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Description	

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Transparent Polymer Blends Composed of Cellulose Acetate Propionate and Poly(epichlorohydrin)

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ABSTRACT:

Structure and properties for binary blends composed of biomass-based cellulose acetate propionate (CAP) and poly(epichlorohydrin) (PECH) have been studied. It is found from the dynamic mechanical measurements that mutual dissolution takes place to some degree with remaining CAP-rich and PECH-rich regions in the blends. As a result of the interdiffusion, leading to fine morphology, the blends exhibit high level of optical transparency although the individual pure components have different refractive index. Furthermore, the mechanical toughness of CAP, which is one of the most serious problems for CAP, is considerably improved by blending PECH. This will have a great impact on industries because the blend technique widens the application of CAP.

Key words: blends; cellulose acetate propionate; miscibility; rheology; mechanical properties

INTRODUCTION

Because of the rapid growth of the global attention to the environment, biomass-based polymers have been focused to a great extent these days. Although natural rubber and natural fibers, known as biomass-based polymers, already have a huge market, there are quite a few consumptions in the field of plastic industry. Consequently, considerable studies have been carried out these days on biomass-based semi-crystalline polymers, such as poly(lactide), poly(3-hydroxybutyrate), and poly(butylene succinate) (Doi and Steinbuchel 2002; Yamaguchi and Arakawa 2006; Arakawa et al. 2007). The final target of these studies is to find out various applications in the replacement of conventional crystalline polymers, such as polyethylene and polypropylene. Meanwhile, there are few studies on glassy polymers from biomass, although glassy polymers from fossil resources have a huge market. Cellulose derivatives, such as cellulose triacetate (CTA), cellulose acetate propionate (CAP), and cellulose acetate butyrate, are transparent glassy polymers (Edgar et al. 2001). Recently, Glasser (2004) summarized the prospects for future application of cellulose-derivatives based on numerous reports. In particular, CAP shows high level of heat resistance, which is comparable with polycarbonate, with an excellent light transmittance. Further, it can be manufactured by various processing methods, such as extrusion and injection-molding, which is quite different from CTA. For the better understanding the processability, Pecorini (1997) studied the fundamental rheological and thermal properties of CAP and the blends with plasticizer. Furthermore, it has been proposed that nanocomposites with layered silicate have a great possibility to improve the various properties (Ray and Bousmina 2005). These advantages make CAP as a candidate of a future glassy polymer instead of conventional ones from fossil resources. As often happen to a glassy polymer, however, CAP shows poor mechanical properties, especially low level of toughness (Pecorini 1997; Brydson 1999). Therefore, reinforcement by rubbery materials has been desired to widen the application.

Regarding the miscibility of CAP with other polymers, Buchanan et al. (1993) have carried out pioneering works. They clarified that some polyesters are miscible with CAP, such as poly(tetramethylene glutarate) and aliphatic polyester composed of dicarboxy acid with C5 and diol with C2 – C6. Furthermore, Waniczek et al. (1985) showed aliphatic polyester is miscible with CAP. Finally, Tatsushima et al. (2005) proved that CAP is miscible with poly(caprolacton), poly(3-hydroxybutyrate), and poly(butylene succinate). As exemplified here, there have been few reports on the blends of CAP with rubbery materials except for the recent work on blends with linear low-density polyethylene (Kosaka et al. 2007).

In this study, rubbery poly(epichlorohydrin) (PECH) is employed as a modifier. It has been known that PECH has a similar solubility parameter to CAP, because both CAP and PECH are miscible with poly(3-hydroxybutyrate) (Scandola et al. 1992; Pizzoli et al. 1994; Park et al. 2005; Masuzawa and Yamaguchi 2006; Yamaguchi and Arakawa 2007).

EXPERIMENTAL

Materials

The samples employed in this study are cellulose acetate propionate (Eastman Chemical, CAP-482-20) which has a degree of substitution of 2.75 ($DS_{Ac} = 0.10$, $DS_{Pr} = 2.65$) and poly(epichlorohydrin) (PECH), (Daiso, Epichlomer H; Mooney viscosity $ML_{1+4}(100\,^{\circ}C) = 55$). The molecular weights of the samples were evaluated by a gel permeation chromatograph, g.p.c., (Tosoh, HLC-8020) with TSK-GEL® GMHXL, in which chloroform was employed as eluant at 40 ºC at a flow rate of 1.0 ml/min. The sample concentration was 1.0 mg/ml. The number-, weight-, and z-average molecular weights as a polystyrene standard are as follows: $M_n = 7.71 \times 10^4$, $M_w = 2.01 \times 10^5$, and $M_z = 4.85 \times 10^5$ for CAP; and $M_n = 1.04 \times 10^5$, $M_w = 1.06 \times 10^6$, and $M_z = 2.80 \times 10^6$ for PECH. The densities of the materials were evaluated following JIS K 7112-A method at 23 ºC and found to be 1227 [kg/m^3] for CAP and 1350 [kg/m^3] for PECH.

The blend samples composed of CAP and PECH with various blend ratios were prepared by a 60 cc internal batch mixer (Toyoseiki, Labo-Plastomill) at 200 °C. The rotor rate was 30 rpm and the mixing time was 5 min. The obtained sample was compressed into a flat sheet with 1.0 mm thickness by a compression-molding machine

(Tester Sangyo) for 5 min at 200 °C under 10 MPa and then plunged into an ice-water bath.

Measurements

The temperature dependence of oscillatory tensile moduli, such as storage modulus *E'* and loss modulus *E"*, in the solid state was measured from -100 to 170 °C using a dynamic mechanical analyzer (UBM, E-4000). The frequency used was 10 Hz and a heating rate was 2 °C/min. The rectangular specimen, in which the width is 1 mm, the thickness is 1.0 mm, and the length is 20 mm, were employed.

The refractive index was evaluated by Abbe refractometer (Atago, NRA 1T) at 25 °C employing α-bromonaphthalene as a contact liquid.

The transparency of the film with 1.0 mm thickness was evaluated by a Haze meter (Toyoseiki, Direct Haze Meter) at room temperature. 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; it is often employed as a measure of the turbidity of a film specimen.

The tensile properties were evaluated by a tensile machine (JTT, Ministar) at 25 °C at a crosshead speed of 50 mm/min. The sample specimens were cut out from the plate by a razor blade following ASTM D-1822 L.

RESULTS AND DISCUSSION

Viscoelastic Properties

The temperature dependences of oscillatory tensile moduli for all samples are shown in Figure 1. Since both CAP and PECH are amorphous materials with different glass transition temperatures, the storage modulus drops off sharply at the glass transition temperatures; 144 ºC for CAP and -19 ºC for PECH.

It is obvious from the figure that CAP shows lower storage modulus *E'* than PECH in the low temperature region, *i.e.*, in the glassy state. Above the glass transition temperature of PECH, however, CAP exhibits higher modulus.

As for the blends, the storage modulus *E'* decreases stepwise, which are obvious especially for the blends with 30 and 50 wt% of PECH. Correspondingly, there are 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. The peak temperature of *E"* located at higher temperature is, however, lower than that for the pure CAP, and vice versa. The phenomena demonstrate that both materials are dissolved into each other to some degree.

[Figure 1]

Figure 2 shows the glass transition temperature, the peak temperature of *E"*, plotted against the PECH content. The solid line in the figure represents the predicted one following Fox-relation as;

$$\frac{1}{T_g} = \frac{\phi_1}{T_{g,1}} + \frac{\phi_2}{T_{g,2}} \qquad (1)$$

where ϕ_i is the volume fraction of *i* component having the following relation with the weight fraction w_i and the density ρ_i as;

$$w_1 = \frac{\phi_1\rho_1}{\phi_1\rho_1 + \phi_2\rho_2} \qquad (2)$$

[Figure 2]

Since the phase separation takes place to some degree, the higher Tg of the blends is located at higher temperature than the predicted line, leading to good heat-resistance. Further, the figure also suggests that glass transition temperature of the PECH-rich phase is almost independent of the blend ratio. For example, CAP/PECH (70/30, w/w) shows double peaks located at 87 and 2 ºC. Therefore, Fox-relation suggests that CAP-rich region contains 75 vol% of CAP and PECH-rich region does 20 vol% of CAP.

Optical Properties

Figure 3 shows the haze value and total transmittance as a function of the weight content of PECH in the blends. Both values are found to be almost independent of the blend components, although PECH and CAP/PECH (10/90, w/w) are slightly hazy, which would be attributed to the light scattering from the surface. The surface of the rubbery materials is not so smooth in this study as compared to the other samples.

[Figure 3]

As seen in the figure, the blends show high degree of transparency, *i.e.*, low level of haze, although dynamic mechanical properties indicate the phase separation. Further, it is found from Abbe refractometer that refractive index of the polymers are as follows; 1.4738 for CAP and 1.5149 for PECH at 25 °C.

The magnitudes of total transmittance T and haze H were theoretically derived by Willmouth (Willmouth 1986) based on the Rayleigh-Debye model (Kerker 1969).

$$T = \frac{\Phi_t + \left(\Phi_s\right)_0^{90}}{\Phi_0} \tag{3}$$

$$H = \frac{\left(\Phi_s\right)_{2.5}^{90}}{\Phi_t + \left(\Phi_s\right)_0^{90}} \tag{4}$$

where Φ_0 the flux of incident beam, Φ_t the directly transmitted one without scattering, and $(\Phi_s)_{\alpha 1}^{\alpha 2}$ the forward scattered one with scattering angle from α1 to α2.

The term $(\Phi_s)_{\alpha 1}^{\alpha 2}$ is dependent upon the number of scattering entities, *i.e.,* radius of dispersion, and the difference in the refractive index between the continuum and dispersed phases. Khanarian evaluated the haze value for immiscible polymer blends and discussed the effect of the particle size and the refractive index difference. As a result, equations (3) and (4) were found to predict the experimental data. Further, it is demonstrated that an immiscible blend, in which the size of dispersion is 0.5 μm, is opaque, *i.e.,* loses transparency, when the difference in refractive index is only 0.004 (Khanarian 2000).

In this study, the mutual dissolution of both components, which is suggested by the shift of glass transition temperatures for both phases, is responsible for the transparent, because it leads to the size reduction of phase separation as well as the depression of the difference in refractive index.

Here, the following simple additional rule is assumed to calculate the refractive index of each phase.

$$n_{blend} = n_{CAP}\phi_{CAP} + n_{PECH}\phi_{PECH} \qquad (5)$$

Following equation (5), the refractive index of the CAP-rich region in CAP/PECH (70/30, w/w) is 1.484 and that of the PECH-rich region is 1.507. In this case, the difference in refractive index is larger than 0.02, which is large enough to scatter the visible light as discussed by Khanarian (2000). Therefore, the size of the phase separation must be smaller than the wavelength of the visible light, at least for the blends containing less than 30 wt% of PECH.

Considering the above discussion, the phase structure was examined employing a scanning electron microscope and an atomic force microscope. However, apparent phase separation was not detected in this study.

Tensile Properties

Figure 4 shows the curves of nominal stress plotted against nominal strain for CAP and blends at 25 ºC, *i.e.*, lower than glass transition temperature of the pure CAP and higher than that of the pure PECH. The horizontal axis is logarithm scale for the purpose to show all curves. As seen in the figure, the initial modulus and yield stress decrease with increasing the content of PECH in blends, whereas the strain at yield point is almost independent of the blend ratio. Furthermore, CAP and CAP/PECH (90/10, w/w) show brittle failure without stress-whitening after passing the yield point. The blends with 30-50 wt% of PECH, however, exhibit strain-hardening after the yield point, demonstrating that they deform in a ductile manner. Consequently, the nominal stress at break point is higher than the yield stress.

[Figure 4]

The yield stress and the toughness, *i.e.*, the area of stress-strain curve, are plotted against the blend ratio in Figure 5. It is found that the yield stress decreases monotonically with the blend ratio. Moreover, the toughness, which is one of the most serious problems for CAP, is improved to a great extent by blending PECH. The result demonstrates that mechanical toughness of CAP is enhanced without losing optical transparency by blending PECH.

[Figure 5]

CONCLUSION

The mechanical and optical properties have been characterized for the binary blends composed of biomass-based cellulose acetate propionate (CAP) and poly(epichlorohydrin) (PECH). The blend shows excellent optical transparency although the dynamic mechanical spectra imply phase-separated morphology. The optical transparency is attributed to the mutual dissolution of both components to some degree, which is responsible for the reduction of the difference in refractive index and will lead to a fine morphology. Finally, the mechanical toughness of CAP is considerably improved by blending PECH, which will widen the application of CAP.

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Figure Captions

Figure 1 Temperature dependence of oscillatory tensile modulus for CAP, PECH, and the blends conducted at 10 Hz; (a) storage modulus E' and (b) loss modulus E''. The numerals in the figure represent the weight fraction of PECH in the blends.

Figure 2 Glass transition temperature, defined as the peak temperatures of E'', plotted against PECH volume fraction. The solid line represents the predicted line by Fox equation assuming the miscibility.

Figure 3 Haze and total transmittance values of CAP/PECH blends for the plaques with 1 mm thickness.

Figure 4 Stress-strain curves for CAP, PECH, and the blends at 25 °C.

Figure 5 Yield stress and toughness plotted against PECH weight fraction.

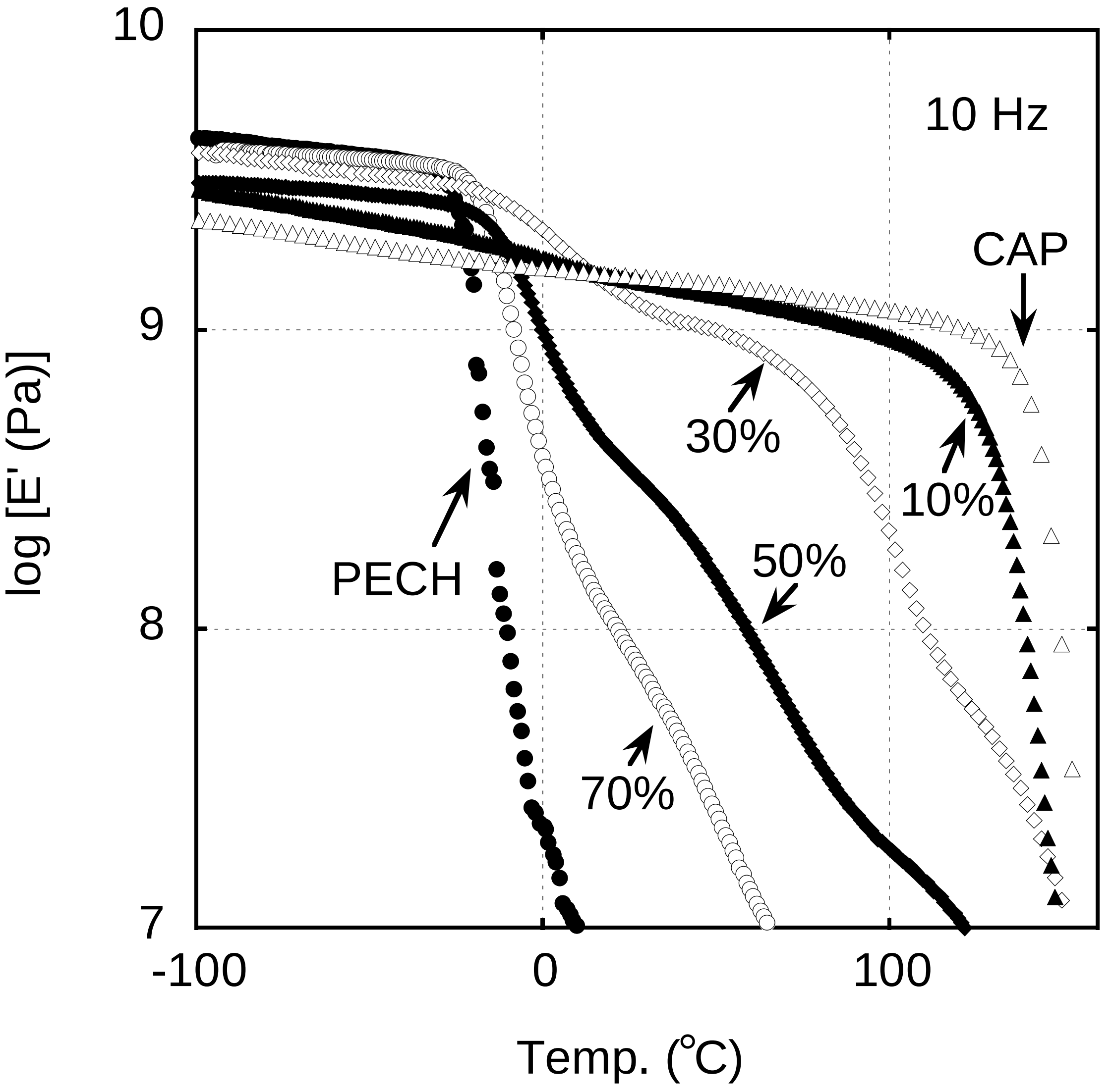


Figure 1(a)

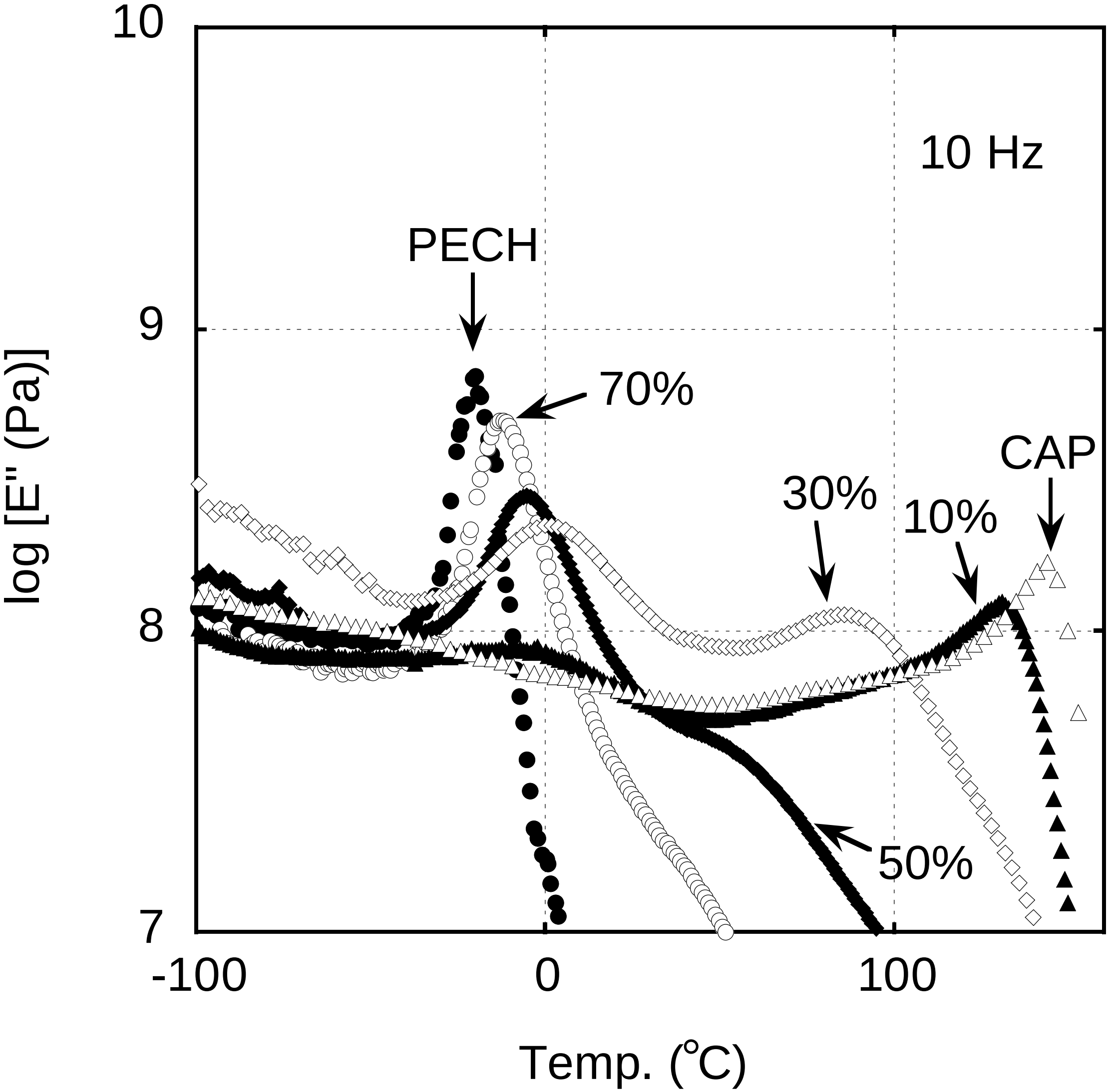


Figure 1(b)

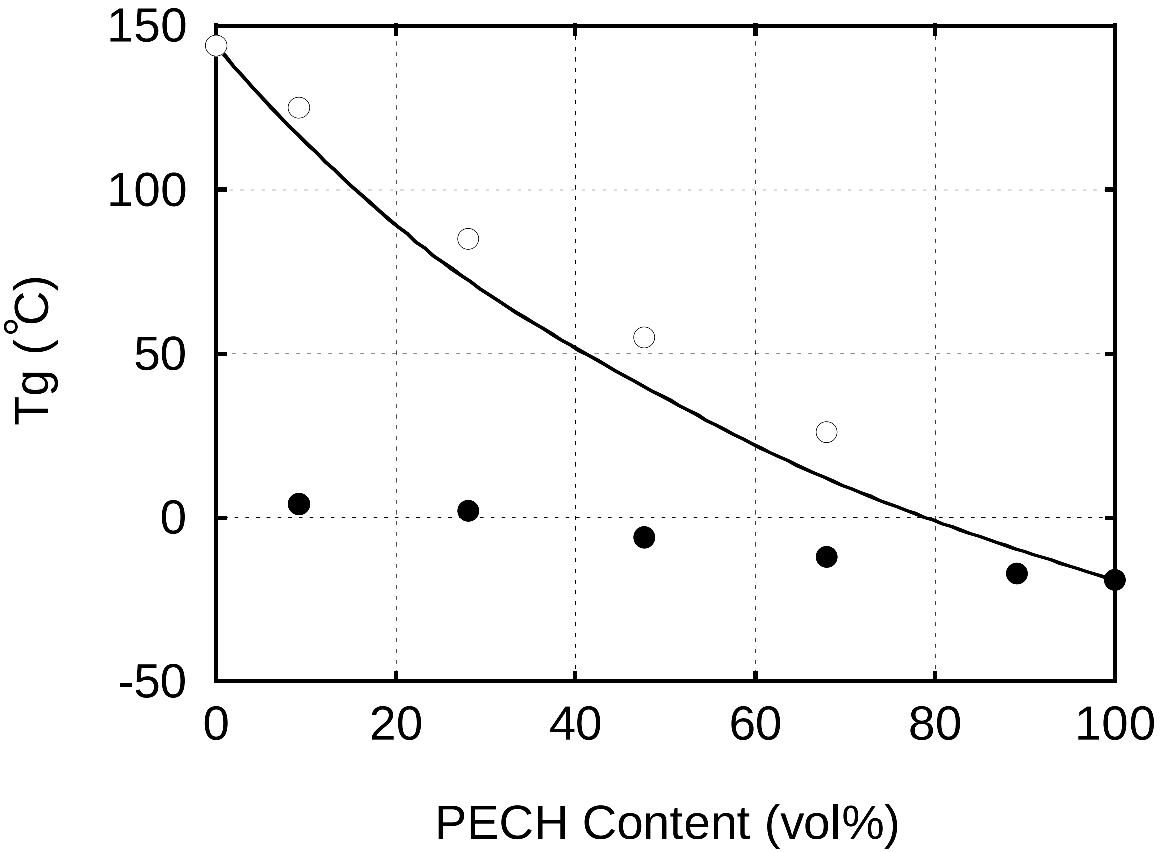
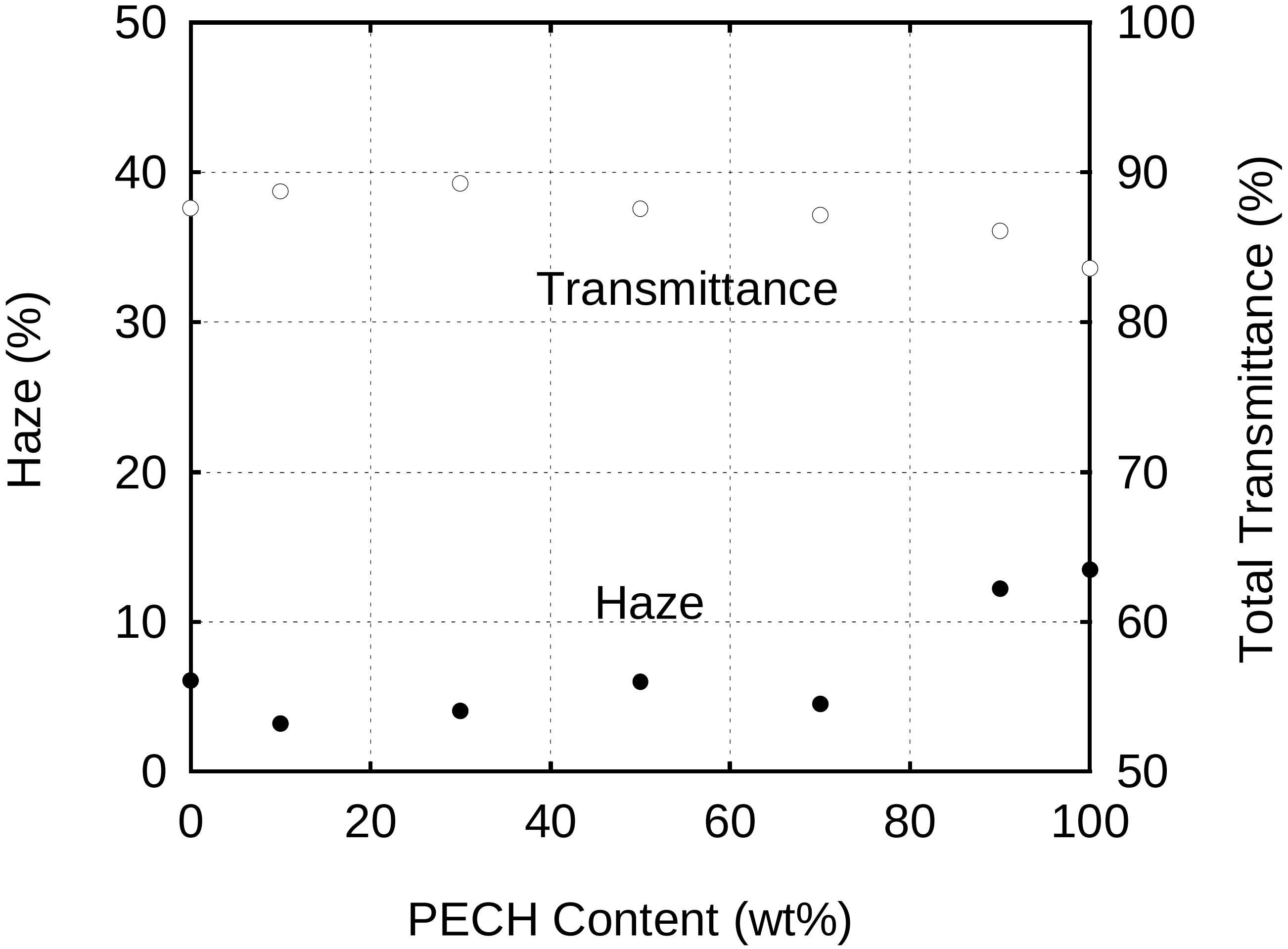


Figure 2



50
40
30
20
10
0
100
90
80
70
60
50
0
20
40
60
80
100
Haze (%)
Total Transmittance (%)
PECH Content (wt%)
Transmittance
Haze

Figure 3

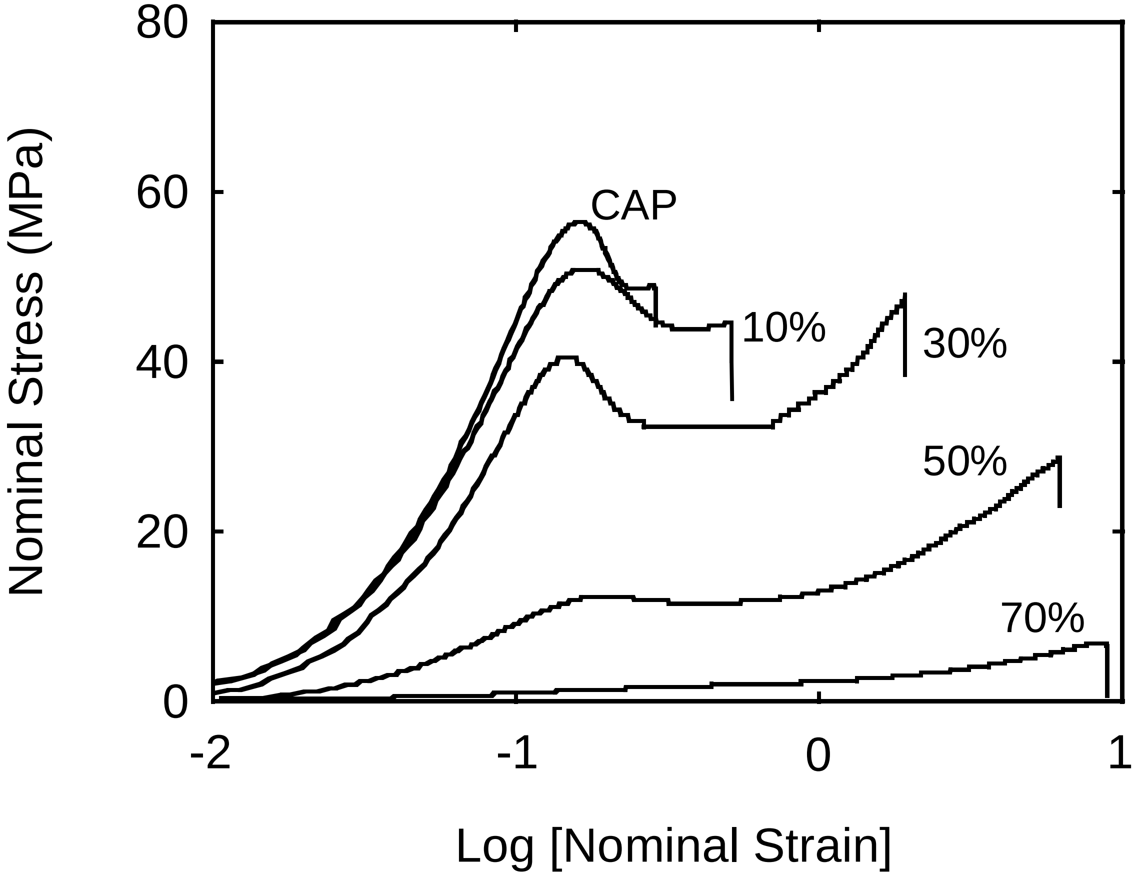

80
60
40
20
0
-2
-1
0
1
Nominal Stress (MPa)
Log [Nominal Strain]
CAP
10%
30%
50%
70%

Figure 4

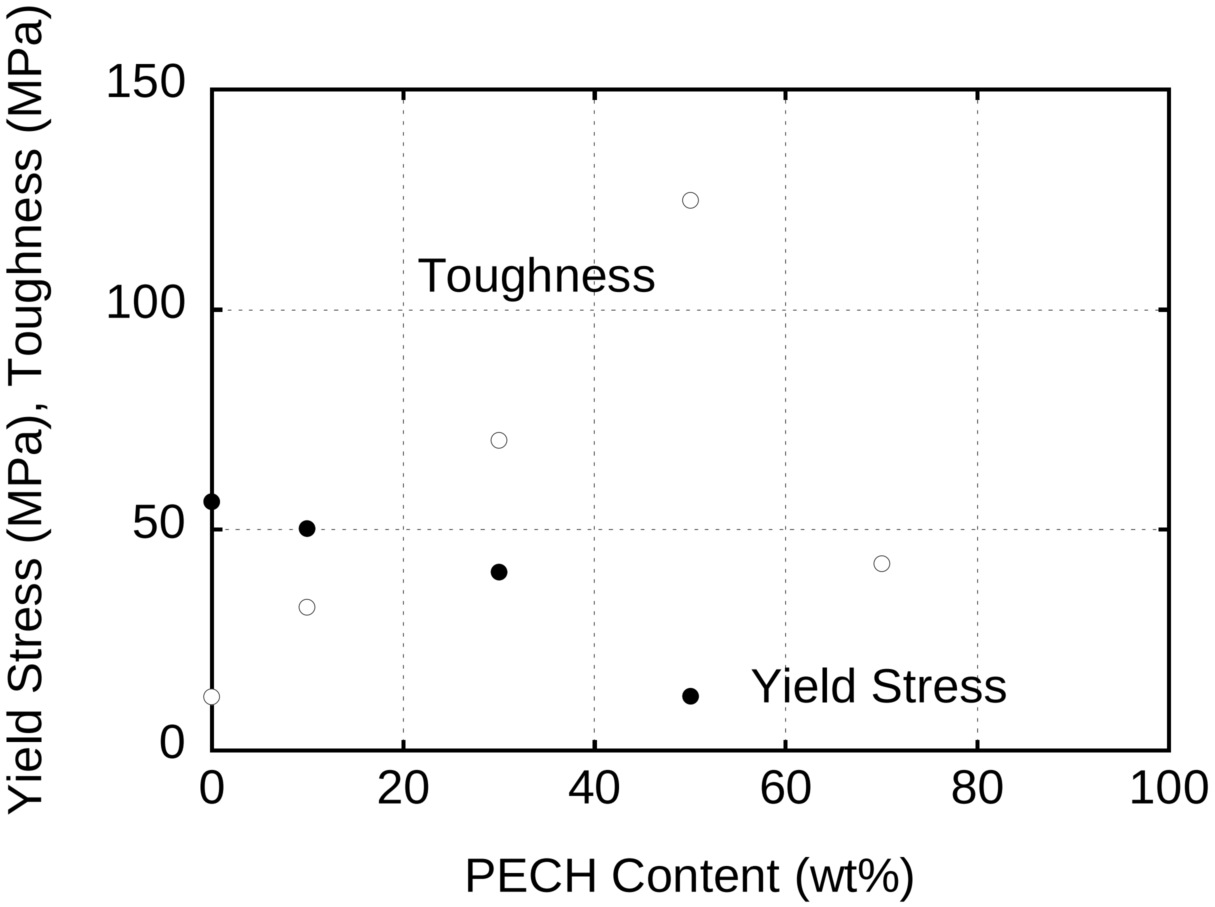

Yield Stress (MPa), Toughness (MPa)
150
100
50
0
0
20
40
60
80
100
PECH Content (wt%)
Toughness
Yield Stress

Figure 5