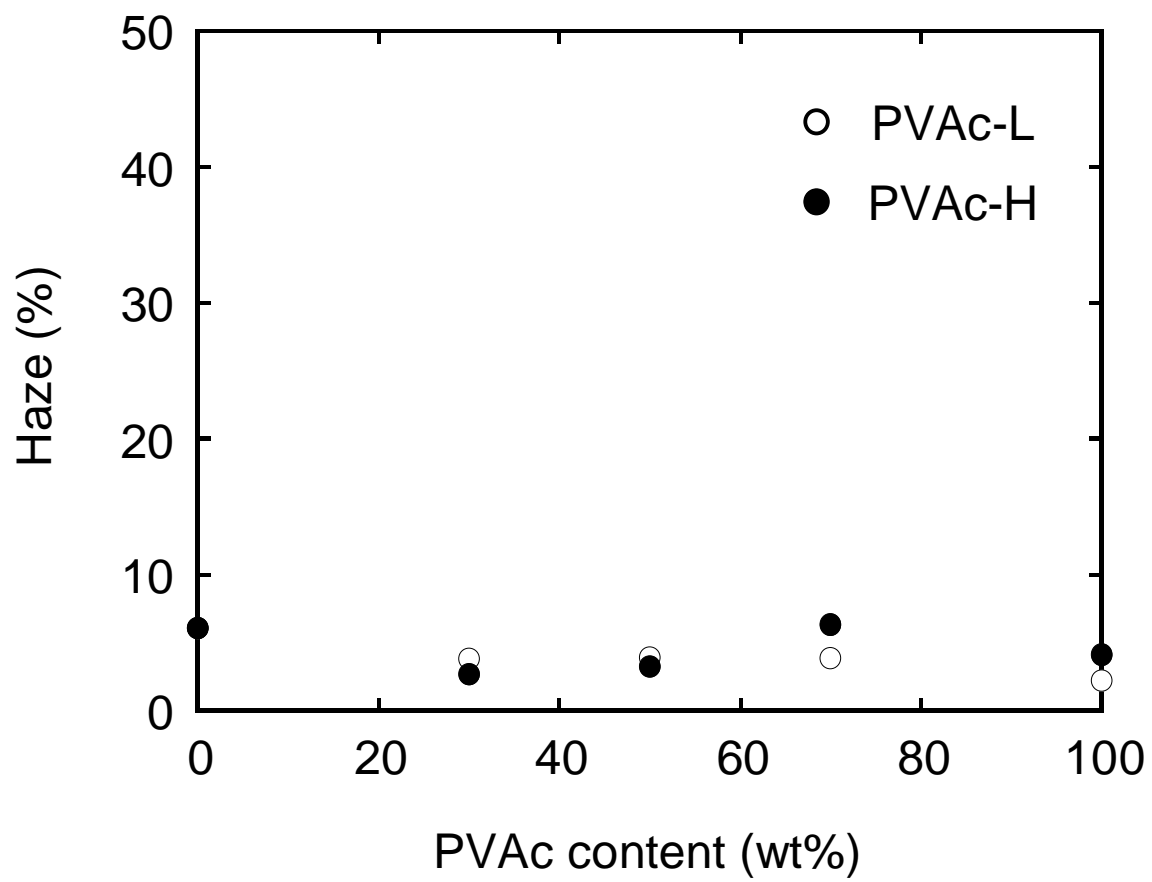


Figure 4

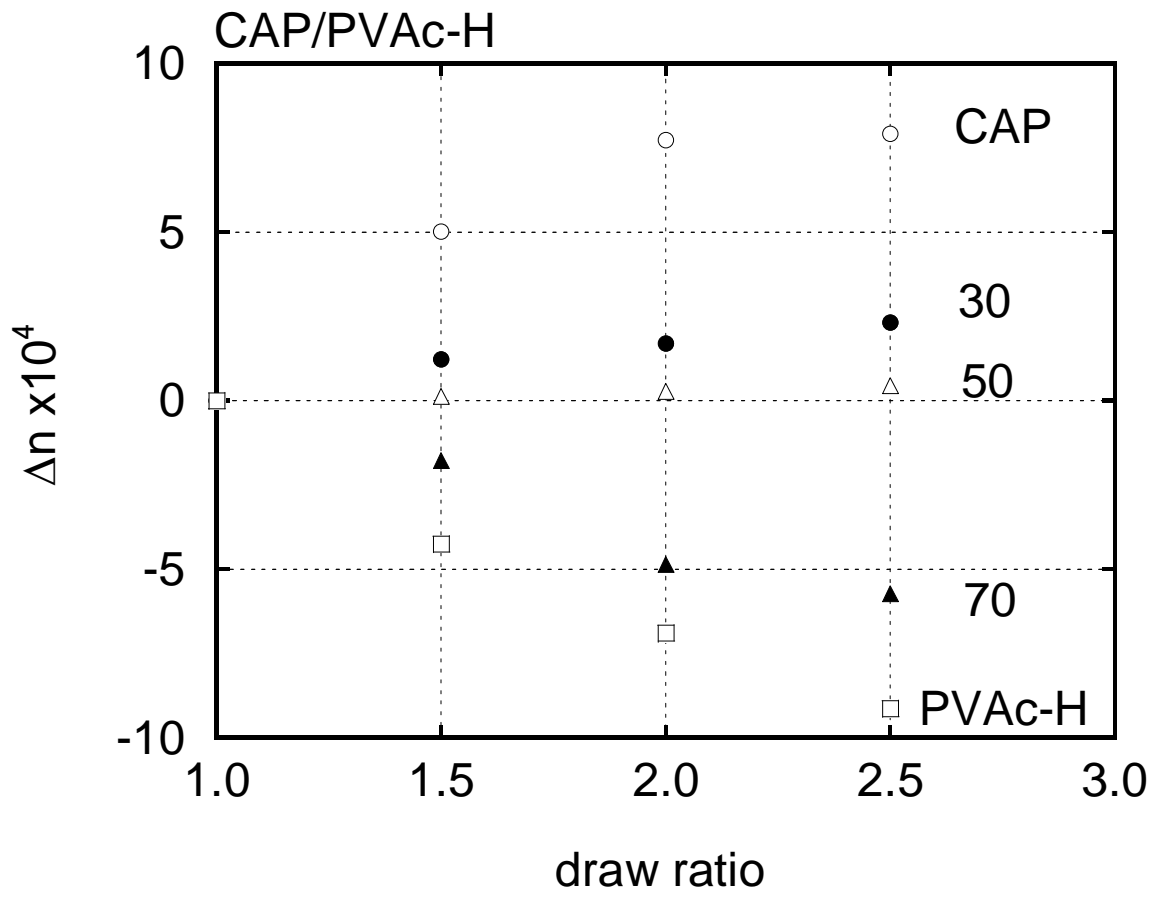


Figure 5

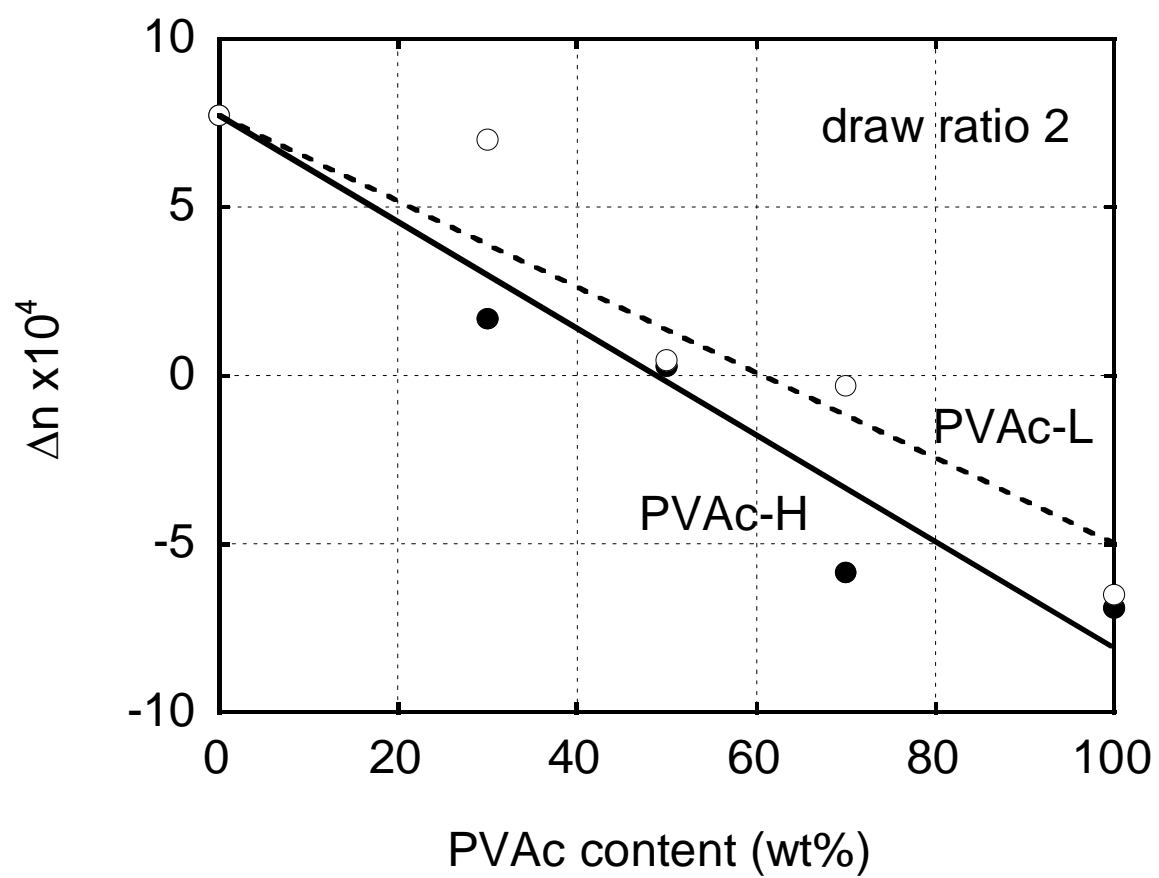


Figure 6