International Journal of Pharmaceutics, 27 (1985) 267–277
Elsevier

IJP 00920

The thermomechanical properties and glass transition temperatures of some cellulose derivatives used in film coating

P. Sakellariou [1], R.C. Rowe [2] and E.F.T. White [1]

[1] *Department of Polymer Science and Technology, University of Manchester, Institute of Science and Technology, Manchester M60 1QD and* [2] *ICI Pharmaceuticals Division, Macclesfield, Cheshire SK10 2TG (U.K.)*

(Received April 10th, 1985)
(Accepted July 30th, 1985)

Key words: cellulose derivatives – film coating – differential scanning calorimetry – differential thermal analysis – glass transition temperatures – tortional braid pendulum

---

Summary

The thermomechanical properties and glass transition temperatures of a number of cellulose derivatives used in the film coating of oral dosage forms have been studied using differential scanning calorimetry (DSC), differential thermal analysis (DTA), and the torsional braid pendulum—a dynamic technique originally invented for following rigidity changes accompanying the curing of polymers. The data from both DSC and DTA showed considerable discrepancies with values in the literature exacerbated by the poor resolution in these techniques which record glass transition temperatures as slight changes in the baseline. When using the torsional braid pendulum all the polymers, with the exception of hydroxypropyl cellulose, exhibited a simple thermomechanical spectrum with a single peak in the damping curve and a corresponding abrupt change in rigidity. The high resolution of the data enabled the glass transition temperatures of these polymers to be measured with a high degree of precision.

Correspondence: R.C. Rowe, ICI Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire SK10 2TG, U.K.

Introduction

The cellulose derivatives ethyl cellulose, hydroxypropyl methylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose phthalate and cellulose acetate phthalate are used extensively in the film coating of oral dosage forms (Rowe, 1985). A knowledge of the thermomechanical properties and glass transition temperatures of such film formers is important since these determine their behaviour in film coating formulations both at ambient conditions and at elevated temperatures during the coating process and subsequent storage. Over the past few years the literature on the glass transition temperatures of these materials has been considerably enriched with authors using both differential scanning calorimetry (Entwistle and Rowe, 1979; Porter and Ridgway, 1983; Okhamafe and York, 1985) and thermomechanical techniques (Osterwald et al., 1982; Rowe et al., 1984). Thermomechanical analysis has also been used to evaluate the softening temperature of these materials (Masilungan and Lordi, 1984). However, because of the various techniques used, there are discrepancies in the data and, as yet, no attempt has been made to collate and corroborate these data. In the present work we have used a dynamic mechanical technique—the torsional braid pendulum—and both differential scanning calorimetry and differential thermal analysis to provide data on both the thermomechanical properties and glass transition temperatures of all the commonly used cellulose derivatives.

Materials and Methods

The film formers studied were ethylcellulose (EC; Grade N50, Hercules Powder, Wilmington, DE, U.S.A.); hydroxypropyl methylcellulose (HPMC; Pharmacoat 606, Shin-Etsu Chemicals, Tokyo, Japan); hydroxypropyl cellulose (HPC; Klucel L, Hercules Powder Co., Wilmington, DE, U.S.A.); hydroxypropyl methylcellulose phthalate (HPMCP, HP50 and HP55; Shin-Etsu Chemicals, Tokyo, Japan); cellulose acetate phthalate (CAP; Eastman, Chemical Products, Kingsport, TN, U.S.A.). All were used as received.

The thermomechanical spectra of the film formers were obtained by means of torsional braid analysis. This is a dynamic mechanical technique that measures the response of a polymer impregnated glass fibre braid to a sinusoidal stress as a function of temperature. The apparatus used was similar to that described by Rowe et al. (1984) but with an improved air bearing and improved data collection and processing (Sakellariou, 1984). Glass braids, 85 mm in length, used in this study, were prepared by doubling a twisted E glass yarn of four strands per yarn and containing 800 filaments. Braids terminated by crimped butt connectors were desized by heating in an air oven at 500°C for 1 h and impregnated by immersion in 15% w/v solution of the film formers in a solvent mixture consisting of equal parts by volume of dichloromethane and methanol and then drying to constant weight at 85°C in an oven. The specimens were tested at a resonant oscillation frequency of ca. 1 Hz and at a heating rate of $1°C \cdot min^{-1}$. The output from the Hall effect detection device which was proportional to the angular displacement was stored, after some signal conditioning, as 1024 data points in a transient recorder (DL 901, Datalab). This digitized signal was then displayed on an oscilloscope or printer before being processed in a microprocessor to eliminate spurious lateral oscillations. A peak fitting routine (Sakellariou, 1984) was used to determine the period of oscillation (P) which is related both to the shear modulus of the system and also the logarithmic decrement (Δ)—a function of the energy loss of the system at each temperature interval. Glass transition temperatures were determined from the peaks in the logarithmic decrement vs temperature spectra while the peak width at half-power height ($W_{\sqrt{2}}$) was used as a measure of the energy dissipation of the material.

Glass transition temperatures were also determined for both powdered samples (10 mg approx.) and solution cast films (vacuum dried at 60°C) using differential scanning calorimetry (DSC-2, Dupont) and differential thermal analysis (DTA, Model 990 Thermal Analyser, Dupont) at a heating rate of $20°\mathrm{C} \cdot \mathrm{min}^{-1}$.

Results and Discussion

No indication of any crystallinity was recorded in the DSC/DTA thermograms for either powdered or solution cast films of any of the polymers; the polymers were therefore considered to be amorphous. All the thermograms showed intense water endotherms despite vacuum drying. It is interesting to note that whereas the water endotherms for the hydroxypropyl methylcellulose, hydroxypropyl cellulose, hydroxypropyl methylcellulose phthalate and cellulose acetate phthalate all occurred between 85 and 100°C, that for the more hydrophobic ethylcellulose occurred at some 10°C lower. In all cases a repeat run on the same sample resulted in a reduction of the water endotherm and a clearer indication of the glass transition temperature (Table 1). Although powdered samples of hydroxypropyl methylcellulose yielded a value of 180°C for its glass transition temperature, a value of 157°C was recorded when using films cast from a solvent mixture of equal parts by volume of dichloromethane and methanol. In the case of hydroxypropylcellulose a transition was recorded at 175–177°C in the DTA thermogram and a small broad endotherm at 177–183°C was observed in the DSC. This transition did not possess the characteristics of the glass transition temperature and is thought to be attributable to either the effects of a localized molecular orientation or viscous flow. The data from the DSC and DTA showed considerable discrepancies with the values in the literature ostensibly using the same techniques. This implies that the values obtained are highly dependent upon the experimental conditions such as sample size, form and preparation, and heating rate. In addition, the situation is exacerbated by the poor resolution of these thermal techniques which record glass transition temperatures as slight changes in the baseline.

The relative rigidity ($1/P^2$) and logarithmic decrement, (Δ) for the temperature range from 20°C to 180°C for all the polymers investigated are shown in Figs. 1–7 with the relevant data summarized in Table 2. Measurements at sub-zero tempera-

TABLE 1

THE GLASS TRANSITION TEMPERATURES OF THE CELLULOSE DERIVATIVES AS DETERMINED BY DSC AND DTA

Polymer	Glass transition temperature (°C)			
	DSC	DTA	Literature	
HPMC	180	169–174	177 [1]	155 [2]
EC	133	133	129 [1]	
HP55	136	133		
HP50	146	146		
CAP	171	170	18.5 [3]	

[1] Entwistle and Rowe (1979).

[2] Okhamafe and York (1985).

[3] Porter and Ridgway (1983).

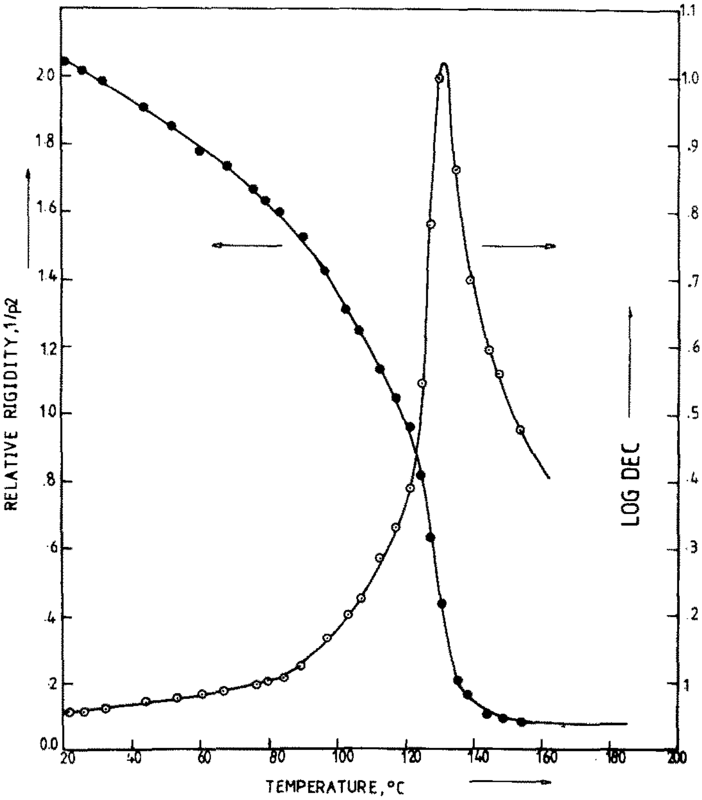

Fig. 1. The thermomechanical spectra of ethyl cellulose. ●, relative rigidity; ○, logarithmic decrement.

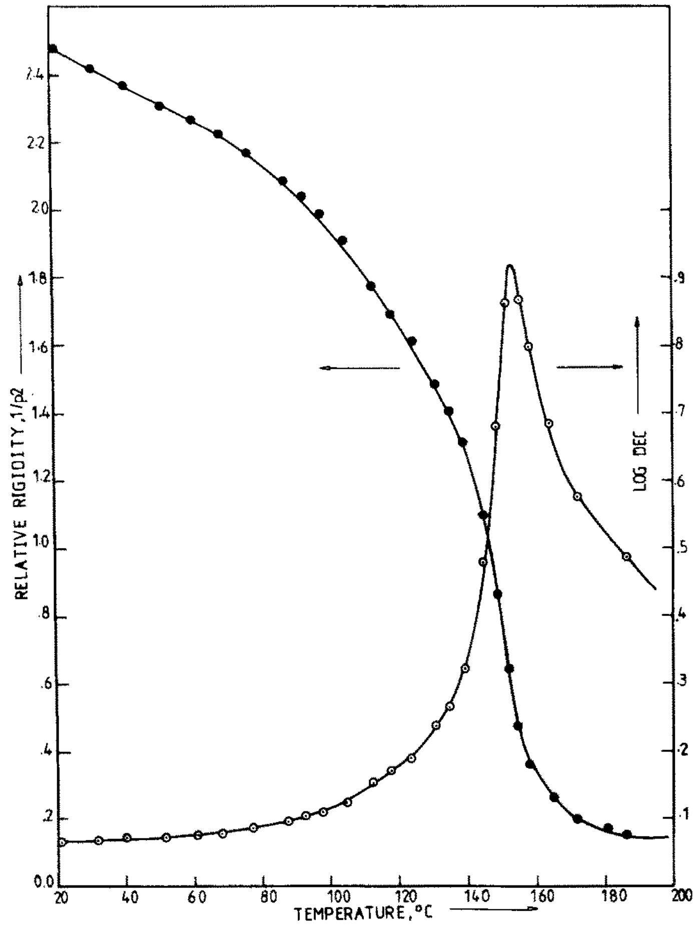

Fig. 2. The thermomechanical spectra of hydropropyl methylcellulose (HPMC a). ●, relative rigidity; ○, logarithmic decrement.

tures down to −40°C showed no transitions or any other change in the spectra and were omitted. All polymers with the exception of hydroxypropylcellulose yielded simple thermomechanical spectra with a single transition in the logarithmic decrement curve and a corresponding abrupt drop in the relative rigidity.

Ethyl cellulose produced a single transition in both damping and relative rigidity at 131.5°C (Fig. 1). The frozen-in molecules began to move more freely at 60–70°C with a maximum energy dissipation at 131.5°C. The glass transition is relatively sharp and complete at 150°C.

The thermomechanical spectra of both batches of hydroxypropyl methylcellulose showed slight but significant differences (Figs. 2 and 3, Table 2) with HPMC(b) exhibiting a broader transition shifted to higher temperatures by 5°C. This is thought to be due to the differences seen in the molecular weight distributions of the two batches with HPMC(a) containing a considerable fraction of low molecular

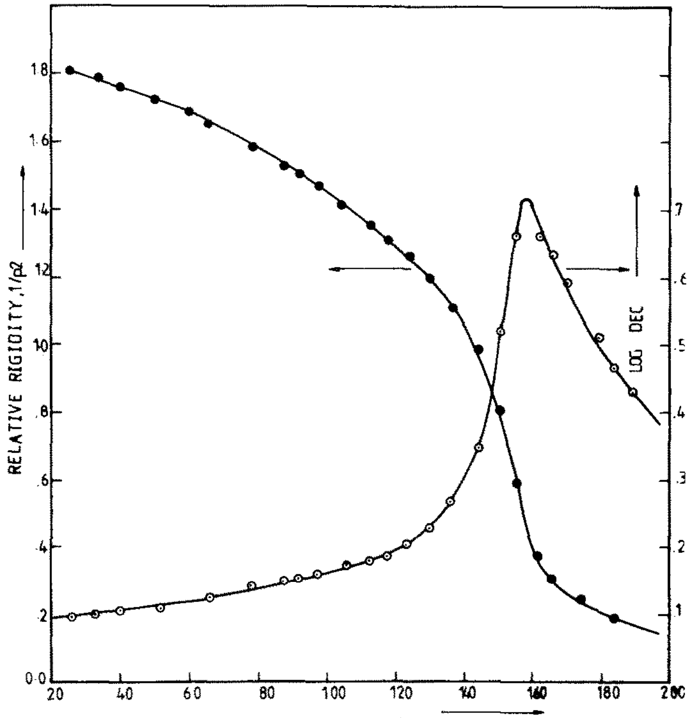

Fig. 3. The thermomechanical spectra of hydroxypropyl methylcellulose (HPMC b). ●, relative rigidity; ○, logarithmic decrement.

weight species and HPMC(b) containing a considerable fraction of high molecular weight species. The shorter chains in HPMC(a) will result in additional free volume and mobility due to the increased number of chain ends causing a reduction in its glass transition temperature.

TABLE 2

THE THERMOMECHANICAL PROPERTIES OF THE CELLULOSE ETHERS SUMMARIZED FROM FIGS. 1-7

Polymer	T_g (°C)	F (Hz)	Δ 20°C	$W_{\sqrt{2}}$ (°C)
HPMC(a)	153.5	0.70	0.07	18.0
HPMC(b)	158.5	0.67	0.09	30.0
EC	131.5	0.60	0.06	11.5
HP50	137	0.52	0.08	13.5
HP55	133	0.59	0.08	11.5
CAP	163	0.60	0.08	11.0
HPC	124	0.36	0.27	–

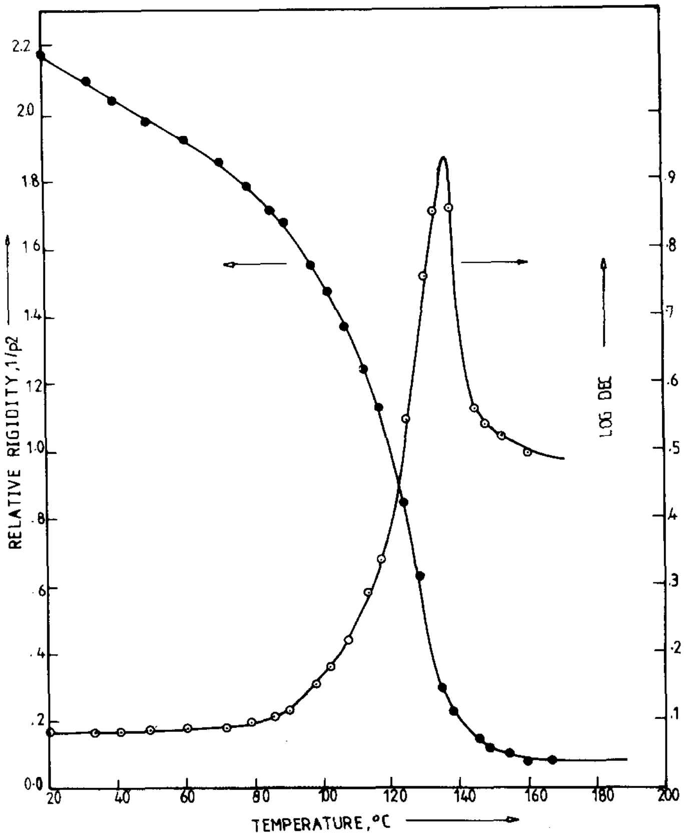

Fig. 4. The thermomechanical spectra of hydroxypropyl methylcellulose phthalate (HP 50). ●, relative rigidity; O, logarithmic decrement.

The two grades of hydroxypropyl methylcellulose phthalate showed significant differences in their glass transition temperatures (Figs. 4 and 5) the HP55 grade with the higher σ-carboxybenzoyl content (25–35% w/w) having a lower glass transition temperature than the HP50 grade with the lower σ-carboxybenzoyl content (20–24% w/w). This was not totally unexpected since the phthalyl groups are very bulky and would be expected to increase free volume and chain mobility. It is interesting to note that Osterwald et al. (1982) quoted a glass transition temperature of 80–90°C for HP55 with a broad transition extending over 70° using a conventional torsion pendulum technique. The influence of the bulky phthalyl groups is again apparent in the data generated for cellulose acetate phthalate (Fig. 6), with a measured glass transition temperature of 163°C, some 27° lower than that previously measured for the fully acetylated cellulose, cellulose triacetate (Gillham and Schwenker, 1966).

The thermomechanical spectra of hydroxypropylcellulose is very much more complicated than the other cellulose derivatives (Fig. 7). The relative rigidity decreases constantly over the temperature range −20°C to +180°C before levelling off. Slight changes in the slope were observed at 65°C, 100°C and 124°C. A number

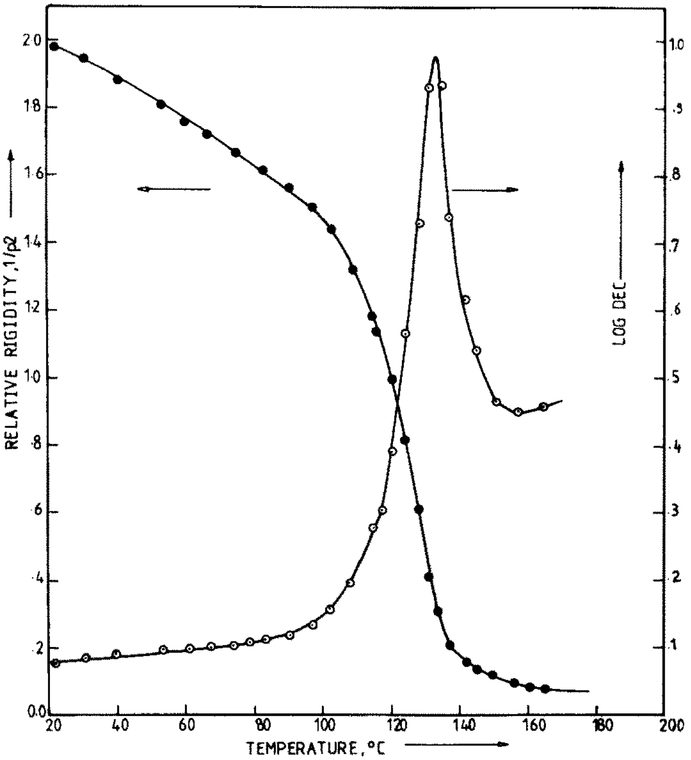

Fig. 5. The thermomechanical spectra of hydroxypropyl methylcellulose phthalate (HP 55). ●, relative rigidity; ○, logarithmic decrement.

of peaks and plateaus can be seen in the logarithmic decrement curves. Two broad peaks that almost merge into one occur at 105°C and 124°C. A broad peak can also be seen at 63–67°C and a plateau at 17°C. At temperatures above 126°C the logarithmic decrement decreases forming a plateau at 145–150°C, a minimum at 162°C and a broad well defined peak at 178°C. Damping at room temperature was distinctly higher than that of the other polymers.

The thermomechanical data for cellulose and cellulose triesters reported in the literature as well as thermal analysis data can be useful in interpreting the behaviour for hydroxypropylcellulose. The transition at 105°C is thought to be due to the evaporation of water and this is supported by an intense water endotherm in the DTA at 100°C. The relaxation at 17°C correlates with the secondary relaxation recorded for the cellulose triesters due to the rupture of weak intermolecular hydrogen bonds, while the transition occurring at 63–67°C is thought to be due to the evaporation of trapped methanol. The glass transition of hydroxypropylcellulose must therefore be related to either of the remaining relaxations at 124°C and 178°C. The only available indication of backbone mobility in hydroxypropylcellulose has been provided by Samuels (1969) who, from studies of IR spectra at elevated temperatures, showed an increasing movement of the backbone via rotations about

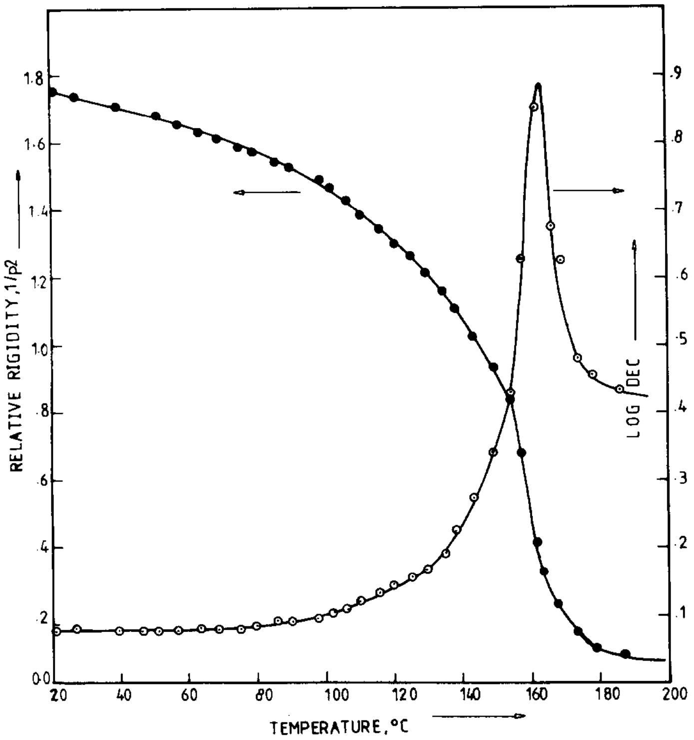

Fig. 6. The thermomechanical spectra of cellulose acetate phthalate. ○, relative rigidity; ●, logarithmic decrement.

C–C and C–O bonds within the temperature range from 120°C to 160°C. Since both DSC and DTA failed to provide a positive indication of a glass transition in the region of 178°C while DSC of water cast HPC films failed to show any transition within the range 140–170°C, it can be concluded that the glass transition temperature of HPC must be related to the relaxation at 124°C. The fact that damping reaches a minimum before the peak at 178°C reinforces the hypothesis that this peak is associated with the softening and commencement of viscous flow of the material. This value also complies with the manufacturer's value for the softening temperature of HPC.

When comparing the data generated by both the thermal analysis and the torsional braid pendulum it must be emphasised that the consistency of glass transition measurements is affected by molecular structure, presence of crystallinity, rate effects, diluents, molecular weight and static methods as compared to dynamic methods (Lee and Rutherford, 1975). Since the torsional braid pendulum is a dynamic method while DSC or DTA are both static methods it would be expected to produce higher values of the glass transition temperature (Williams et al., 1955). Nevertheless, in the method reported here a frequency of about 1 Hz was used and hence the data should be reasonably comparable. Heating rate effects constitute a

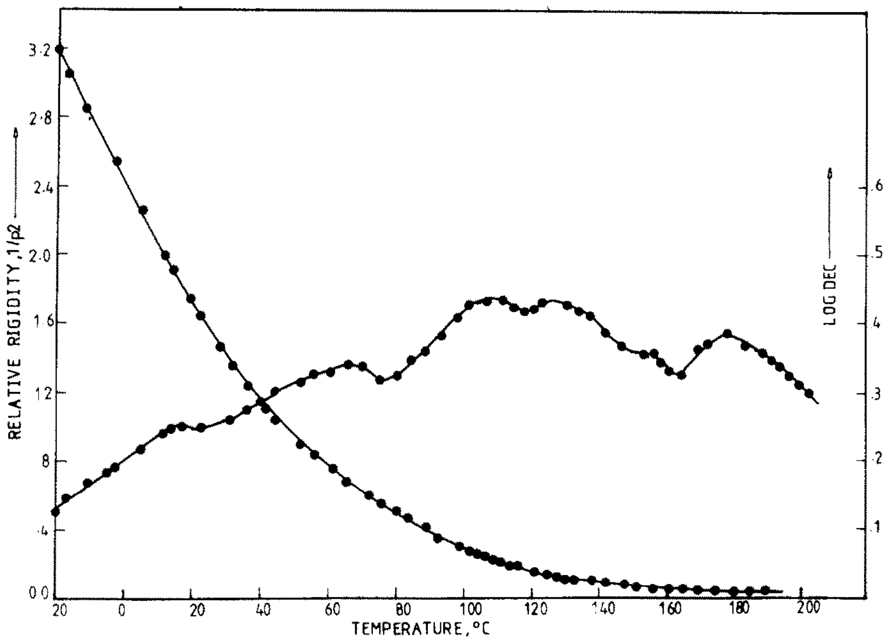

Fig. 7. The thermomechanical spectra of hydroxypropylcellulose. ○, relative rigidity; ●, logarithmic decrement.

significant source of error in most techniques since it is imperative that the sample reaches equilibrium at the temperature and frequency imposed throughout the test. Consequently too high a rate of heating will not permit the attainment of equilibrium, will reduce the time available for the molecules to respond and hence will cause the glass transition temperature to shift to higher temperatures. With the torsional brain pendulum a sample of 10 mg was heated at ca. 1°C · min^{-1} while in DSC and DTA the same sized sample was heated at 20°C · min^{-1}. Taking into account the much lower sample mass/sample surface area ratio of the braids compared to the DSC/DTA samples, it would be expected that the latter would yield higher values for the glass transition temperature by some 9°C at maximum (Nielson, 1963).

While most of the polymers did, in fact, show such a variation, the HPMC samples exhibited differences of between 16 and 26.5°C with respect to the DSC/DTA values. It is thought that with this polymer, sample preparation is an important variable with samples prepared from casting from solvent yielding lower values of glass transition temperature than powdered samples due to unavoidable solvent retention. Solvent retention may be the cause of the very low readings of glass transition temperatures reported by Porter and Ridgway (1983) for cellulose acetate phthalate (18.2°C) and Abdul-Razzak (1980) for hydroxypropyl methylcellulose (53–58°C). No transitions in these regions were found for either the thermal analysis or the torsional braid pendulum method used in this study.

In conclusion it can be seen that torsional braid pendulum is a very useful tool in determining the thermomechanical properties and glass transition temperatures of the cellulose derivatives used as film formers in coatings for oral dosage forms. The technique produces data of high precision and resolution, a significant improvement to the standard DSC and DTA methods in current use and enables more informed assessments to be made of the potential behaviour of film formers in practical tablet coating operations.

References

Abdul-Razzak, M.H., The mechanical properties of hydroxypropyl methylcellulose films derived from aqueous systems, M. Phil. thesis, Council for National Academic Awards, 1980.

Entwistle, C.A. and Rowe, R.C., Plasticization of cellulose ethers used in the film coating of tablets. J. Pharm. Pharmacol., 31 (1979) 269–272.

Gillham, J.K. and Schwenker, R.F., Thermomechanical and thermal ánalysis of fiber-forming polymers. Appl. Polym. Symp., No. 2. (1966) 59–76.

Lee, W.A. and Rutherford, R.A., In Bandrup. J. and Immergut, E.J. (Eds.), Polymer Handbook, Wiley Interscience, 2nd Edn., 1975, pp. 111–139.

Masilungan, F.C. and Lordi, N.G., Evaluation of film coating compositions by thermomechanical analysis I. Penetration mode. Int. J. Pharm., 20 (1984) 295–305.

Nielson, L.E., Mechanical Properties of Polymers, Reinhold Press, New York, 1963.

Okhamafe, A.O. and York, P., Interaction phenomena in some aqueous-based tablet coating polymer systems. Pharm. Res., 2 (1985) 19–23.

Osterwald, H., Eisenbach, C.D. and Bauer, K.H., Wirkungsweise und Optimierungsmoglichkeiten de Anwendung von Weichmachen in Filmuberzugen. Acta Pharm. Technol., 29 (1982) 34–43.

Porter, S.C. and Ridgway, K., An evaluation of the properties of enteric coating polymers: measurement of glass transition temperature. J. Pharm. Pharmacol., 35 (1983) 341–344.

Rowe, R.C., Materials used in the film coating of oral dosage forms. In Florence, A.T. (Ed.), Materials used in Pharmaceutical formulation, Critical Reports in Applied Chemistry, Vol. 6, Society of Chemical Industry, Blackwell Scientific Publications, 1985, pp. 1–36.

Rowe, R.C., Kotaras, A.D. and White, E.F.T., An evaluation of the plasticizing efficiency of the dialkyl phthalates in ethyl cellulose films using the torsional braid pendulum. Int. J. Pharm., 22 (1984) 57–62.

Sakellariou, P., Polymeric interactions in tablet coating films, Ph. D. thesis, University of Manchester Institute of Science and Technology, 1984.

Samuels, R.J., Solid-state characterization of the structure and deformation behaviour of water-soluble hydroxypropylcellulose. J. Polym. Sci., A2, 7 (1969) 1197–1258.

Williams, M.L., Landel, R.F. and Ferry, J.D., Temperature dependence of relaxation mechanisms in amorphous polymers and other glass forming liquids. J. Am. Chem. Soc., 77 (1955) 3701.