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Thermal Analysis of Polyvinyl Chloride

- Influence of Plasticizer on Glass Transition -

1. Introduction

Polyvinyl chloride (PVC) is used as an all-purpose plastic in a wide variety of fields ranging from industrial materials such as pipes and wire coating materials to general consumable materials such as film and sheets. One characteristic that makes PVC different from other polymers is the ability to greatly adjust the elasticity and hardness of end products through the addition of plasticizer.

Differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA) can evaluate the fluctuations of the glass transition points of plasticized PVC. This brief introduces examples of DSC and TMA measurements of the glass transition point fluctuations of plasticized PVC with different dioctyl phthalate (DOP) concentrations.

2. Measurements

Three types of PVC samples were used: non-plasticized PVC and plasticized PVC containing 10wt% and 20wt% DOP.

DSC220C and TMA210C units were connected to a SSC5200H Desk Station for the measurements.

For the DSC measurement conditions, a 10mg sample was placed an aluminum open type sample container. The measurement temperature range was -20°C to 120°C and a heating rate of 10°C/min was used. For the TMA measurements, an expansion/compression probe was used and the load was 3g. The measurement temperature range was -40°C to 120°C with a heating rate of 5°C/min.

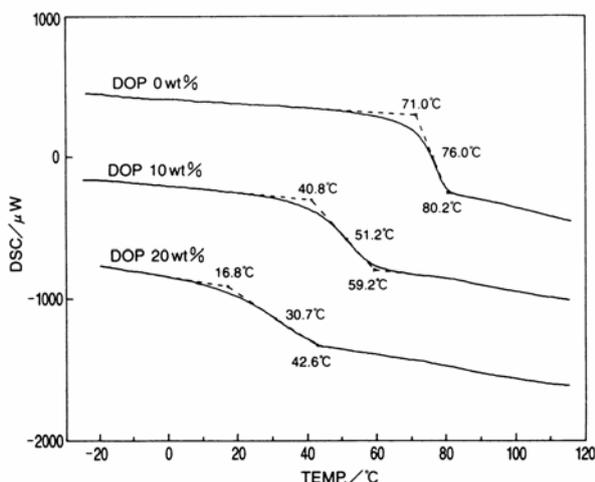


Figure 1 DSC Measurement Data for Each PVC Samples

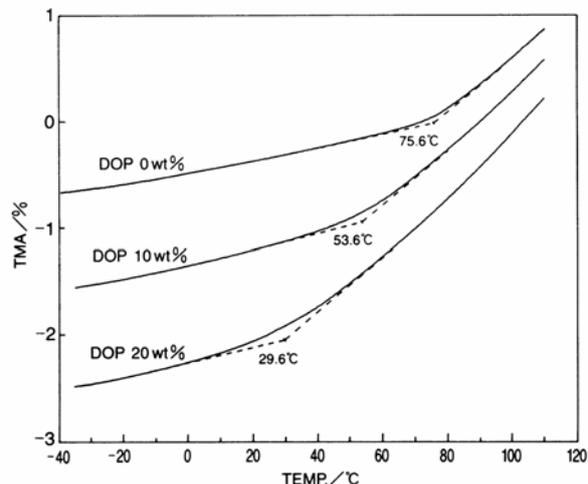


Figure 2 TMA Measurement Data for Each PVC Samples

Table 1 Analysis Results of the Glass Transition Temperature of PVC Samples By DSC, TMA and DMS Measurements

DOP (wt%)	DSC				TMA ^{*5} (°C)	DMS ^{*6} (°C)
	Tig (°C) ^{*1}	Tmg (°C) ^{*2}	Teg (°C) ^{*3}	ΔC_p (J/g°C) ^{*4}		
0	71.0	76.0	80.2	0.311	75.6	76.8
10	40.8	51.2	59.2	0.273	53.6	52.9
20	16.8	30.7	42.6	0.191	29.6	32.5

*1 Onset temperature of Tg

*2 Mid-point temperature of Tg

*3 End temperature of Tg

*4 Specific Heat Capacity difference before and after Tg

*5 Intersection of the extrapolation line

*6 Peak temperature of loss modulus (E'') at measurement frequency 1Hz

3. Measurement Results

Figures 1 and 2 show the DSC and TMA results for the PVC samples, which had DOP concentrations of 0, 10, and 20wt%. Table 1 shows the TMA and DSC analysis results for the glass transition temperatures. For reference, Table 1 includes the glass transition temperatures by dynamic mechanical spectrometer (DMS)¹⁾.

In the DSC measurement data (Figure 1), the shift of the baseline accompanying the glass transition for each PVC sample can be observed. The glass transition temperature shifted lower as the DOP concentration increased. The figure also shows that the temperature range of glass transition (difference between the start point (Tig) and the end point (Teg)) widens as the DOP concentration increases. This indicates that DOP plasticization widened the relaxation temperature width in glass transition. Moreover, the specific heat capacity (ΔC_p) accompanying the glass transition decreases as the DOP concentration increases. These changes in the specific heat capacity are considered the result of increased molecular weight between the entanglements, in addition to the dilution of PVC components that accompanies increases in DOP concentration.

In the TMA measurement results (Figure 2), the change point of the expansion ratio accompanying the glass transition of the PVC samples can be observed. As seen in the DSC measurement data (Figure 1), as the DOP concentration increases, the glass transition temperature shifts lower.

Table 1 show that the glass transition temperatures were consistent for each sample across all measurement methods.

4. Summary

In this brief, DSC and TMA measurements were used to research the effects of plasticizers on the glass transition of PVC samples. Various changes were observed in the three sample types used (non-plasticized PVC and plasticized PVC containing 10wt% and 20wt% DOP). As the DOP concentration increased, the glass transition temperatures shifted lower and the transition areas widened. Furthermore, changes in specific heat capacity were seen.

Reference

- 1) Nobuaki Okubo, DMS Application Brief No.25, Hitachi High-Tech Science Corporation (1994)