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Kinetic examination of the mechanical transition of polymethyl methacrylate films prepared from aqueous dispersions

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Abstract

The activation energy of the phase transition of cast polymethyl methacrylate films produced from an aqueous dispersion (Eudragit NE30D) has been estimated from Dynamic Mechanical Thermal Analysis. The value was found to lie between 170 and 350 kJ mol^{-1}, the variation arising from the different specimen test geometry and testing conditions. From experiments conducted at a range of frequencies and temperatures it was found possible to utilise the concept of frequency shift to produce a master curve, which could relate viscoelastic properties over the temperature range of 5–55 °C and a frequency range of 0.1 to 50 Hz. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Activation energy; Dynamic mechanical thermal analysis; Phase transition; Polymethyl methacrylate dispersions (Eudragit NE 30D)

1. Introduction

Many tablet and pellet coating processes involve applying the polymers as solution or dispersion and subjecting them to heating processes to remove solvent and/or cause coalescence of the polymer molecules to form films. The application of heat involves mechanical transitions in the polymer and how polymer systems respond to these changes has a considerable influence on the performance of the films. Lafferty et al. (2002a) have described the application of dynamic mechanical thermal analysis (DMTA) to the study of polymer films produced from aqueous dispersions of polymer used in film coating. The rate at which these changes occur and the energy changes involved are equally important in providing an understanding of the systems, especially as the polymers undergo a change from the liquid to the solid state. Thus, it would be beneficial to understanding if these properties could be measured. Transition state and barrier theories provide an explanation for the temperature dependence of viscoelastic behaviour (Ward, 1985).

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1.1. Theory

The theory assumes that under an applied stress, the change in molecular conformation is accompanied by a change in energy state. This change in energy state can be compared to the reacting species, which form an activated complex before forming reaction products. The rate of crossing the energy barrier is equal to kT/h where k is the Boltzmann constant, T is the absolute temperature and h is the Planks constant. The probability of forming the activated complex is $e^{\Delta G/RT}$ where ΔG is the Gibbs free energy and R is the gas constant. The frequency v of molecular jumps between the two isomeric states of the molecules can be represented by:

$$v = \frac{kT}{h} e^{-\Delta H/RT} \tag{1}$$

This equation states that the frequency of molecular jump depends upon the barrier height and not the free energy difference between the equilibrium sites.

Eq. (1) can be rewritten as

$$v = v_o e^{-\Delta H/RT} \tag{2}$$

where v_o is frequency at $T = \infty$ and ΔH is the enthalpy of the transition. Eq. (2) is in the form of the Arrhenius equation. It is then assumed that the viscoelastic behaviour can be directly compared to a molecular reaction controlled by a process with a constant activation energy. Tan δ (phase lag angle i.e. ratio of the storage to the loss modulus) is measured at frequencies v, and v_1 and v_2 and it is assumed that the peak temperature in the tan δ response can be related by the equation:

$$\frac{v_1}{v_2} = \frac{e^{\Delta H/RT_1}}{e^{\Delta H/RT_2}} \tag{3}$$

The activation energy for the process can therefore be obtained by examination of a material over a range of at least 3 decades of frequency and by plotting the $\log_e$ of the frequency as a function of the reciprocal temperature at which the peak tan δ occurs. It is possible to interrelate the time and temperature dependence of the viscoelastic properties of polymers, as it has been identified that there is a general equivalence between time and temperature (Ferry, 1980). Thus two curves for measurements of viscoelastic properties at a range of frequencies, at different temperatures, can be superimposed by keeping one end fixed and shifting the other horizontally and parallel to the log frequency axis. If an arbitrary temperature T_2 is taken to fix one curve and ω is the frequency at one point on the curve at T_2 with viscoelastic property V_s, then the other curve will have the same value of the viscoelastic property at a different temperature T, and at a frequency ω. The shift factor a_T required to superimpose the two curves is the displacement $\log \omega_s - \log \omega$ along the frequency axis and may be defined as

$$\log a_T = \log \omega_s - \log \omega = \log \frac{\omega_s}{\omega} \tag{4}$$

and is a parameter, which is a function only of temperature.

Williams et al. (1955) were the first workers to notice this ability to provide a master curve for viscoelastic properties, provided that the data was collected over a wide enough range of temperatures. The master curves are, therefore, produced by using equivalent time and temperature and superimposing data obtained, where these differing conditions apply.

This approach will be used in this study to determine the activation energy for the phase transitions in polymethyl methacrylate (Eudragit NE 30D) cast films, when subjected to changes in temperature.

2. Materials and methods

Cast films of Eudragit NE 30D (Rhône-Poulenc, Darmstadt, Germany) were prepared as described previously (Lafferty et al., 2002b). Two different instruments examined the thermal mechanical properties of the films. (1) Single cantilever bending of films 20 × 10 mm and 5 mm thickness was undertaken with a DMTA (Polymer Laboratories, Loughborough, UK) at a temperature range 0–75 °C (heating rate 3 °C min^{-1}) with frequencies of 0.2, 0.3, 1, 3, 10 and 50 Hz. (2) Parallel plate compression on 6 mm diameter (5 mm thick) disc specimens was carried out with DMA (Perkin Elmer, High Wycombe, UK) at a temperature range 0–75 °C (heating rate 3 °C min^{-1}) at frequencies of 1, 2, 3, 5, 10, 15, 20, 25, 30, 40, 50 Hz. All experiments were carried out in triplicate.

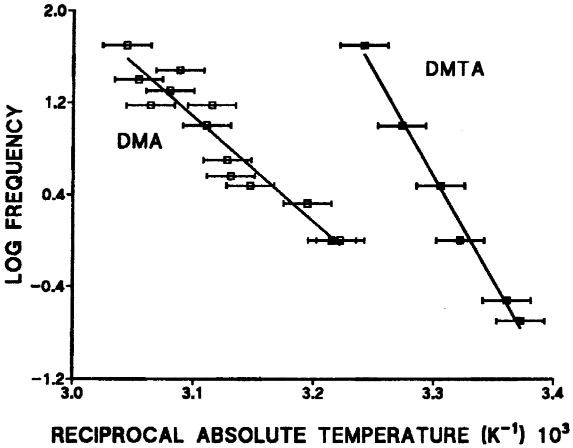

Fig. 1. The relationship between the frequency at which the peak tan * occurs and the reciprocal of the absolute temperature for Eudragit NE30D cast films. (Activation energy for the α process determined by DMTA (■) = 350 ± kJ mol^{-1}, correlation coefficient = 0.99 and by DMA (□) = 174 ± 50 kJ mol^{-1}, correlation coefficient = 0.95).

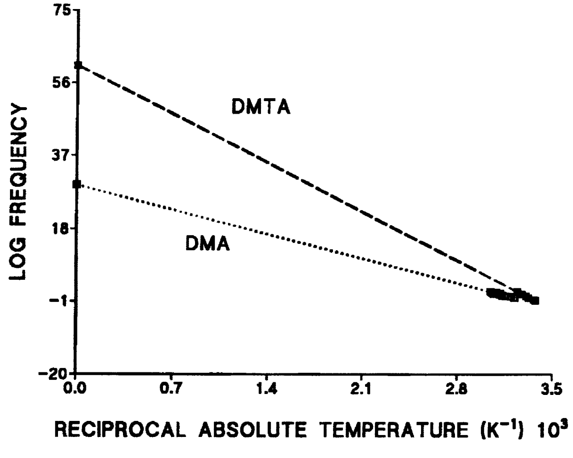

Fig. 2. Frequency at which the peak tan δ occurs as a function of the reciprocal temperature, extrapolated to predict the frequency of the activation energy data to predict the frequency at infinite temperature.

3. Results and discussion

The frequency at which the peak tan δ occurred at each temperature was monitored. When the log of this frequency was plotted as a function of the reciprocal of the absolute temperature, linear graphs were obtained for each instrument (Fig. 1). The activation energies can be derived from the slopes of these graphs. The value determined by the cantilever bending was 350 ± 80 kJ mol^{-1} and for the parallel plate compression 174 ± 50 kJ mol^{-1}. These differences could arise from the difference in specimen size and the mode of application of stress. Clarke and Braden (1989) found an activation energy of 428 ± 15 kJ mol^{-1} for polymethyl methacrylate determined in a bending mode. Thus the values obtained here are a similar order of magnitude. As the current results show a linear dependence of log frequency and reciprocal absolute temperature it should be possible to extrapolate the graph to frequency at infinite temperature. Such extrapolations were large (see Fig. 2) and resulted in estimates of 10^{30} Hz for the bending and 10^{60} Hz for compression. These values are far higher than the 10^{12}, which is the approximate frequency of molecular vibration. Hence it is likely that the curves do represent an α transition, i.e. motion of the polymer backbone.

3.1. *Time/temperature superimposition*

The results were taken from the single cantilever stress system operating in isothermal mode over a temperature range of 5–55 °C (heating rate 5 °C min^{-1}) at frequencies of 0.2, 0.3, 1, 3, 5, 10, 20 and 50 Hz). The results for storage modulus, loss modulus and tan δ are shown in Fig. 3a, b, and c. From these results the Williams et al. (1955) master curve was suc-

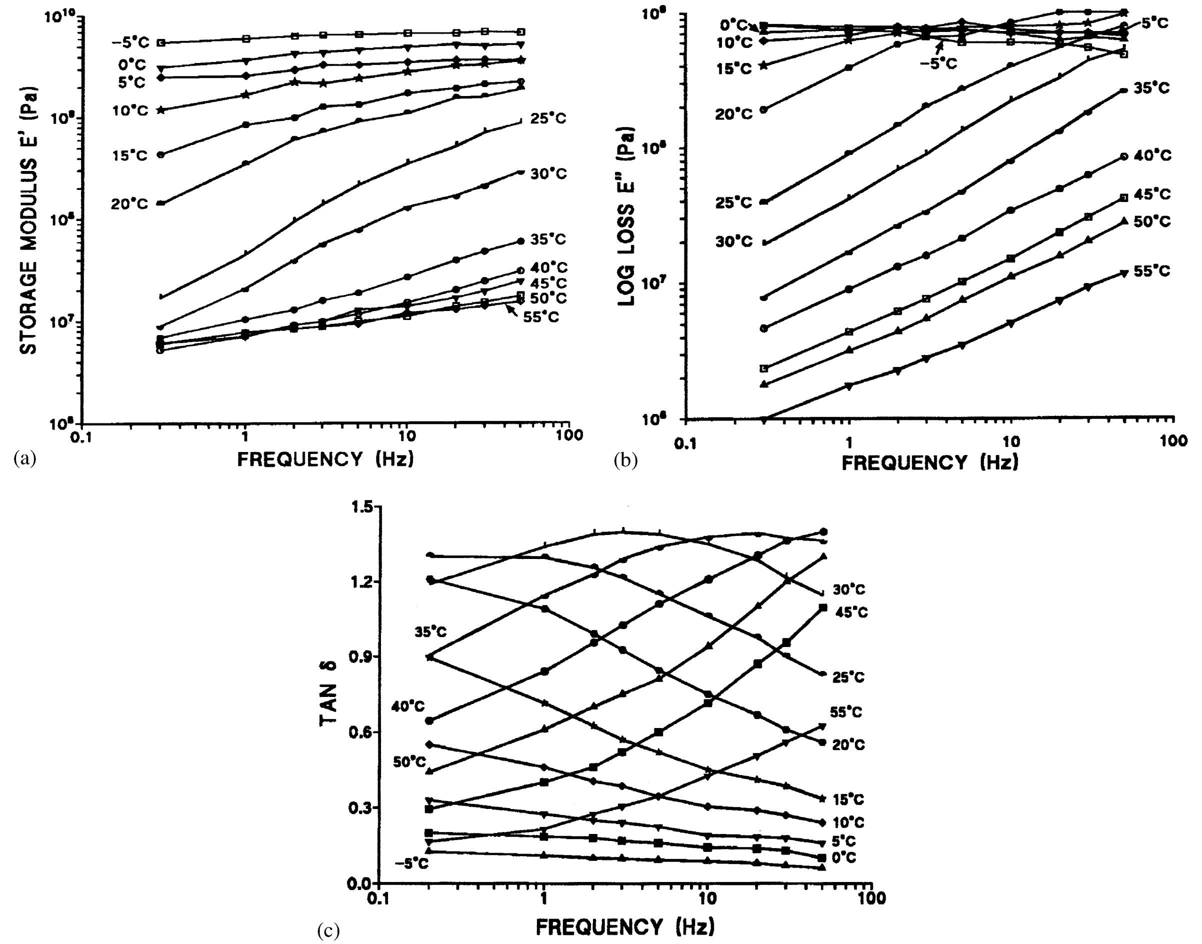

Fig. 3. The (a) storage modulus, (b) the loss modulus and (c) tan δ for films of Eudragit NE30D examined using DMTA in isothermal mode.

cessfully produced for the loss and storage moduli (Fig. 4) indicating that these viscoelastic properties can be put onto a common temperature time base. It follows therefore, for this film, experiments carried out under one set of temperature conditions could be used to predict the viscoelastic behaviour of the material at another temperature.

The results can also be used to derive a further estimate for the activation energy by determination of the shift factor a_T and plotting as a function of the absolute temperature (see Fig. 5). The slope of this line represents the activation energy for the process and provides a value of 270 ± 20 kJ mol^{-1} which lies between the two values obtained from the graphs of log frequency against absolute temperature.

4. Conclusions

The application of DMTA therefore can provide estimates of the activation energies for changes of state of the polymethyl methacrylate polymer. The value was found to lie in the range 175–350 kJ mol^{-1}. It was also found possible to produce a Williams Landel and Ferry (WLF) master curve, which could relate the values of the viscoelastic parameters of storage and loss modules determined under one set of temperature

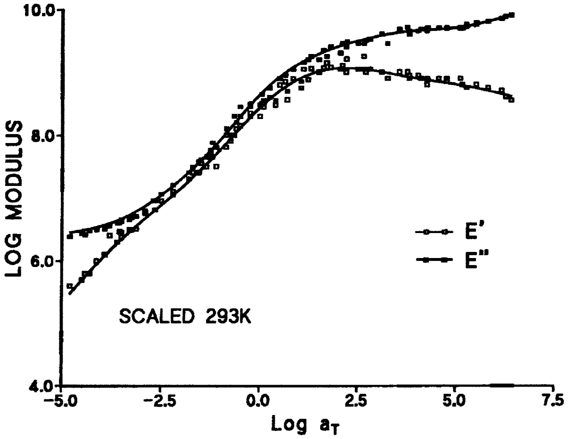

Fig. 4. The Williams, Landell and Ferry (WLF) master curve generated from the storage and loss modulii, data for Eudragit NE30D cast films.

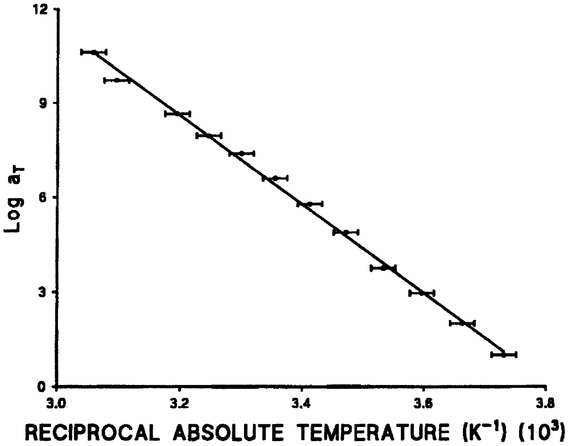

Fig. 5. The shift factor a_T generated from the WLF theory as a function of the reciprocal absolute temperature. (Activation energy for the a process from WLF theory, 270 ± 20 kJ mol^{-1}, correlation coefficient = 0.998.)

conditions to those measured under different conditions of time and temperature.

References

Clarke, R.L., Braden, M., 1989. Modified Arrhenius equation for the frequency dependence of the transition temperature of polymers. Biomaterials 10, 349–352.

Ferry, J.D., 1980. Viscoelastic Properties of Polymers, third ed. Wiley, New York.

Lafferty, S.V., Newton, J.M., Podczeck, F., 2002a. Dynamic Mechanical Thermal Analysis of polymer films prepared from aqueous dispersion. Int. J. Pharm. 235, 107–111.

Lafferty, S.V., Newton, J.M., Podczeck, F., 2002b. Characterisation of the mechanical properties of polymer films formed from aqueous polymer dispersions by creep testing. Int. J. Pharm. 239, 143–148.

Ward, M., 1985. Mechanical Properties of Solid Polymers, second ed. Wiley, New York, p. 49.

Williams, M.L., Landel, R.F., Ferry, J.D., 1955. The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming systems. J.Am. Chem. Soc. 77, 3701–3707.