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Stress relaxation behaviour of compacts of sodium chloride and polyethylene

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Summary

Using a specially constructed jig, precise measurements of force–time and displacement–time profiles were recorded during the consolidation of sodium chloride and polyethylene. It was found that after compression, sodium chloride underwent an immediate pressure decay to a far greater extent than polyethylene, which was shown to deform predominantly by elastic deformation. Mixtures of varying proportions of sodium chloride and polyethylene indicated that up to the critical level of 3% w/w polyethylene, there was a corresponding reduction in the overall plasticity of the binary mixture; whilst from 3–10% an improvement in plasticity was recorded. A clearly defined direct relationship was found to exist between plastic flow, compact thickness and pressure decay. With regard to the tensile strength of the compacts, it was shown that sodium chloride hardens with age, but that with a polyethylene content of 2% and above, the elasticity of the polyethylene was such that tablets were produced that were so structurally weak that they had zero tensile strengths. This significant finding meant that relatively small amounts of an elastic constituent could produce a compact with no practical strength and that predominantly elastic materials should therefore be avoided in tablet formulations.

Introduction

During the compression process, energy is imparted to the particulate material which bonds the particles together to form coherent compacts. However, not all the compaction energy is utilised in bonding; some will be used to deform the particles both elastically and plastically and to cause brittle fracture. The factors influencing the compaction of materials that deform plastically have been reviewed by Jones (1981). He emphasised that the rate of application of the applied force was an important variable, since slow com-

pression and decompression would allow some degree of stress relaxation to occur before the load was removed. In the case of the plastically deforming material sodium chloride, stress relaxation occurs the instant compression ceases and has been found by Rees and Shotton (1970) and Rue and Barkworth (1980) to account for the high, time-dependent strength of sodium chloride compacts. Using an instrumented tablet machine to study stress–time relationships for a variety of drugs and excipients, Baba and Nagafuji (1965) demonstrated two basic findings, namely that: (a) an increase in relaxation coincided with both a reduction in applied force and particle size; and (b) on tableting, a creep recovery led to the swelling of tablets containing starch and lactose.

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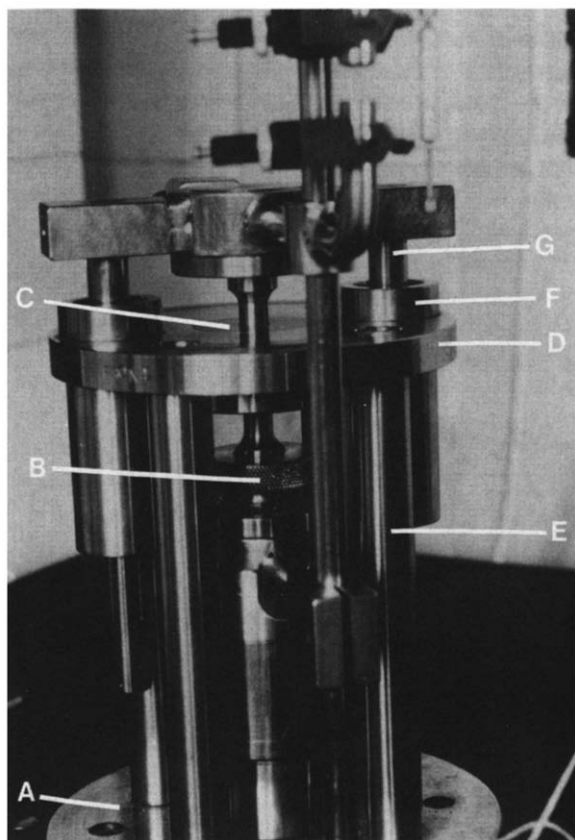
Shlanta and Milosovich (1964) also demonstrated a time-dependent effect as did Cole et al. (1975) who measured both the load and resultant deformation of sodium chloride, potassium chloride and potassium citrate. They concluded that stress relaxation was due to certain materials undergoing plastic flow once the maximum load had been applied. Hiestand et al. (1977) investigated the effect of stress relaxation on capping and showed that materials that capped also exhibited slower stress relaxation. Their findings clearly identified the time-dependent relationship between stress relief and plastic deformation. Using the Maxwell model, David and Augsburger (1977) were able to classify various materials according to their degree of plastic flow under compaction. By adopting mechanical strength of tablets as a measure of ultimate bonding potential, David and Augsburger showed that there was an interdependence between highest attained strength and maximum plastic flow. Most pharmaceutical formulations do not, however, consist of predominantly plastically deforming powders, but are composed of mixtures of plastic, elastic and brittle materials. Therefore, the aim of this study was to investigate the stress relaxation properties of sodium chloride and polyethylene, which are examples of respectively plastic and elastic materials.

Materials and Methods

The materials used were sodium chloride (analytical reagent grade, B.D.H. Chemicals Ltd., Poole) and polyethylene ('sclair', Rotec Chemicals Ltd., Bedford). Blends of binary mixtures of different concentrations were prepared using a turbula mixer. Single components and mixtures were dried and stored over silica gel until compressed.

An Instron Universal Testing Instrument (Model 1121) fitted with a 10 kN load cell was used to compress the powders. A force of 8 kN, which was equivalent to a compaction pressure of $112.6 \text{ MN} \cdot \text{m}^{-1}$, was used at preset compaction speeds of 2, 20 or $50 \text{ mm} \cdot \text{min}^{-1}$. At the instant at which the top punch exerted its maximum pressure of $112.6 \text{ MN} \cdot \text{m}^{-1}$ the load was stopped and

the crosshead allowed to 'float'. Force-time curves were plotted directly on a flat bed recorder. A special jig was constructed to enable the powders to be compressed uniformly and also to provide a method for measuring accurately punch displacement, both during loading and throughout the stress relaxation period. In the past the measurement of force-displacement has suffered both from lack of precision and also from the inability to detect very small changes in displacement during the compression cycle. To heighten the degree of detection and precision and minimise instrumental errors this special jig was designed and constructed (Fig. 1). The principal function of the jig was to simultaneously monitor both force-time and force-displacement relationships during a single compression. The base of the jig (A) was bolted to the base plate of the Instron crosshead unit. Into the base was secured the bottom punch held in a screw-thread holder (B). The die (C) was placed in the jig table (D) which in turn was bolted to the base by means of four legs (E) extending upwards from the jig base. The bottom punch was stationary and positioned, by means of the screw-thread holder, so that it entered the die to the same extent each time a compression was carried out. Also attached to the table were two frictionless bearings (F) through which two complementary legs (G) from the upper punch holder fitted smoothly, such that when powder was placed into the die, the top punch rested lightly on the powder. Top punch displacement, during both compression and decompression stages, was determined by attaching an Instron extensometer (model G51-12MA, 25 mm — 50%) between the top punch and jig base. Adjustment was such that the extensometer could be removed after each compression cycle; the compact ejected manually and the extensometer replaced in exactly the same position for the next measurement. Using an Instron Calibration Unit, the extensometer was accurately calibrated allowing displacements of $1\text{--}2 \mu\text{m}$ to be resolved. By feeding displacement (X-axis) and load (Y-axis) to an independent X-Y recorder, force-displacement and force-time profiles could be recorded simultaneously. Tensile strength of the compacts produced was measured using a Heberlein strength tester with plattens covered with filter paper.



A = Base
B = Screw-thread holder
C = Die
D = Jig table
E = Four legs
F = Two frictionless bearings
G = Legs

Fig. 1. The stress relaxation jig which enables punch displacement to be measured to $1\text{--}2\ \mu\text{m}$.

Results and Discussion

Fig. 2 illustrates the pressure decay (force)–time relationships for the two materials. It can be seen that sodium chloride and polyethylene undergo an immediate pressure decay; sodium chloride decaying to a far greater extent than polyethylene. The large decrease in pressure for sodium chloride after the maximum load has been applied is accounted for by plastic flow reducing the force acting on the load cell. Deformation by plastic flow is well documented for sodium chloride. However, polyethylene, which is considered to be

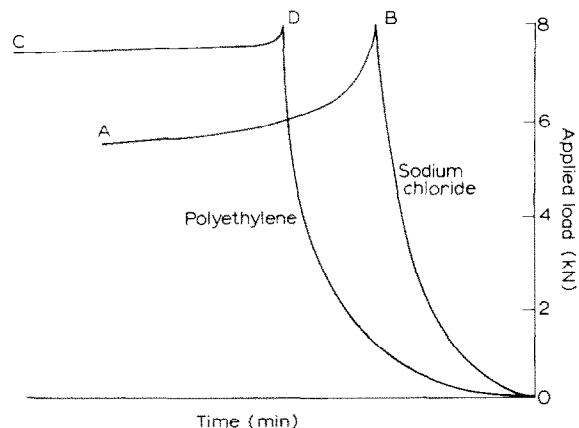


Fig. 2. Pressure decay–time profiles for polyethylene and sodium chloride. Maximum applied pressure $112.6\ \text{MN}\cdot\text{m}^{-2}$; compression speed $2\ \text{mm}\cdot\text{min}^{-1}$; relaxation time A, B = C, D = 40 min.

predominantly an elastic material, also exhibited an immediate pressure decay though not of the same magnitude as sodium chloride. Polyethylene can be considered to be a viscoelastic material and under an applied load does deform plastically to some extent as shown in Fig. 2. By mixing various proportions of polyethylene with sodium chloride, the stress relaxation of these mixtures could be similarly recorded (Fig. 3). It can be seen that as the polyethylene content increases up to 3% w/w there is a corresponding reduction in plasticity of

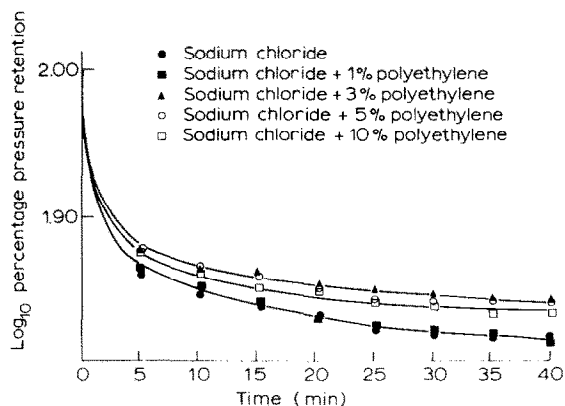


Fig. 3. Stress relaxation (pressure) of sodium chloride with and without the addition of varying amounts of polyethylene. All materials compressed to a maximum applied pressure of $112.6\ \text{MN}\cdot\text{m}^{-2}$ at a crosshead speed of $50\ \text{mm}\cdot\text{min}^{-1}$.

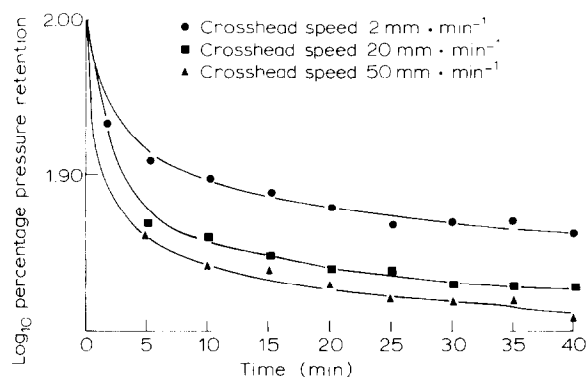


Fig. 4. Stress relaxation (pressure) of sodium chloride compressed to a maximum applied pressure of $112.6 \text{ MN} \cdot \text{m}^{-2}$.

the overall mixture; whilst from 3 to 10% w/w stress relaxation increases over the 40-min time interval. It would seem that small quantities of an elastic material like polyethylene interferes with the plastic flow of sodium chloride, which in turn reduces the amount of stress relaxation after the maximum pressure of $112.6 \text{ MN} \cdot \text{m}^{-2}$ has been applied. Interestingly, however, it can be seen that higher concentrations of polyethylene up to 10% w/w improved the plasticity of the compacts, indicating that the plastic component of polyethylene was now predominating and as a result increases the stress relaxation of the sodium chloride-polyethylene mixture. The influence of speed of compaction or dwell time on stress relaxation is shown in Fig. 4 (sodium chloride) and for sodium chloride-polyethylene mixtures in Fig. 5. Dwell time plays a major role in the compaction process as can be seen from these figures. With sodium chloride an increase in compression speed from 2 to 20 to 50 mm/min produced respective decays of 14.4, 15.2 and 16.4%. It was thus found that a shorter dwell time increased the extent of plastic flow; a conclusion that was difficult to explain. Inclusion of 3% polyethylene, at all three speeds, reduced the amount of stress relaxation, whilst a higher concentration of polyethylene (10%) again improved the plasticity of the compacts. Very little data has been published concerning the effect of varying the compression speeds on the compaction properties of materials, though of the work that has been reported (Ritter and Sucker,

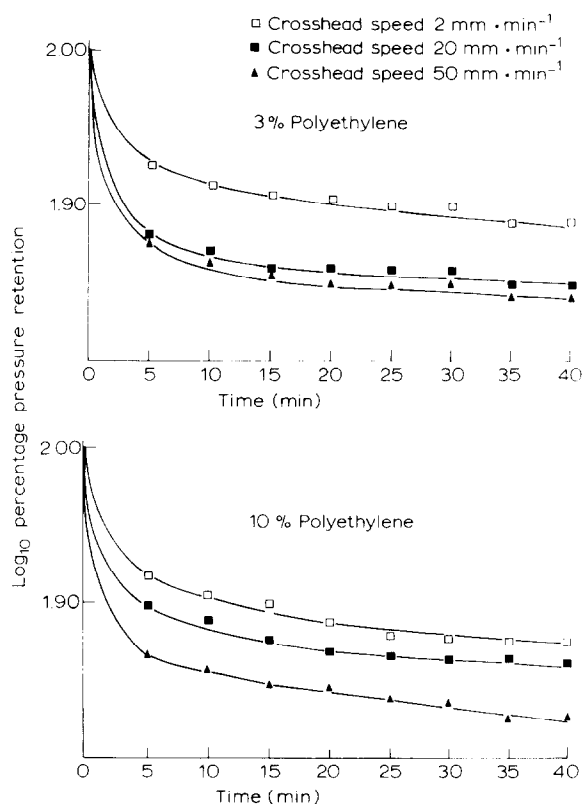


Fig. 5. Stress relaxation (pressure) of sodium chloride plus polyethylene compressed to a maximum applied pressure of $112.6 \text{ MN} \cdot \text{m}^{-2}$.

1980; Vezin et al., 1983) very much higher compaction speeds have been utilised than in this work.

The experimental technique allowed simultaneous measurements to be made of compact thickness in the die. The extensometer precisely measured the displacement of the top punch after the maximum load had been applied. An increase in axial displacement corresponded directly with a reduction in compact thickness and volume. Fig. 6 depicts the results obtained over a 40-min relaxation time. As expected sodium chloride plastically deformed and as a result a large reduction in compact volume was recorded (as an increase in axial displacement). With polyethylene, however, it elastically recovers, post-compaction and as a result there is a reduction in axial displacement indicating that the material undergoes instant

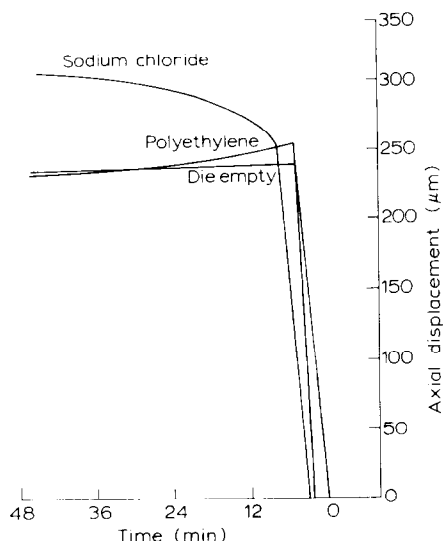


Fig. 6. Displacement-time profiles for sodium chloride and polyethylene. Maximum applied pressure $112.6 \text{ MN} \cdot \text{m}^{-2}$; compression speed $2 \text{ mm} \cdot \text{min}^{-1}$; relaxation time 40 min.

expansion after the load has been applied. A combination of sodium chloride and varying proportions of polyethylene produced the time-displacement curves shown in Fig. 7. As can be seen increasing the amount of polyethylene up to 3%

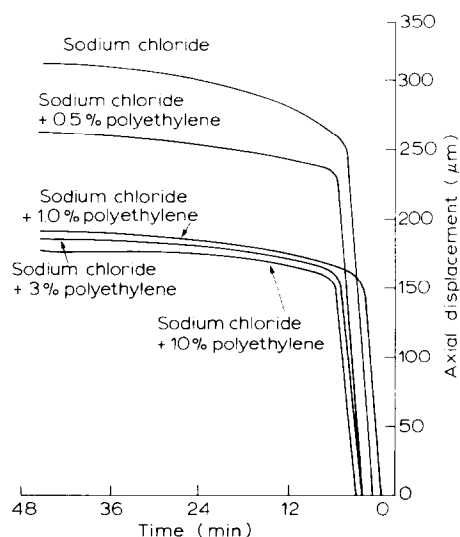


Fig. 7. Displacement-time profiles for sodium chloride (mean particle size $355 \mu\text{m}$) as a single component and diluted with polyethylene. Maximum applied pressure $112.6 \text{ MN} \cdot \text{m}^{-2}$; compression speed $2 \text{ mm} \cdot \text{min}^{-1}$; relaxation time 40 min.

w/w considerably reduced the plasticity of sodium chloride resulting in thicker compacts due to the elastic recovery of the polyethylene. Increasing the concentration of polyethylene up to 10% only marginally increased the thickness of the compacts and as found before this was due to the plastic component of polyethylene now predominating and so reducing the overall elasticity of the binary mixture once the critical concentration of 3% polyethylene had been reached.

The interrelationship between pressure decay and displacement is illustrated in Fig. 8. The respective profiles are similar in shape. As sodium chloride plastically flows a corresponding reduction occurs in compact thickness which in turn results in a reduction in the pressure applied to the load cell by the compact. There is therefore a clearly defined direct interdependence between plastic flow, compact thickness and pressure decay. York and Bailey (1977) compared changes in the heights and diameters of compacts of sodium chloride and found that large dimensional changes occurred after 15–20 min. They defined a correlation between reduction in dimension and decrease in porosity. There seems little doubt that, in the case of sodium chloride, plastic flow accounts for such changes. By increasing compression speed, a corresponding increase in both pressure decay and displacement were observed; the measured displacement at 20 and $50 \text{ mm} \cdot \text{min}^{-1}$ being greater than that at $2 \text{ mm} \cdot \text{min}^{-1}$.

Tensile strength profiles of sodium chloride

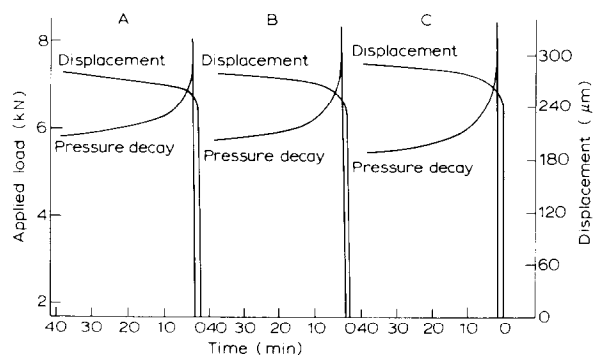


Fig. 8. Time-dependent stress relaxation at maximum applied pressure for sodium chloride. A: compression speed $2 \text{ mm} \cdot \text{min}^{-1}$. B: compression speed $20 \text{ mm} \cdot \text{min}^{-1}$. C: compression speed $50 \text{ mm} \cdot \text{min}^{-1}$.

with and without polyethylene as a function of compression speed are shown in Fig. 9. With respect to sodium chloride alone, all compacts displayed identical tensile strengths irrespective of compression speed. As expected, the compacts hardened and higher tensile strengths were recorded after 40 min. With the inclusion of 0.5% w/w polyethylene the lowest compression speed produced compacts of lowest strength, being significantly lower than at the two higher speeds. Such a difference is consistent with a reduced pressure decay arising as a result of both decreased particle bonding and elastic recovery. The highest compression speed generated the hardest compacts, both immediately after compression and after ageing for 40 min. Increasing the polyethylene content to 1% completely negated compact adhesion, irrespective of the compression speed. Tensile strengths were zero, but increased with age. At concentrations of polyethylene of 2% and above, the elasticity of polyethylene was such that coherent compacts could not be produced with measurable tensile strengths even after ageing. Compression speed played no part in modifying the situation and was therefore of little consequence. It would thus seem that the inclusion of concentrations above the critical value of 2% of polyethylene produced a compact that elastically recovered to such an extent that the resultant tablet was structurally weak and produced a compact with zero tensile strength. The evidence for this hypothesis was conclusive. Reduced pressure decay (indicative of significant elastic recovery) and diminished axial displacement (indicating that plastic flow was impaired) all correlated with a fall

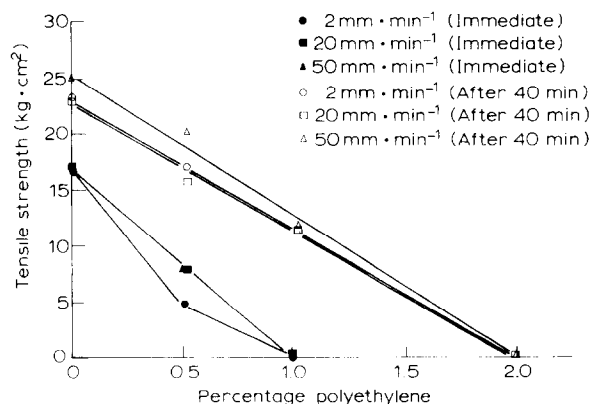


Fig. 9. Tensile strength profiles of sodium chloride with and without polyethylene after compression at $112.6 \text{ MN} \cdot \text{m}^{-2}$.

in tensile strength to zero. The significance of this finding is of paramount importance in tablet formulation design. The inclusion in a formulation of relatively small amounts of an elastic constituent can, as shown here, produce compacts with little practical strength and highly elastic materials like polyethylene should therefore not be considered as suitable ingredients for inclusion in tablet formulations.

With regard to compression speed, although some variations in behavioural patterns are just perceptible, it would appear that at the relatively low speeds operating in the present study, only slight modifications in compaction characteristics were observed. Only by making a comparison of relatively slow and extremely fast speeds could significant differences be anticipated. The Instron machine is not capable of producing precise measurements at high compression speeds, as found on normal tableting machines and such experiments would best be determined on a compaction simulator.

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