SHORT COMMUNICATIONS

Dynamic Mechanical Behaviors of Poly(vinyl alcohol) Film with High Syndiotacticity

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Poly(vinyl alcohol) (PVA-st) which had a high molecular weight of about 5.5×10^5 and a high syndiotacticity was successfully prepared through the photo-emulsion polymerization of vinyl pivalate (VP) followed by saponification.^{1,2} The ratios of syndiotactic, isotactic and heterotactic triad determined from NMR spectroscopy for this polymer were 39.3, 11.3, and 49.4%, respectively.

Crystal melting peak (T_m) of the PVA-st was observed at 248°C on DSC thermogram as shown in Figure 1, whereas that of the high molecular weight PVA (PVA-HW³, $\bar{M}_n = 5.2 \times 10^5$) derived from vinyl acetate (VAc) was at 229°C and that of the commercial PVA (PVA-C, $\bar{M}_n = 7.7 \times 10^4$) given by usual radical polymerization was at 231°C.

As for PVA-st, PVA-HW, and PVA-C, the heats of fusion estimated from their endothermic peaks on DSC thermograms were approximately all equal in quantities and the apparent degrees of crystallinity determined by density measurement for three polymers were similarly comparable to each other (PVA-st, 29; PVA-HW, 31; PVA-C, 28%).

The differences in the stereoregularities and molecular weights among the PVA homologs seemed to be reflected on the dynamic

mechanical properties. Therefore, the temperature dependence of dynamic strage modulus E' and loss tangent for undrawn films of three polymers cast from 1,1,1-3,3,3-hexafluoro-2-propanol solutions was measured.

The results are shown in Figure 2.

α_a dispersion of PVA is generally assigned to a mode of relaxation of amorphous phase. The peaks of the α_a dispersion for three polymers were observed at the temperature range of about 60° to 70°C. The lowering of E' of PVA-st at glass transition region was less than that of PVA-HW or PVA-C and the magnitude of E'

Figure 1. DSC curves of PVA films: —, PVA-st; ---, PVA-HW; — · —, PVA-c; scanning speed, 10°C min⁻¹.

Figure 2. Temperature dependence of dynamic storage modulus E' and $\tan \delta$ for PVA films: $\circ$, PVA-st; $\triangle$, PVA-HW; $\square$, PVA-C; frequency, 110 Hz.

for PVA-st, even this undrawn film, remained at $10^{10} \text{ dyn cm}^{-2}$. Though PVA-st and PVA-HW had approximately same molecular weight, a marked difference of E' between both polymers in and above the glass transition region was confirmed. Information obtained from the dynamic mechanical and thermal properties of PVA-st suggested that better structural regularity of molecular chain and effective intermolecular force by strengthening of the hydrogen bond were brought into PVA-st by the abundance of syndiotacticity.

These facts gave us the expectation that the drawn and heat-treated fibrous samples of

PVA-st may display a mechanical properties superior to those of undrawn film described above.

Preparation of Cast Film of PVA-st

VP was polymerized by irradiating with a high pressure mercury lamp at 0°C for 10 h in the presence of water and LWZ (polyoxyethylene nonyl phenyl ether sodium sulfate) as an emulsifier. The resulting PVP was dissolved in tetrahydrofuran and saponification in 25% KOH–MeOH mixed solution at 60°C for 15 min under N_2 atmosphere. The desired PVA with high molecular weight and high syndiotacticity was obtained.

The PVA-st was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol in concentration of about 1%, then the solvent was allowed to evaporate at room temperature, followed by vacuum drying. Cast film obtained was subjected to dynamic mechanical measurement. Sample was 40 mm long, 2 mm wide, and 0.03 mm thick in shape.

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REFERENCES

1. T. Yamamoto, S. Yoda, O. Sangen, R. Fukae and M. Kamachi, *Polym. Prepr. Jpn.*, **37**, 333 (1988).
2. T. Yamamoto, S. Yoda, O. Sangen, R. Fukae, and M. Kamachi, *Polym. J.*, **21**, 1053 (1989).
3. T. Yamamoto, S. Seki, M. Hirota, and M. Kamachi, *Polym. J.*, **19**, 1417 (1987).