International Journal of Pharmaceutics, 22 (1984) 57–62
Elsevier

IJP 00742

An evaluation of the plasticizing efficiency of the dialkyl phthalates in ethyl cellulose films using the torsional braid pendulum

R.C. Rowe, A.D. Kotaras [1] and E.F.T. White [1]

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

(Received April 9th, 1984)
(Accepted June 21st, 1984)

Summary

The plasticizing efficiency of the dialkyl phthalates when added to ethyl cellulose has been evaluated by measuring the glass transition temperatures of formulations using the torsional braid pendulum—a dynamic mechanical technique originally invented for following the rigidity changes accompanying the curing of polymers. The plasticizing efficiency of the four phthalates used was found to be diethyl > dimethyl > dibutyl > dioctyl. In the case of dioctyl phthalate phase separation was so pronounced that there was little effect on the glass transition temperature of the ethyl cellulose. Measured values for the glass transition temperatures were compared with predicted values using a suitable mixture-rule model. Agreement was limited to the case of diethyl phthalate at plasticizer concentrations below 20% w/w.

Introduction

Ethyl cellulose, either alone or in combination with water-soluble polymers, is widely used in coatings for the preparation of delayed or sustained release films (Coletta and Rubin, 1965; Shah and Sheth, 1972; Persson et al., 1981). Since the integrity of the film and the absence of flaws or cracks are all important factors in controlling the release of a drug from such a preparation, it is imperative that the

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

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film formulation be optimized with this in mind. The efficiency of plasticizers, e.g. the dialkyl phthalates, which are often added to such films to increase their flexibility and minimize the incidence of flaws, is very important since it is generally desirable to use the least amount of such materials as is necessary to effect the specific change in physical properties. A property that can be well defined and measured for most polymers is the glass transition temperature. This is a function of chain mobility and, since the purpose of a plasticizer is to increase chain mobility, it offers an experimental method for evaluating plasticizer efficiency. In this work the glass transition temperatures of ethyl cellulose alone and in combination with increasing concentrations of the dialkyl phthalates have been measured using a dynamic mechanical technique—the torsional braid pendulum.

Materials and Methods

The ethyl cellulose used was grade N50 (Hercules, Wilmington, DE, U.S.A.) with a nominal viscosity (5% w/w solution in a solvent mixture of toluene–ethanol (80:20% w/w) measured at 25°C) of 50 MPas and an ethoxyl content 48.5% w/w. The dialkyl phthalates—dimethyl, diethyl, dibutyl and dioctyl—were standard laboratory reagents and were used as received.

The method employed to determine the glass transition temperature of the various formulations was the torsional braid pendulum originally invented for following the rigidity changes accompanying the curing of polymers (Lewis and Gilham, 1962). This is a dynamic mechanical technique which measures the response of a polymer-impregnated glass fibre braid to a sinusoidal stress as a function of temperature. When a polymer in its linear viscoelastic region is subjected to an oscillatory stress, the strain lags behind the stress by a phase angle, δ. Such a cyclic deformation is energy dissipative, the ratio of stress to strain being represented by a complex modulus, G^*, which may be resolved into an in-phase elastic component, G', and an out-of-phase energy dissipative component, G''. These components are defined as:

$$G' = G^* \cos \delta \tag{1}$$

$$G'' = G^* \sin \delta \tag{2}$$

From this it can be seen that:

$$\tan \delta = \frac{G''}{G'} \tag{3}$$

For a damped natural resonance oscillation produced by a torsional braid pendulum it is convenient to measure the logarithmic decrement, Δ, from the amplitudes of successive swings since this is equivalent to $\pi \tan \delta$ provided that $\Delta < 1$ which is always the situation in this work. Hence, it can be seen that both

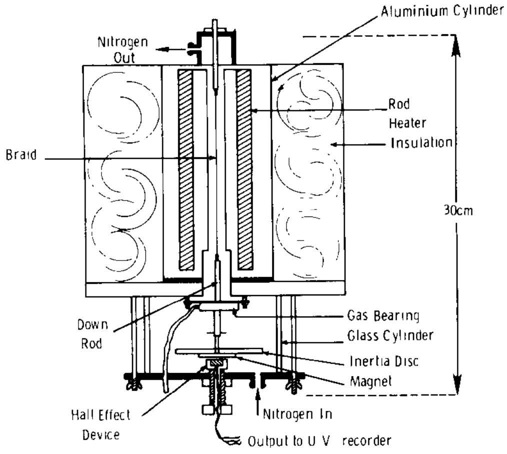

Fig. 1. A schematic diagram of the torsional braid pendulum.

tan δ and Δ are measures of the damping and therefore the degree of segmental motion taking place within a polymer. Damping at temperatures above and below the glass transition temperature is small but rises to a maximum at the glass transition temperature itself. The overall shape of the damping vs temperature curve is also important, a sharp peak denoting a good polymer/plasticizer compatibility, a broad peak denoting poor compatibility.

The apparatus used here was similar to that described by Watts (1977) which consisted of an aluminium cylinder and heating block enclosing a multi-filament, glass roving, braid impregnated by the formulation under test (Fig. 1). The upper end of the braid was attached to a removable bearing assembly while the lower end was attached to an inertia disc to which was fixed a magnet. The oscillations of the disc were followed by means of a Hall effect detection device enclosed in a glass cylinder and base plate. The whole apparatus was purged with nitrogen and a temperature increase of 1°C/min was achieved by the use of heaters embedded in the aluminium block controlled by a specially designed heating control circuit.

The braids used in this study were prepared by first removing the size by heating in an oven at 500°C for 1 h followed by immersion for 3 h in a 2.5% w/v solution of the formulation dissolved in a toluene–ethanol solvent mixture (80 : 20% w/w) and then drying to constant weight in an oven at 70°C. The output from the Hall effect detection device (poportional to the displacement) was transmitted to a UV recorder giving rise to a damped sine curve. From this graph the logarithmic decrement—the natural logarithm of the amplitude of two successive waves—was obtained.

Results and Discussion

The glass transition temperature of the ethyl cellulose was found to be 135°C which compares favourably with that previously measured by differential scanning

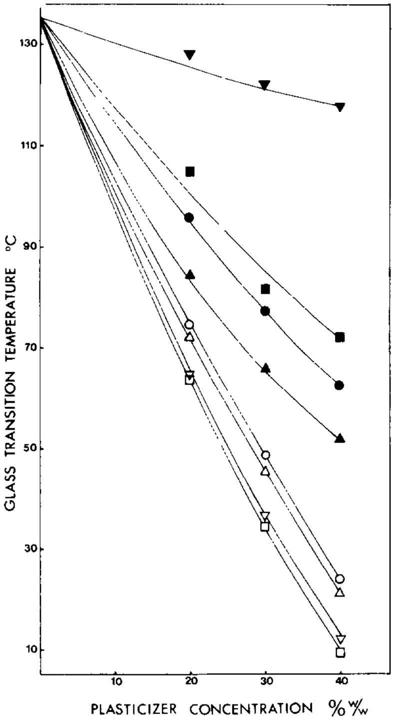

Fig. 2. The effect of plasticizer type and concentration on the glass transition temperature of ethyl cellulose. ●, dimethyl phthalate ▲, diethyl phthalate; ■, dibutyl phthalate; ▼, dioctyl phthalate—values measured using torsional braid pendulum. ○, dimethyl phthalate; △, diethyl phthalate; □, dibutyl phthalate, ▽, dioctyl phthalate—values calculated using Eqn. 4.

calorimetry (Entwistle and Rowe, 1979). The effect of the addition of increasing concentrations of the dialkyl phthalates on the glass transition temperature is shown in Fig. 2. It can be seen that the rank order of plasticizer efficiency as assessed by the greatest decrease in the glass transition temperature per unit amount incorporated was diethyl phthalate > dimethyl phthalate > dibutyl phthalate > dioctyl phthalate. In the case of dioctyl phthalate there was very little decrease in glass transition temperature even at a concentration of 40% w/w. The shape of the damping peak indicated good compatibility with the dimethyl and diethyl phthalates at all concentrations although there was a little broadening of the peak at the highest concentration used. With dibutyl phthalate broadening of the peak occurred at 30% w/w concentration while with dioctyl phthalate there was pronounced phase separation with very broad peaks at all concentrations.

It is interesting to note that these results are in good agreement with those predicted from intrinsic viscosity measurements on the same batch of polymer (Entwistle and Rowe, 1979) and from measurements on other batches of polymer with different nominal viscosities and hence molecular weights but the same ethoxyl content (Kent and Rowe, 1978; Bøgelund, 1983). In all cases a maximum intrinsic

TABLE 1

INTRINSIC VISCOSITY MEASUREMENTS FOR ETHYL CELLULOSE DISSOLVED IN THE DIALKYL PHTHALATES

Plasticizer		Intrinsic viscosity ($dl \cdot g^{-1}$)		
	Grade of polymer:	N7[1]	N20[2]	N50[3]
Dimethyl phthalate		0.583	0.877	1.382
Diethyl phthalate		0.722	1.061	1.430
Dibutyl phthalate		0.510	1.047	0.947
Dioctyl phthalate			0.532	0.539

[1] Kent and Rowe, 1978.
[2] Bøgelund, 1983.
[3] Entwistle and Rowe, 1979.

viscosity and hence maximum compatibility was shown in the case of diethyl phthalate (Table 1).

The results are also in good agreement with those expected from solubility parameter values. The solubility parameter of ethyl cellulose is 21.1 $MPa^{1/2}$ (Burrell, 1975) while those of dimethyl phthalate, diethyl phthalate, dibutyl phthalate and dioctyl phthalate are 21.9 $MPa^{1/2}$, 20.5 $MPa^{1/2}$, 19.0 $MPa^{1/2}$ and 16.2 $MPa^{1/2}$, respectively. It would be expected, therefore, that compatibility would be best with the lower members of the series with the optimum occurring with diethyl phthalate.

It is interesting to compare the actual measured values of the glass transition temperatures of the formulations with those predicted using the simple mixture–rule equation derived by Kelley and Bueche (1961):

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d V_d T_{gd}}{\alpha_p V_p + \alpha_d V_d} \qquad (4)$$

where T_g is the predicted glass transition temperature; α_p and α_d are the coefficients of volumetric expansion of the polymer and the plasticizer, respectively; V_p and V_d are the volume fractions of the polymer and plasticizer, respectively; and T_{gp} and T_{gd}

TABLE 2

CONSTANTS USED IN EQN. 4

	T_{gp} (°C)	α_p^1 (°C^{-1})	T_{gd}^2 (°C)	α_d^2 (°C^{-1})
Ethyl cellulose	135	4.8×10^{-4}	–	–
Dimethyl phthalate	–	–	−80	7.8×10^{-4}
Diethyl phthalate	–	–	−85	7.6×10^{-4}
Dibutyl phthalate	–	–	−97	7.8×10^{-4}
Dioctyl phthalate	–	–	−89	7.6×10^{-4}

[1] Kelley and Bueche, 1961.
[2] Bondi, 1968.

are the glass transition temperatures of the pure polymer and plasticizer, respectively. Fig. 2 shows the predicted results using the constants as shown in Table 2. It can be seen that the only curve to be anywhere near comparable to the measured results was the one predicted for diethyl phthalate and even this deviated at the higher plasticizer concentrations.

The reasons for the large deviations between theory and practice lie in the assumptions made in the derivation of eqn. 4. This expression was specifically derived for ideally compatible systems in which plasticization is simply a dilution effect of the polymer matrix involving an increase in free volume and hence is not necessarily applicable to the system under test where phase separation occurs. The closeness of the predicted and measured curves for the diethyl phthalate, especially at low plasticizer concentrations, indicates that, in this case, the assumptions are reasonably valid, i.e. there is good plasticizer/polymer compatibility and plasticization is by an increase in free volume. However, at higher concentrations of the diethyl phthalate and with all the other dialkyl phthalates the assumptions are invalid due to decreased compatibility.

In conclusion it can be seen that diethyl phthalate was the best plasticizer of those examined. At 30% w/w concentrations it lowered the glass transition temperature of the ethyl cellulose very close to 60°C—the temperature of the tablet coating process. By lowering the glass transition the toughness of the ethyl cellulose film should be greatly improved thus enabling the tablet coating to withstand the stresses occurring during the coating process. Dimethyl and dibutyl phthalates were less effective because of increasing incompatibility problems and in the case of dioctyl phthalate phase separation was so pronounced that incorporation had little effect on the glass transition temperature of the ethyl cellulose. The torsional braid pendulum has proved to be a very useful tool in this work.

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