

α and β Relaxations of PVC and Calculation of the Activation Energy of the β Event



Summary

The use of the PerkinElmer® DMA 8000 for the analysis of the α (T_g) and β relaxations of PVC is shown in this application note. All relaxations are frequency dependant and the results of a multi frequency experiment show clear events for both α and β relaxations. The activation energy of the transition is calculated using the Arrhenius equation.

Introduction

Dynamic Mechanical Analysis (DMA) is one of the most appropriate methods to investigate relaxation events. The glass transition (T_g) is a key process in any material and is sometimes referred to as the α transition. Normally at a lower temperature, other relaxation events can sometimes be observed for polymeric materials. The β relaxation is normally attributed to a polymer backbone conformation reorganization. The activation energy of this process can be determined by performing an Arrhenius plot of the data. As frequency is essentially a rate expression with units of s^{-1} the natural log of frequency can be plotted against 1 over temperature. The slope of this line is equal to negative the activation energy divided by the gas constant.

The DMA 8000 works by applying an oscillating force to the material and the resultant displacement of the sample is measured. From this, the stiffness can be determined and $\tan \delta$ can be calculated. $\tan \delta$ is the ratio of the loss component to the storage component. By measuring the phase lag in the displacement compared to the applied force, it is possible to determine the damping properties of the material. $\tan \delta$ is plotted against temperature and glass transition is normally observed as a peak since the material will absorb energy as it passes through the glass transition.

Results and conclusion

Figures 1 and 2 show an expanded view of the temperature range 50 °C to 120 °C. This is the region of the glass transition for PVC. The $\tan \delta$ graph shows clear peaks representing the glass transition and as expected, the actual T_g is frequency dependant which is characteristic for relaxation events.

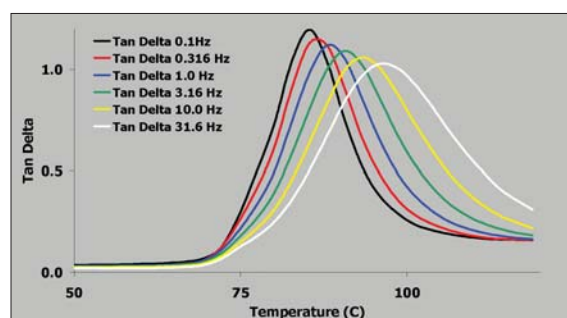


Figure 1. $\tan \delta$ glass transition of PVC.

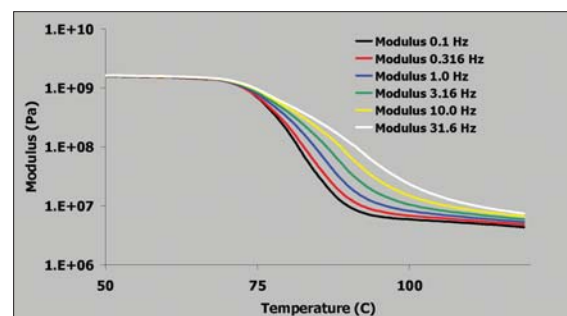


Figure 2. Modulus through glass transition of PVC.

Experimental

Multi-frequency temperature scan of PVC.

A bar of PVC was clamped in the single cantilever bending clamps and cooled with LN₂ to -100 °C. The experiment was started, collecting data at all the frequencies during the same experiment.

Equipment	Experimental Conditions	
DMA 8000	Sample:	PVC
1L Dewar	Geometry:	Single Cantilever Bending
	Dimensions:	5.2 (l) x 9.7 (w) x 1.5 (t) mm
	Temperature:	100 °C to 120 °C at 2 °C min ⁻¹
	Frequency:	0.1 to 100 Hz (7 discrete frequencies)

As shown in Figure 2, the modulus of the material decreases as the glass transition is passed. Again, as expected, this is observed to be frequency dependant. Both the modulus and tan δ graphs show typical behavior of polymeric materials on passing through T_g.

The temperature range is expanded to show -100 °C to 50 °C in Figure 3. In this region, it is possible to observe the β relaxation event. Due to the frequency dependence, it is possible to categorically ascribe this event as a relaxation. In order to better show the event, polynomial best fits have been overwritten on the graph for some of the frequencies.

The Arrhenius equation can be expressed as

$$\ln(F) = \ln(A) - \frac{E_a}{RT}$$

where F is frequency, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is temperature. A plot of ln frequency against 1/temperature is known as an Arrhenius plot.

The Arrhenius plot with a line of best fit and the equation of that line is highlighted in Figure 4. The slope is equal to the negative of the activation energy divided by the gas constant. The activation energy for the β relaxation of PVC is 77kJmol⁻¹. This is effectively the energy barrier the material has to overcome in order to undergo the structural reorganization of the β relaxation. Similarly, the activation energy of the T_g could have also been calculated.

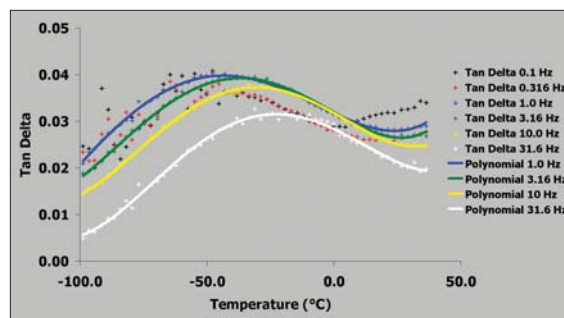


Figure 3. β relaxation for PVC.

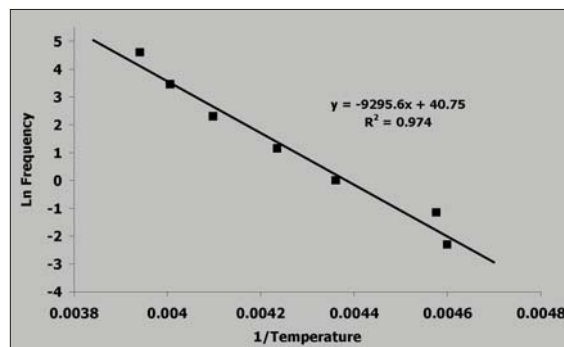


Figure 4. Arrhenius plot.