Dynamic Viscoelastic Measurements of Polyvinyl Chloride
- The Effects of Plasticizers -

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1.   Introduction

The addition of plasticizers is a simple method to lower the glass transition of thermoplastic polymers and give end products their required flexibility. Plasticizers are most often used with the flexible polyvinyl chloride (PVC) products (such as film, sheets and wire coverings) but are also used with polyvinyl acetate, polyvinylidene chloride and polyamide (nylon). There are various types of plasticizers, including phthalate ester, phosphoester and fatty acid ester plasticizers, and their use is dependant on the objective or application.

Dynamic viscoelastic measurements can evaluate changes in the viscoelastic behavior of plasticized polymers. This effective method is often used to test the required properties of end products because it can evaluate property differences caused by different plasticizer types and concentrations.

In this brief, the effects of plasticizers on the dynamic viscoelastic behavior of PVC are measured. PVC was plasticized using di-octyl phthalate (DOP), a common plasticizer. This brief reports the differences in viscoelasticity when PVC is plasticized and the changes caused by different plasticizer concentrations.

2.   Experiment

Three samples were tested: non-plasticized PVC and plasticized PVC containing 10wt% and 20wt% DOP. Each sample was press molded flat to a thickness of approximately 2mm to create a viscoelasticity measurement sample.

SDM5600H Rheol. station was connected to a DMS120 dynamic mechanical spectrometer (bending module) for the measurements. The deformation mode was bending and the measurement frequencies were 0.5, 1, 2, 5, and 10Hz. The measurement temperature range was -120°C to 150°C with a heating rate of 2°C/min.

3.   Measurement results

Figure 1 shows the viscoelasticity spectrum of PVC. This figure shows results of the simultaneous measurement of the temperature and frequency dispersions. The lines are the *E'*, *E"*, and tan δ curves for the five frequencies between 0.5Hz and 10Hz. The PVC measurement results (Figure 1) show two dispersions, α and β, starting from the high temperature side. The α-dispersion is considered the main dispersion (glass transition) and β-dispersion is considered the local mode relaxation[1] .
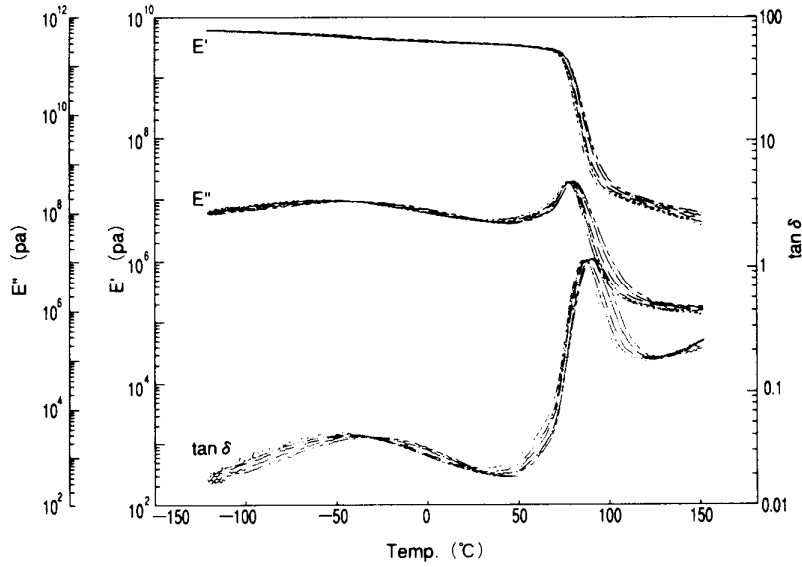
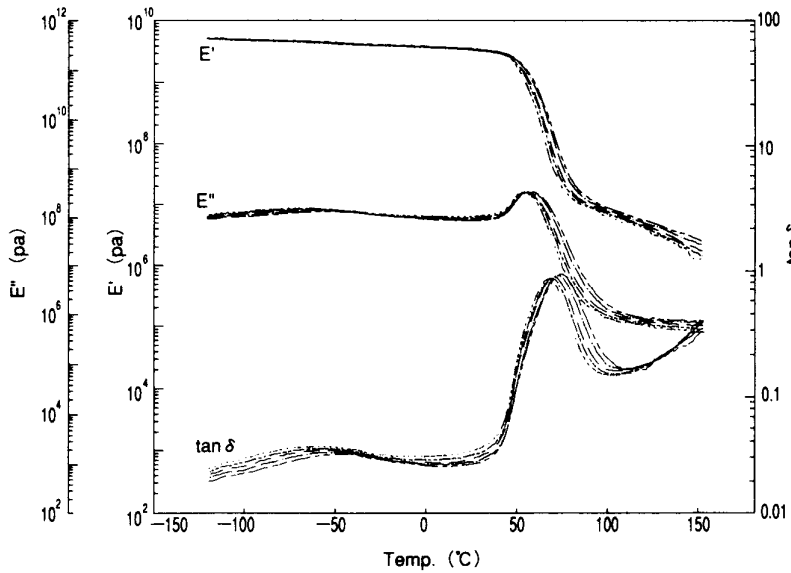Figure 1   Dynamic viscoelasticity spectrum of PVC

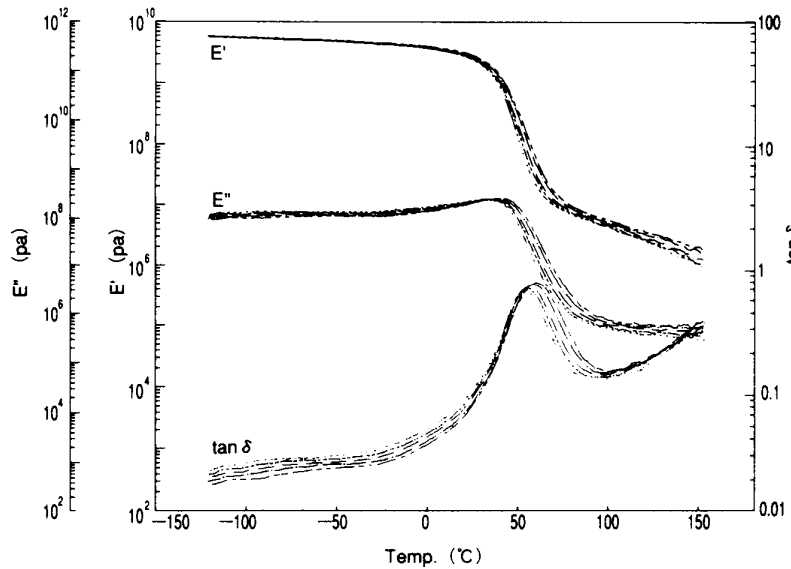Figure 2   Dynamic viscoelasticity spectrum for plasticized PVC of 10wt% DOP

Figure 3   Dynamic viscoelasticity spectrum for plasticized PVC of 20wt% DOP

Figure 2 and 3 shows the dynamic viscoelasticity spectrum for PVC samples containing 10wt% and 20wt% DOP respectively. When PVC is plasticized, the main dispersion (glass transition) shifts to a lower temperature. As the plasticizer concentration increases, the main dispersion shifts even lower.

Figure 4 shows the E' curve and Figure 5 shows the tanδ curve for the 1Hz frequency results of Figures 1 to 3. Figure 6 shows the analysis results of the apparent activation energy ΔE[2] that accompanies the main dispersion of each measurement sample.
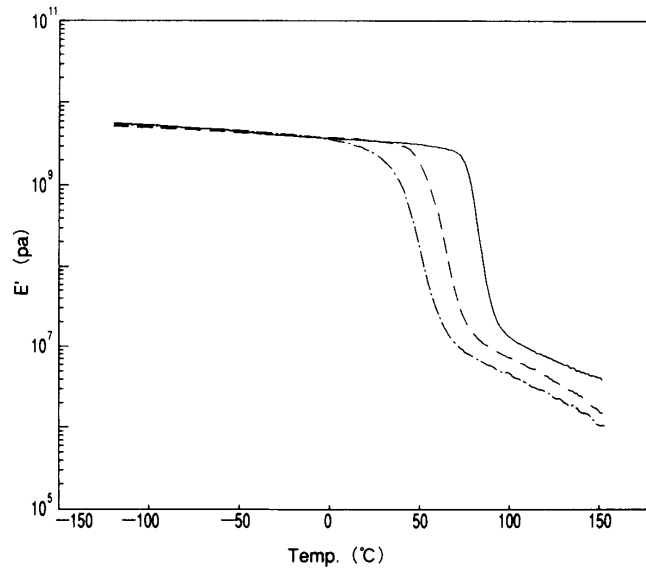

Figure 4   Comparison of E' curves for DOP 0wt%, 10wt% and 20wt%
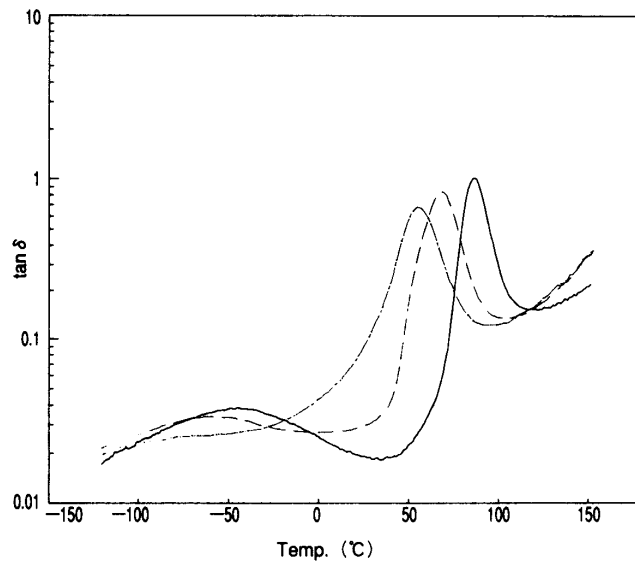Frequency: 1Hz
——————— : DOP 0%
- - - - - - - : DOP 10%
- · - · - · - : DOP 20%

Figure 5   Comparison of tanδ curves for DOP 0wt%, 10wt% and 20wt%
Frequency: 1Hz
——————— : DOP 0%
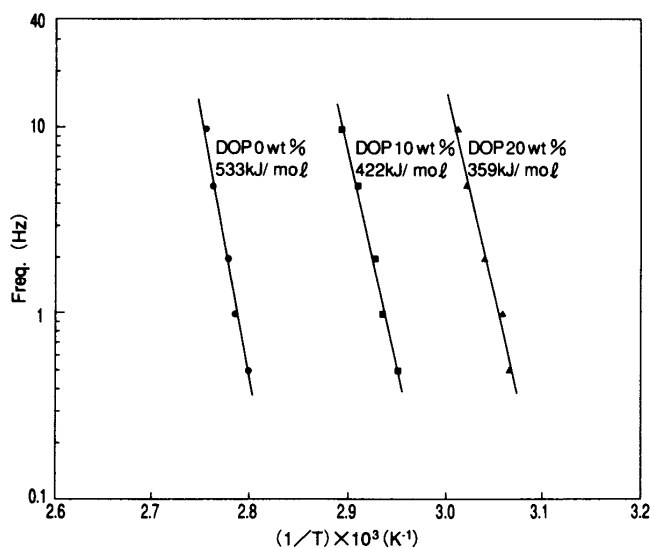- - - - - - - : DOP 10%
- · - · - · - : DOP 20%

Figure 6　Analysis Results for Apparent Activation Energy

Table 1　Storage Modulus, Main Dispersion Peak Temperature
and Main Dispersion Apparent Activation Energy

DOP concentration (wt%)	E' (Pa)[*1]		Peak temperature (°C)[*1]		ΔE[*2] (kJ/mol)
	-100°C	120°C	E''	$\tan\delta$	
0	5.3×10^9	7.4×10^6	78.6	85.9	533
10	5.0×10^9	4.2×10^6	52.9	67.7	422
20	5.3×10^9	2.7×10^6	32.5	54.0	359

1 Value for a measurement frequency of 1Hz
2 Results calculated from the $\tan\delta$ peak during main dispersion

Table 1 lists the storage modulus E' at -100°C and 120°C, the peak temperature the loss modulus E'' and $\tan\delta$ at main dispersion, and the apparent activation energy ΔE. The storage modulus E' results (Figure 4, Table 1) show that roughly the same elastic modulus rate was obtained for the glassy region of all measurement samples. However, the elastic modulus rate in the rubbery plateau region after glass transition decreased as the DOP concentration increased. This decrease in elastic modulus rate occurs due to the dilution of the polymer component that accompanies an increased plasticizer concentration and the increase in molecular weight between the entanglements[3].

The $\tan\delta$ curve results (Figure 5, Table 1) show that the peak temperature of the main dispersion shifts lower and the width of the peak widens as the DOP concentration increases. The widening of the peak indicates that the DOP plasticizers widened the temperature range of relaxation in glass transition. Moreover, a comparison of the apparent activation energy ΔE that accompanies the main dispersion (Figure 6, Table 1) shows that the activation energy decreases as the DOP concentration increases. This result indicates that the higher the plasticizer concentration, the easier it is for glass transition to occur.

4.   Conclusion

In this brief, dynamic viscoelastic measurements were used to investigate the effects of plasticizers on PVC viscoelasticity. Measurements of the three PVC samples (non-plasticized PVC and plasticized PVC with 10wt% and 20wt% DOP) showed that increasing the DOP concentration lowers the glass transition temperature. Furthermore, changes in viscoelasticity were observed, such as the lowering of storage elastic modulus E' in the rubbery plateau region.

References
1)   Yasaku. Wada, "Solid Properties of Polymers", Baihukan (1971)
2)   Nobuaki Okubo, Application Brief DMS No.7, Hitachi High-Tech Science Corporation (1990)
3)   F, Bueche, "Physical Properties of Polymers", Interscience, New York (1962)