International Journal of Pharmaceutics, 92 (1993) 137–141

IJP 03136

Compaction stress relaxation interpreted using a hyperbolic relation [1]

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(Received 5 October 1992)
(Accepted 18 November 1992)

Key words: Stress relaxation; Powder compaction; Hyperbolic relationship; Deformation; Viscoelastic behavior

Summary

Stress relaxation experiments were used to quantify the time-dependent deformation of four materials. The experimental data fitted a hyperbolic relationship. This enabled quantification of (i) the instantaneous rate of stress relaxation $\Delta F/\Delta t$ at time zero when peak load was reached, (ii) the total visco-elastic force, ΔF_0 remaining at time zero, and (iii) the relaxation half-life, t'.

Introduction

The visco-elastic behaviour of a material can be studied by holding a specimen at constant strain and recording the stress relaxation that occurs over a period of time. In the case of a particulate solid undergoing compaction in a die, stress relaxation occurs as a result of time-dependent deformation of the material under stress, facilitated by the presence of void spaces within the compact. As this process proceeds, the stress reduces and the driving force for further stress relaxation diminishes. It is relatively straightforward from an experimental standpoint to hold the compact at constant bulk strain, whereas maintaining a constant stress to measure creep compliance (Tsardaka, 1990) is technically more difficult.

A number of investigators (Shlanta and Milosovich, 1964; Baba and Nagafuji, 1965; Cole et al., 1975; David and Augsburger, 1977; Hiestand et al, 1977; Rees and Rue, 1978; Shott, 1983) have applied this stress relaxation technique to study pharmaceutical powder compaction. Several of them (Baba and Nagafuji, 1965; David and Augsburger, 1977; Hiestand et al., 1977; Rees and Rue, 1978; Shott, 1983) attempted to fit the data to mathematical models in order to permit more detailed analysis.

Materials and Methods

Four particulate solid materials, commonly used in the formulation of compressed tablets,

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[1] Paper presented at the 6th International Conference on Pharmaceutical Technology, Association de Pharmacie Galénique Industrielle, Paris, June 1992.

were studied; they represent a wide range of different types of consolidation behaviour when a compression load is applied: microcrystalline cellulose (Avicel PH102, FMC Corp., U.S.A.); partially pregelatinised corn starch (Starch 1500, Colorcon Ltd, U.K.); anhydrous lactose (Sheffield Products, U.S.A.); dibasic calcium phosphate dihydrate (Emcompress, Edward Mendell, U.S.A.).

Helium air pycnometry (Model 1302, Micromeritics, U.S.A.) was used to measure the apparent particle density of each material and, thus, to determine the compression weight required to produce a compact of 2.21 mm theoretical thickness at zero porosity when pressed between flat punches in a 12.7 mm diameter die. Samples of each material, weighed to ± 0.5 mg, were stored at 25°C/53% relative humidity for 1 week prior to testing. The powder samples were compressed using a tensile testing machine (T22K, J.J. Lloyd Instruments Ltd, Fareham, U.K.) fitted with a compression cage. Applied force was monitored using a pre-calibrated 20 kN load cell (Grade B, J.J. Lloyd Instruments Ltd, Fareham, U.K.). A constant stress module (T510, J.J. Lloyd Instruments Ltd, Fareham, U.K.), interfaced to the drive mechanism of the rig, enabled the load to be increased to the required level of either 2 or 6 kN, at the selected platen rate of 10 mm min^{-1}. When the drive mechanism stopped, the distance separating the punch faces was maintained constant. As stress relaxation occurred within the powder bed, held under these conditions of constant strain, the force decay was monitored for 5 min. Assuming that the cross-sectional area of contact between the punch faces and the compact remained effectively constant throughout the test, the recorded force is directly proportional to the mean axial stress.

Preliminary measurements were made to ascertain the need for correction of the data to compensate for measurable deformation of the components of the compression rig. With no powder in the die and with the punch faces in direct contact, no significant decrease in force could be detected, under identical loading conditions to those used in the tests.

Each stress relaxation curve was generated from 500 data points processed by a microcomputer (BBC Master series, Acorn Computers, Cambridge, U.K.). Six replicate samples of each material were tested.

Results and Discussion

The difference between peak force, F_{max} at time zero and the force, F_t at time t, quantifies the force decay, ΔF associated with stress relax-

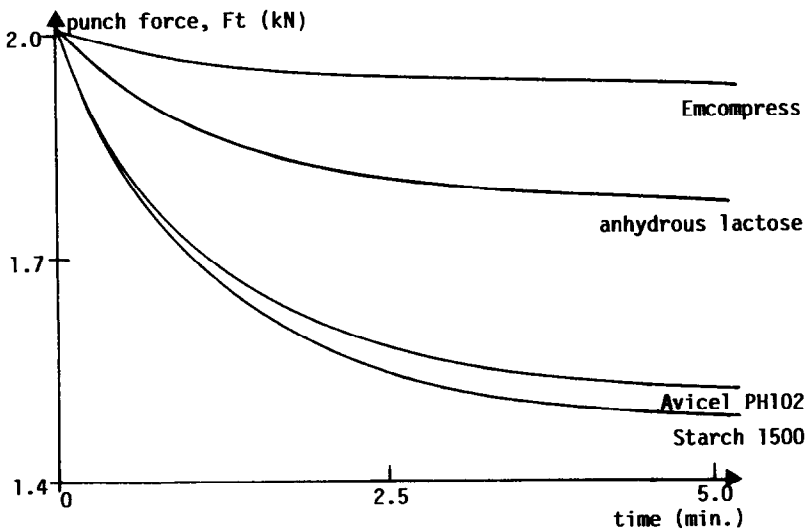

Fig. 1. Stress relaxation results for materials loaded to 2 kN at 10 mm min^{-1}, showing the decreasing punch force with time.

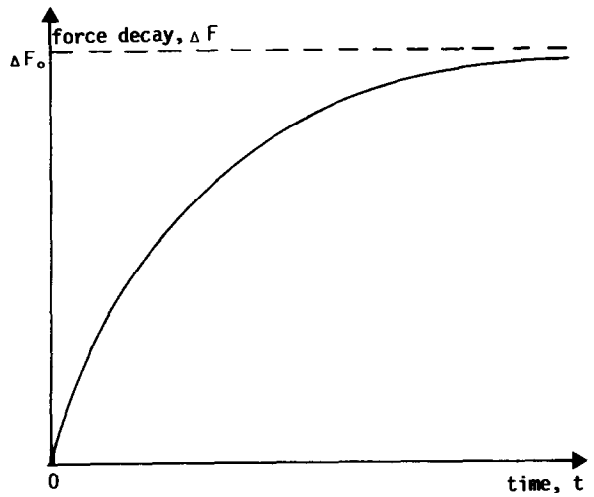

Fig. 2. Typical increase in the force decay, ΔF as a function of time, showing the value approaching the asymptotic value, ΔF_0.

ation. Fig. 1 shows a plot of the total force, F_t as a function of time. Clearly, as visco-elastic deformation proceeds at constant strain, the applied load diminishes to a constant value, $F_{t\infty}$ at infinite time.

Thus, when $t = t_\infty$, the force decay ΔF becomes equal to the limiting value ΔF_0, i.e., $(F_{max} - F_{t\infty})$.

If force decay, ΔF is plotted against time, a curve of the form shown in Fig. 2 is obtained, where the asymptote is given by ΔF_0. This curve may be described by the hyperbolic equation:

$$(t + t')(\Delta F_0 - \Delta F) = K \tag{1}$$

The relevance of the constants, t' and K is explained by expanding Eqn 1 as follows:

$$t\Delta F_o - t\Delta F + t'\Delta F_o - t'\Delta F = K \tag{2}$$

But $t = 0$ when $\Delta F = 0$

Therefore,

$$t'\Delta F_0 = K \tag{3}$$

Substituting in Eqn 2, and rearranging, gives:

$$t\Delta F_0 = t\Delta F + t'\Delta F \tag{4}$$

Dividing through by $(\Delta F \cdot \Delta F_0)$ gives:

$$t/\Delta F = t \cdot (1/\Delta F_0) + t'/\Delta F_0 \tag{5}$$

or,

$$t/\Delta F = (t + t')/\Delta F_0 \tag{6}$$

According to Eqn 5, a plot of $t/\Delta F$ against time, t, will be rectilinear (Fig. 3).

At short relaxation times, $t \approx 0$ and $(t + t')/\Delta F_0$ becomes $t'/\Delta F_0$. Eqn 6 then reduces to:

$$t/\Delta F = t'/\Delta F_0 \tag{7}$$

where $t'/\Delta F_0$ represents the intercept in Fig. 3.

Thus the reciprocal of this intercept quantifies the rate of stress relaxation, $\Delta F/\Delta t$ immediately after peak load is applied. Here Δt represents a short time period from time zero.

Furthermore, Eqn 5 shows that, by taking the reciprocal of the gradient, $1/\Delta F_0$ in Fig. 3, the total force decay at infinite time, ΔF_0 is obtained.

The value of t' is given by the product of the intercept, $t'/\Delta F_0$ and the reciprocal slope, ΔF_0. From Eqn 6, t' is the time at which the peak force, F_{max} has decreased by half of the total visco-elastic force, ΔF_0 remaining at time zero; it therefore is equivalent to a half-life of stress relaxation.

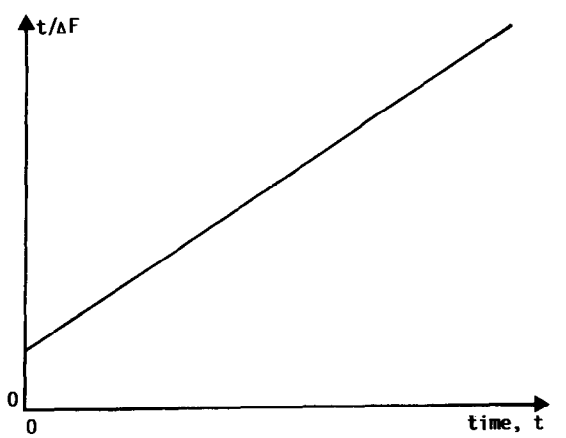

Fig. 3. Linear transform of the hyperbolic graph shown in Fig. 2, according to Eqn 5.

The experimental stress relaxation data for the four materials gave the results presented in Table 1 for the derived visco-elastic parameters, ΔF_o, $\Delta F/\Delta t$ and t'. The high values for the correlation coefficient, r clearly demonstrate that, by transforming the data according to Eqn 5, excellent linear correlation was obtained between $t/\Delta F$ and time, t, as shown in Fig. 3. The proposed method of linearising stress relaxation data, therefore, enabled precise quantification of the instantaneous rate of stress relaxation, $\Delta F/\Delta t$ at a specified applied force, as well as the total remaining visco-elastic force, ΔF_o at time zero, and the half-life, t' of the visco-elastic force decay.

The data were also analysed according to the method proposed by Baba and Nagafuji (1965). When the relative force, $F_t/F_{t\infty}$ was plotted against logarithm of time, there was clear evidence of deviation from linearity at short relaxation times. This gave values of the correlation coefficient which, in every case, were lower than those listed in Table 1: the r values ranged from 0.983 to 0.992 for starch and cellulose, 0.964 to 0.992 for lactose, and 0.900 to 0.961 for dicalcium phosphate. So, irrespective of consolidation mechanism, the hyperbolic relationship gave better linearisation of the stress relaxation results.

One difficulty associated with fitting experimental stress relaxation data to, say, a Maxwell model (David and Augsburger, 1977) is the need to know the equilibrium, or asymptotic value of the force, at infinite time. The difference between this value and the recorded force at any particular time gives the amount of the visco-elastic force remaining within the system at that time. Graphical estimation of the asymptote introduces errors. Consequently, an additional advantage of the present approach is that it provides a solution to this problem of determining ΔF_o.

Rees and Rue (1978) suggested that, since a pharmaceutical compaction process is of short duration, it is the behaviour of materials during the early stages of stress relaxation that is of special interest. In practice, that is the most difficult part of the stress relaxation profile to define. This may be a further advantage of the hyperbolic model proposed here, as it provides a means

TABLE 1

Results derived, using Eqn 5, from experimental stress-relaxation data obtained after compaction at different platen-rates and peak loads

	r	Peak load (kN)	Platen rate (mm/min)	ΔF_o (N)	$\Delta F/\Delta t$ (N s^{-1})	t' (s)
Starch 1500	0.999	2.02	10	485.4	38.3	12.7
	0.999	2.03	50	476.2	41.5	11.5
	0.999	6.04	10	1250	94.3	13.3
	0.999	6.05	50	1282	104.2	12.3
Avicel PH102	0.999	2.09	10	456.6	35.2	13.0
	0.999	2.09	50	456.6	38.3	11.9
	0.999	6.04	10	943.4	64.9	14.5
	0.999	6.11	50	952.4	73.5	13.0
Anhydrous lactose	0.999	2.04	10	215.1	22.6	9.5
	0.999	2.02	50	233.6	28.9	8.1
	0.999	6.02	10	485.4	31.6	15.4
	0.999	6.24	50	543.5	36.8	14.8
Emcompress	0.987	2.02	10	48.22	10.8	4.5
	0.993	2.18	50	59.28	8.4	7.1
	0.994	6.06	10	136.6	9.4	14.5
	0.996	6.26	50	152.2	12.5	12.2

for calculating the rate of force decay, $\Delta F/\Delta t$ immediately after the known peak load is applied.

As shown in Table 1, an increase in the compaction load raised the value of ΔF_0 for all four materials. This effect was most marked in the case of Starch 1500 although, in proportional terms, the change for Emcompress was equally large. The 5-fold increase in platen rate had no apparent effect on ΔF_0 for starch and cellulose, but increased the value by about 10% for lactose, and by 10–20% for dicalcium phosphate. The effect of strain rate on the two latter materials is explained by the results for stress relaxation rate at peak load, $\Delta F/\Delta t$ shown in Table 1; clearly, they will undergo less rapid deformation than starch or cellulose as the compaction load is applied, and therefore will exhibit higher values of visco-elastic force remaining at time zero (ΔF_0), when the platen rate is increased.

The relaxation half-lives, t' for Starch 1500 and Avicel PH102 showed no significant dependence on peak load or loading rate. In contrast, the values for anhydrous lactose increased by over 50%, and for Emcompress by up to 225%, when the peak load was raised from 2 to 6 kN. This seems to indicate that compaction load had more effect on the long-term relaxation rate as measured by t' than on the short-term rate as quantified by the $\Delta F/\Delta t$ values. There was no obvious trend in the effect of loading rate on the half-lives of lactose or dicalcium phosphate. It is interesting that the half-lives for all four materials recorded at 6 kN load were very similar, ranging from 12.2 to 15.4 s.

Conclusion

Experimental stress relaxation data for Starch 1500, Avicel PH102, anhydrous lactose and Emcompress showed excellent fit to a hyperbolic relationship.

Linear transformation of the hyperbolic stress relaxation profile enabled three visco-elastic parameters to be quantified. These were the total visco-elastic force, ΔF_0 remaining at time zero, the instantaneous relaxation rate, $\Delta F/\Delta t$ and the relaxation half-life, t'.

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