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Thermodynamic analysis of compact formation; compaction, unloading, and ejection
II. Mechanical energy (work) and thermal energy (heat) determinations of compact unloading and ejection

Mark T. DeCrosta [a,b,*], Joseph B. Schwartz [b], Rodney J. Wigent [b], Keith Marshall [c]

[a] *SmithKline Beecham Pharmaceuticals, Collegeville, PA, 19426, USA*
[b] *Philadelphia College of Pharmacy and Science, Philadelphia, PA19104, USA*
[c] *Keith Marshall Associates, Brick, NJ 08723, USA*

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Abstract

A compaction calorimeter, previously described (DeCrosta, M.T., Schwarz, J.B., Wigent, J.B., Marshall, K., 2000. Thermodynamic analysis of compact formation: compaction, unloading, and ejection. I. Design and development of a compaction calorimeter and mechanical and thermal energy determination of powder compaction. Int. J. Pharm. 198, 113–134.), was utilized to evaluate the thermodynamics of the unloading and ejection of compacts of Avicel® pH102, Emcompress®, Fast-Flo #316®, Starch 1500, and acetaminophen (APAP). A constant strain waveform, applied by a compaction simulator, enabled the separate thermodynamic evaluation of unloading from compaction. The brittle materials, Fast-Flo #316® and Emcompress®, displayed the most unloading work, and the plastic/self-lubricating materials, Avicel® and Starch 1500, displayed the least. Unloading heat values were negative for all materials, except APAP. APAP's positive heat values indicated the breaking of bonds during unloading as a result of its highly elastic nature. Positive internal energy changes of unloading, which indicate the net breaking of bonds, were observed for APAP and Emcompress® over the compaction forces tested. Negative energy changes for Starch 1500, Fast-Flo #316®, and Avicel® became positive with increasing compaction forces. Ejection work increased with increasing compaction force for the brittle materials, whereas smaller ejection work values for Avicel®, Starch 1500, and APAP remained constant. Increasing negative heat values as a function of compaction force were observed for Fast-Flo #316® and Emcompress®. Negative internal energy values for ejection were observed for Fast-Flo #316® and Emcompress®, which indicates net bond formation as a result of high shear of the compact with the die wall. Internal energy changes for Starch 1500, Avicel®, and APAP, were approximately zero, indicating the absence of net bonding or bond formation during the process. © 2001 Published by Elsevier Science B.V.

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* Corresponding author.

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1. Introduction

A compaction simulator fitted with a calorimeter can be utilized to separate the thermodynamic processes of compaction, unloading, and ejection of the tablet cycle by the use of constant strain (position) punch waveform (Rubinstein et al., 1991). This waveform is only capable of a compaction simulator (Celik and Marshall, 1989; Celik and Lordi, 1991; Rubinstein et al., 1991), which has hydraulic actuators to move both the lower and upper punches independently. Previous investigations (Coffin-Beach, 1982; Coffin-Beach and Hollenbeck, 1983; Ragnarsson and Sjogren, 1983a; Rowlings, 1989; Rubinstein et al., 1991; Rowlings et al., 1995; Wurster et al., 1995) of material compaction have used hydraulic presses, which apply a constant stress (force) waveform during compaction. In addition, industrial tableting machines usually compress to constant thickness (Rubinstein et al., 1991). The thermodynamic evaluation of the applied work during compaction can be over-estimated using a constant stress waveform as opposed to a constant strain waveform. Materials that are plastic (Yu et al., 1988) and flow (creep) under pressure will enable the punches to move closer together applying additional work. Brittle materials (Roberts and Rowe, 1986a, 1987) under load may also allow additional work to be applied from additional compression, i.e. volume reduction.

To accurately assess the work of the tableting process, the sub-processes of compact unloading (Ketolainen et al., 1993) and ejection, in addition to powder compaction, also need to be determined. Decompression, in the 'pure' sense, is the increase in volume of the compact as a result of the elastic recovery of the compacted material. If the compact has a large elastic component, the compact may 'cap or laminate' during/after unloading (Rippie and Danielson, 1981; Casahoursat et al., 1988; Yu et al., 1988; Dwivedi et al., 1992), or after ejection. This occurs when a significant number of bonds within the compact cannot withstand the elastic recovery. In this report, 'decompression' will be used interchangeably with the accurate term 'unloading' to be consistent with the majority of published reports.

An ejected compact is the net result of bond formation and bond breakage during the tableting subprocesses of compaction, unloading, and ejection. The ejection event imparts a significant stress on the compact from unequal distributions of force throughout the compact. The ejection process also produces significant shear at the edges of the compact, which can result in additional consolidation.

The availability of particle surface area for particle contacts, and, therefore, bonding, can be measured by determining the porosity level of the compact. Celik and Marshall (1989) were the first to report work and force as a function of porosity. Porosity is the measure of the total intra- and interparticulate voids of a compact. Porosity has an indirect correlation with the quantity of particle surface area for contact. As porosity is reduced, more surface of the particles come into contact, which increases the possibility of interparticulate bonding. Percentage porosity ($\%E$) is calculated form the following equation:

$$\%\ E = 100[1 - (V_t/V_c)] = 100[1 - (H_t/H_c)] \quad (1)$$

where V_t is the volume of the compact at 0% porosity, V_c is the volume of the compact under pressure, H_c is the thickness of the compact under pressure, and H_t is the thickness of the material at 0% porosity. In the present research, work, heat, and internal energy change, will be reported against percentage solids as well as maximum compaction force. Percentage solids (% Solids) is the quantity of material, excluding voids, i.e. air, contained within a compact. The percentage solids of a compact is calculated by subtracting $\%E$ from 100: at 100% solids, no voids are present, and hence, $\%E$ equals 0:

$$\%\ \text{Solids} = 100 - \%E. \quad (2)$$

The present research utilized a constant strain (punch position) waveform for tableting where previous investigations (Coffin-Beach, 1982; Coffin-Beach and Hollenbeck, 1983; Celik and Marshall, 1989; Oates and Mitchell, 1989; Rowlings et al., 1995; Wurster et al., 1995) have used a constant stress (force) profile. A constant strain waveform produces a specific punch displacement during compaction. The force necessary to move the punches the desired distance is a function of the deformation mechanism of the material being compressed. This force is not known until after the compaction event.

Materials held under constant stress conditions may yield creep, hence additional punch movement, and therefore additional compaction work. This additional work is inherent in Coffin-Beach's and Rowlings' work where compaction pressures were held for 3.3 min and 40 s, respectively. Plastic materials will flow under certain forces and, therefore, yield additional punch movement/work under constant stress conditions. Brittle materials allow additional work as a result of additional particle fracture and consolidation.

Work, for a tablet press system, is mechanical energy that is derived from force and displacement measurements (Higuchi et al., 1953, 1954; Nelson et al., 1955; Rankell and Highuchi, 1968; Ragnarsson and Sjogren, 1983b, 1985; Oates and Mitchell, 1989, 1994; Hoblitzell and Rhodes, 1990; Pesonen and Paronen, 1990a; Dwivedi et al., 1992; Wray, 1992; Ketolainen et al., 1993). Simply, an applied force, F, over a distance, dX, provides the information to determine work:

$$W = \int F dX. \tag{3}$$

In order to derive the total work (Celik and Marshall, 1989) of unloading (W_{un}) and ejection (W_e), several parameters need to be measured:

$$W = \left(\int_{X=0}^{X_{max(up)}} F_{up} dX_{up} \right) + \left(\int_{X=0}^{X_{max(lp)}} F_{lp} dX_{lp} \right) \tag{4}$$

where F_{up} and F_{lp} are the forces of the upper and lower punches determined from load cell measurements; X_{up} and X_{lp} are the contributions of the upper and lower punches (respectively) to the decrease in the distance between them, as measured by the linear variable differential transducers (LVDTs); $X = 0$ is the distance between the punches where pressure is initially observed; and $X_{max(up)}$ and $X_{max(lp)}$ are the distances observed at maximum pressure for the upper and lower punches, respectively. The work of unloading and ejection for each punch includes frictional work and work due to elastic deformation of the punches under pressure. Blank compaction runs yielded negligible frictional work and heat due to lubrication of the punch tips and die.

Decompression is the increase in compact volume, i.e. tablet thickness, that may result when the punches within the die move apart. Work during compact unloading, i.e. force removal, results from the 'elastic recovery' of the compact applying a force on the punch tips as they are moving apart. This elastic recovery produces an increase in compact thickness within the die. Compacts that do not display 'elastic recovery' will not produce forces when the punches are withdrawn. Other factors that may be contributable to forces observed as punches are withdrawn, are the speed of withdrawing the punches or the presence/length of a constant stress/strain portion during tableting. If the punches are withdrawn more rapidly than the elastic recovery of the compact, forces may not be observed during the process. Constant strain/stress application may allow additional plastic flow or fragmented particles to fill voids that would not be observed during a typical production tableting cycle. This additional plastic flow or fragmented particle void filling may give rise to little/no forces observed during unloading. An observed elastic recovery force results in negative unloading work, i.e. negative energy work values (Joules), from work done by the system (compact) on the surrounding (punch tips). (Ketolainen et al. (1993) observed that unloading work was found to increase with increasing compaction force, for Avicel® and Emcompress® when tableted on an eccentric press. Dwivedi et al. (1992) determined the in-die recovery (decompression) of granular acetaminophen (APAP), Emcompress®, spray-dried lactose, and Avicel® pH102. The unloading work rank order, on a Joule per gram basis, of the materials was Avicel® > Fast-Flo #316® and APAP > Emcompress®.

Work of the unloading process has been investigated by few authors (Coffin-Beach, 1982; Yu et al., 1988; Dwivedi et al., 1992; Ketolainen et al., 1993). These authors evaluated the work of compact (tablet) unloading by the application of a dynamic tablet waveform (Coffin-Beach, 1982; Dwivedi et al., 1992; Ketolainen et al., 1993), recompressions of compacts (Coffin-Beach, 1982;

Yu et al., 1988), or by determining the in-die tablet elastic recovery upon removing the applied force (Dwivedi et al., 1992). In contrast to compression, values of unloading work are negative. This is due to the force of the system (tablet) placed on the surroundings (punch tips) as a result of the axial elastic recovery of the compact as the compression load is released.

During the tableting cycle, work is placed on the compact during ejection by forces required to remove it from the die. The required force, and resulting work (Jarvinen and Juslin, 1974; Lammens et al., 1980, 1981; Bechard and Down, 1992; Ketolainen et al., 1993), is dependent on friction between the compacted particles with the die wall, as well as additional compaction of the tablet as it is ejected from the die. In this investigation, a lubricant solution was used to swab the punch tips and die wall to minimize frictional forces of the compact with the die. If lubrication is sufficient, ejection work will be mainly attributable to tablet compaction. After ejection of the tablet from the die, the tablet may be capable of recovering elastically in both the radial and the axial direction. The determination of ejection work is the last 'link' in performing a complete mechanical energy assessment of compact formation.

The present research evaluates the quantity of work and heat during the tablet sub-processes of compact unloading and ejection by the application of a compaction simulator previously described (DeCrosta et al., 2000). The mechanical evaluation of the sub-processes was attained by using a computerized waveform for compaction and unloading, and a manual initiation of compact ejection. Compaction of the material was accomplished by the application of a constant strain waveform. Unloading and ejection internal energy changes are calculated from heat and work determinations of these processes. Unloading and ejection work, heat, and internal energy change are reported graphically with respect to percentage solids content in addition to maximum compaction force.

2. Materials and methods

Powders for tableting were chosen to encompass brittle, plastic, elastic, and viscoelastic compaction behavior with either good or poor compactibility. These powders include commonly used excipients as well as powders that do not form compacts, i.e. polyethylene, or form capped tablets, i.e. acetaminophen. These materials are: Acetaminophen USP dense powder-Mallinckrodt Specialty Chemicals Company, Raleigh, NC (lot #5543993B723); Avicel® pH 102 (microcrystalline cellulose)-FMC Corporation, Philadelphia, Pennsylvania (lot #2233); Emcompress® (dibasic calcium phosphate dihydrate, USP)-Mendell, Patterson, New York (lot #7002X); Fast-Flo #316® lactose (spray-dried lactose monohydrate)-Foremost, Baraboom, Wisconsin (lot #2RL223); low-density polyethylene (average molecular weight 35 000)-Aldrich Chemical Company, Milwaukee, WI (lot #02526LG); Starch 1500 (modified corn starch)-Colorcon, Indianapolis, IN (lot #201010). A common particle size of 150–212 μm for all materials, except 212–300 μm for polyethylene, was used in this investigation due to the effects of varying particle size (York, 1978, 1992; Roberts and Rowe, 1986b; Esezobo and Pilpel, 1987; Pesonen and Paronen, 1990b; Riepma et al., 1990, 1991, 1992). Acetaminophen tablets capped. Polyethylene exhibited no permanent bonding, as was exhibited by its free-flowing powder after compaction. Polyethylene could not be accurately evaluated due to some melted particles 'lodging' between the punch tips and the aluminum die.

Compaction of the test materials was performed utilizing a 'Compaction Calorimeter', previously described (DeCrosta et al., 2000). Compaction was performed with 19 mm round fiberglass punch tips contained in a Delrin calorimeter. Compaction and unloading of the powders were accomplished using a 'step like' double-ended punch waveform with 0.03 s increments for a tableting cycle of 122.85 s. The upper punch displacement was 8 mm, and the lower punch displacement was 5 mm. The punch displacement speed for both compaction and unloading was 6.7 mm/s for the upper punch and 4.2

mm/s for the lower punch. The speed of ejection was 200 mm/s. The compaction of the powder occurred in 1.2 s with a subsequent period of 121.65 s (122.85–1.2 s) at constant strain. Forces of 12–45 kN were used during compaction. The punch tips and aluminum die were swabbed between compactions with a cotton 'Q-tip' that was previously immersed in a 2% lubricant (stearic acid/acetone) solution. The lubricant was used to reduce frictional forces between the punches and die during compaction, unloading, and ejection. Force and displacement measurements were made by load cells and linear variable transducers, respectively, previously described by Celik and Marshall (1989). In-die compact thickness, and, hence, in-die porosity, was varied by adjusting the lower punch start position. Four different compact thicknesses, i.e. porosity/percentage solids levels, were evaluated for each material except Starch 1500, which had five different thicknesses. Compacts were made in triplicate at each thickness.

True density, bulk density, moisture content, and mass of the materials are displayed in Table 1. True densities of the test materials were determined by Helium pycnometry (Accupyc Model #1330-Micromeritics, Norcross, GA) with an equilibration rate of 0.005 psig/min. True densities of the materials were needed to determine the mass of each powder that would be equivalent to a theoretical thickness of 3.81 mm and a true volume of 1.0774 cm^3 at zero porosity when compacted. True densities were measured for the compacts and displayed no significant difference compared to their respective powders. Bulk densities were determined by weighing the mass corresponding to a 50 ml volume in a volumetric cylinder. Moisture contents of the materials, by determining their weight loss on drying, were performed gravimetrically using a Motorola Computrac MAX50 (Motorola, Mansfield, MA).

The temperature during the tableting cycle was monitored by a metal oxide thermistor (model 5611, Hart Scientific, Pleasant Grove, UT), which was silver epoxied to the aluminum die. Temperature was monitored using a rating period of 5 s and a resolution of 0.0001°C. Compaction was not initiated until the temperature difference between rating periods was less than 0.001°C for 1 min. Temperature data were collected during this period. The compaction and unloading events were controlled by the waveform previously stored by a computer link to the compaction simulator. The ejection of the compact was initiated manually by hitting any key on the computer keyboard. Ejection was not initiated until a temperature difference between rating periods was less than 0.001°C for 1 min.

3. Results and discussion

Increased tensile strength (Krycer et al., 1982; Leuenberger, 1982; Jetzer et al., 1983; Esezobo and Pilpel, 1987; Celik, 1992) of ejected compact has been shown to be a function of increased compaction forces. Accurately stated, the tensile strength of the compact is a measure of the net

Table 1
Bulk density, true density, moisture content of powders, and mass of materials compacted

Material	Approximate bulk density[a] (g/cm^3)	True density[b] (g/cm^3)	Moisture content[c] (%)	Mass of material compacted (g)
Acetaminophen	0.642 (0.007)	1.2938 (0.0001)	0.12 (0.01)	1.6886 + 0.0005
Avicel® pH 102	0.312 (0.012)	1.5672 (0.0033)	3.07 (0.15)	1.3940 + 0.0005
Emcompress®	0.858 (0.011)	2.3083 (0.0009)	0.75 (0.01)	2.487 + 0.0005
Fast-Flo #316®	0.563 (0.011)	1.5423 (0.0023)	0.75 (0.05)	1.6220 + 0.0005
Starch 1500	0.670 (0.008)	1.5002 (0.0001)	8.09 (0.16)	1.6092 + 0.0005

[a] Sample size $n = 4$, standard deviations are in parentheses.
[b] Sample size $n = 6$, standard deviations are in parentheses.
[c] Sample size $n = 2$, standard deviations are in parentheses.

result of the material's behavior during the subprocesses of compaction, unloading, and ejection. During compaction, forces increase where brittle materials may fracture or plastic materials may flow. The increased forces yield an additional particle surface area that is available for particle contact. This increase in particle surface contact promotes the greater possibility for increased bonding (adhesion and/or cohesion).

The removal of applied forces during unloading is thought to be the 'net' breaking of bonds for brittle and plastic materials, but to different degrees. Bonds are broken during unloading due to their lack of surviving axial elastic recovery of the compact. Bonds may be formed during unloading as a result of plastic flow caused from elastic 'rebounding' of particles/bonds. In the present research, both acetaminophen (APAP), an elastic material, and Emcompress®, a brittle material, displayed a net breaking of bonds as a result of the unloading process throughout their tested compaction forces. The other materials indicated some breaking of bonds at higher applied compaction forces, i.e. above approximately 30 kN. Below 30 kN, data showed that either bonds were predominantly formed or that there was no net breaking or forming of bonds.

3.1. Unloading work

Unloading work for materials in the present research yielded positive work values. These positive values are in contrast to previous investigators (Dwivedi et al., 1992; Ketolainen et al., 1993). The waveform for compact formation includes a compaction portion (punches moving toward each other), unloading (punches moving away from each other), and ejection (lower punch moves upward to remove the compact from the die). These punch movements are observed for 'blank' runs, i.e. without materials, by the compaction simulator. However, when runs were made with the test materials, it was observed that the punches moved toward each other during the initial unloading part of the waveform. Positive work values resulted from this punch movement. This contrasting punch movement, i.e. punches moving toward each other instead of apart, may be attributable to the actuating valve(s) 'overcompensating' when initiating the punches to move apart after an approximately 2 min constant strain period. This contrast may also be attributable to some artifact of the position transducers that regulate the movement of the punches, whereas the strain transducers (LVDTs) measure punch movement. Additional compression, i.e. volume reduction, and/or consolidation, i.e. bond formation, occurred due to the punches moving towards each other during the early part of the unloading waveform. True unloading, i.e. punches moving apart, does occur after the initial stage of the unloading waveform.

From Fig. 1, Emcompress® displayed the largest positive unloading work values. This may result from brittle fracture of the compact during unloading and the subsequent/simultaneous additional compaction of the fragmented particles by the punch tips' elastic recovery. APAP displayed the second largest unloading work values over the range of 22–42 kN compaction force. APAP is a material that is known to be elastic and cap during unloading and/or ejection. The elastic recovery, as force is reduced, can also provide broken bonds and subsequent/simultaneous compaction as observed by Emcompress®. Fast-Flo #316® provides unloading work larger than either Starch 1500 or Avicel® from 20 to 30 kN. However, at 40 kN, Starch 1500 shows work comparable to APAP. This force may give rise to elastic recovery of the compact on unloading. Avicel®, which is known to be the most plastic of the materials, displays the smallest work values as a result of its small elastic component.

From Fig. 2, it is possible to differentiate the materials more easily. The figure depicts unloading work as a function of percentage solids content of the compacts. Emcompress® shows large increases in unloading work with small increases in percentage solids. APAP also displays large increases, but these occur between 85 and 88% solids. Below this solids content, there may not be sufficient consolidation and, therefore, small unloading work values. The plastic materials, Starch 1500 and Avicel®, display considerable increases in unloading work as the percentage solids increases from 88 to 90%. The particles occupying

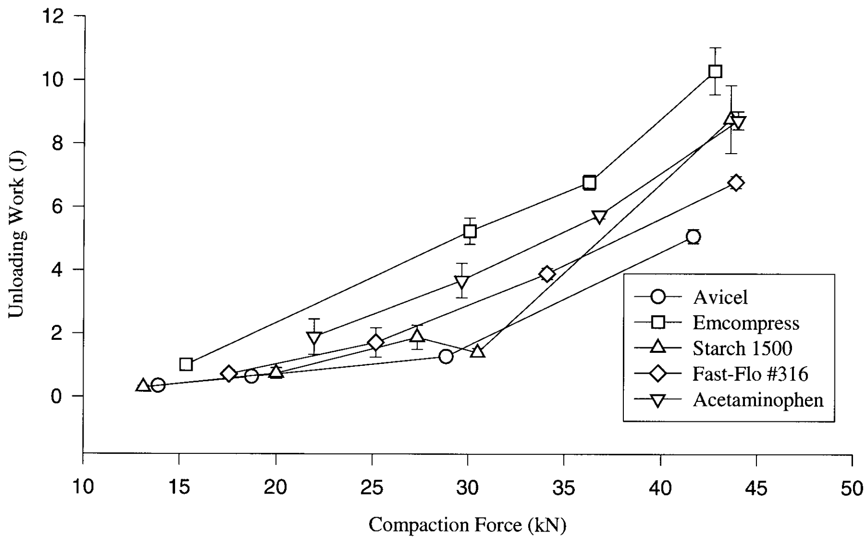

Fig. 1. Unloading work vs. maximum compaction force. (All points displayed are sample means of $n = 3$ with 2s error bars).

voids at these percent solids levels may contain considerable strain. This strain may be released during unloading resulting in fractured particles and additional consolidation. From the displayed curves, Avicel® appears to have the least elastic component and resulting consolidation. In summary, the brittle materials displayed more elastic recovery than plastic materials as the percentage solids content increases. This results in increased brittle fracture and subsequent/simultaneous consolidation during reduction of applied force(s) (unloading).

3.2. Unloading heat

As a result of removing the force applied to the punches during compaction, the compact will expand if there is sufficient elasticity. The elastic 'rebound' of the compact can produce broken bonds, hence, a positive (+) unloading heat, or bonds could possibly be formed producing a negative (−) heat. In addition, interparticulate and die-wall friction could liberate heat during the process.

Fig. 3 depicts the heat as a result of the unloading process. Most of the materials display negative heats from unloading that results from bond formation and interparticulate and particle-die wall friction. At forces of less than 30 kN, the rank order of the unloading heats for the materials are: Avicel® > Fast-Flo # 316® > Emcompress® > Starch 1500. Avicel® and Fast-Flo # 316® appeared to have a greater bond formation and/or friction than Emcompress® and Starch 1500, as indicated by their larger heat values. At forces larger than 40 kN, the rank order changes to: Fast-Flo # 316® > Emcompress® > Avicel® > Starch 1500. The rate of change of unloading heat as a function of compaction force is greater for the brittle materials, Emcompress® and Fast-Flo # 316®, than for the plastic materials, Avicel® and Starch 1500. The brittle materials may invoke a larger friction effect than the plastic materials. In a relative sense, the unloading heats are 1/10 to 1/20 the compaction heats. This indicates that 1/10 to 1/20 the quantity of bonds formed or friction during compaction is present during unloading. As an example, at 40 kN compaction force, −60 J of compaction heat and −3 J of unloading heat are generated for Avicel®. For Emcompress®, −30 J of heat are generated during compaction and −3 J during unloading. This indicates that unloading plays less of a role than compaction in the tableting cycle.

Evaluating APAP, positive unloading heats are displayed below 40 kN. This indicates that the breaking of bonds is dominating the unloading process at these forces. Frictional forces may play a role but they are 'over-shadowed' by the bonds being broken. However, above 40 kN, a slight negative heat is displayed by APAP. This indicates the presence of bond formation and/or friction. Starch 1500 shows an unloading heat of approximately zero from 12 to 20 kN, indicating that the heat loss to bonds breaking is equivalent to bonds being formed or friction forces present.

Fig. 4 depicts unloading heat as a function of percentage solids. As the void spaces are reduced with increasing solids content, Emcompress® and Fast-Flo #316® display greater changes in heat with percentage solids increases than do Avicel® and Starch 1500. This may indicate that Emcompress® and Fast-Flo #316® exhibit a greater friction or produce more/stronger bonds than the plastic materials during unloading. Avicel® is known to produce strong tablets, but this may be due to the strength of the bonds and not the number of bonds formed. Plastic materials flow more easily and occupy voids more efficiently. As a result, more/stronger bonds are formed during compaction, or less friction occurs. During unloading of these plastic materials, there is less stored energy for bond formation than in the brittle materials. Brittle materials are fractured into smaller particles under force and must be 'forced' into voids. As a result, there is more stored energy for bond formation during unloading. This may be a factor contributing to their larger heat values. APAP displays positive heat for the narrow percentage solids range of 85–87%. However, at 88%, APAP shows bond formation, which results in a positive heat value. Plotting heat as a function of percentage solids appears to be more discriminating than plotting as a function of compaction force.

3.3. Unloading internal energy change

The change in internal energy of compact unloading, (ΔE_{un}), is the net result of the work (W_{un}) applied by the system (compact) on the surroundings (punch tips) and heat (Q_{un}) absorbed or liberated by the system during unloading.

$$\Delta E_{un} = W_{un} + Q_{un}. \tag{5}$$

Bonds breaking absorb heat, i.e. a positive (+) Q, where the forming of bonds liberate heat, i.e. a negative (−) Q. In addition, frictional forces, which include interparticulate friction as well as particle-die wall friction, generate heat. The resultant heat of unloading is the net of these three confounded sources of heat.

Fig. 5 depicts the change in internal energy of the compact during unloading as a function of

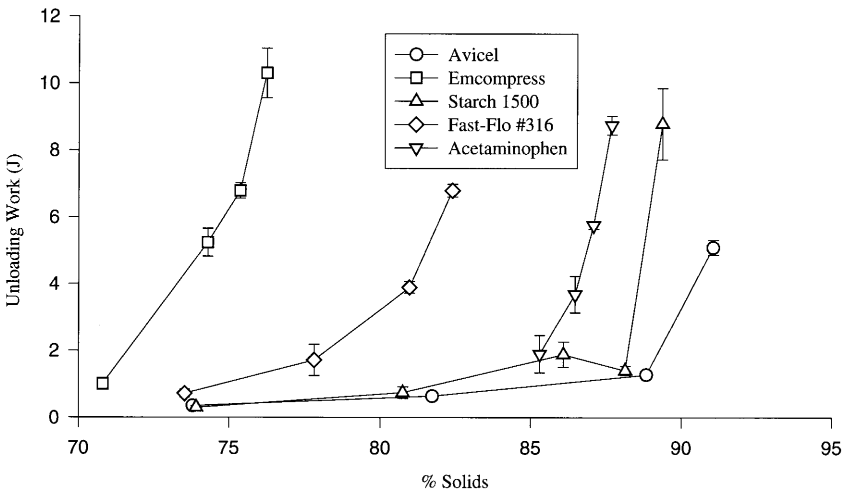

Fig. 2. Unloading work vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

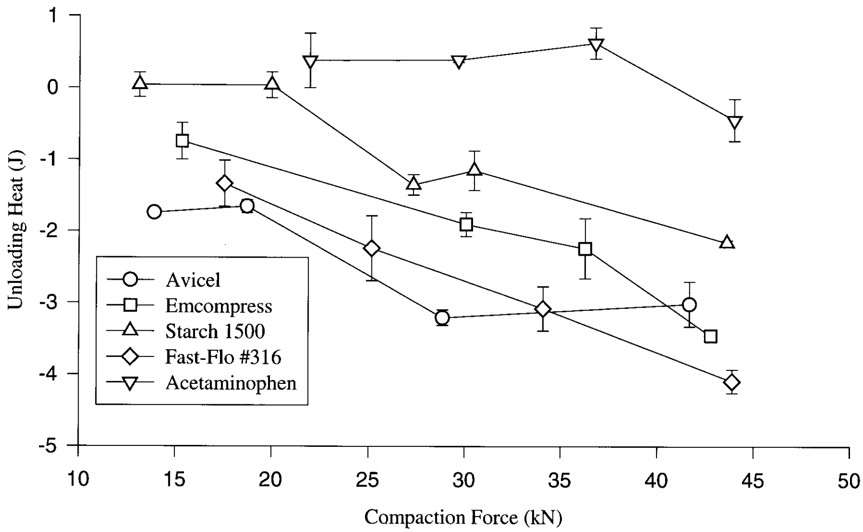

Fig. 3. Unloading heat vs. maximum compaction force. (All points displayed are sample means of $n = 3$ with 2s error bars).

applied compaction force. Both positive and negative internal energy changes were observed when evaluating the test materials. Positive energies indicate bond breaking where negative energies show bond formation. At compaction forces below 30 kN APAP, Emcompress®, and Starch 1500 displayed positive energies where Fast-Flo # 316® and Avicel® displayed negative energies. APAP is known to be highly elastic, causing compacts of the material to cap during unloading and/or ejection. The two brittle materials, Fast-Flo # 316® and Emcompress® show contrasting energies below 30 kN. Emcompress® shows positive internal energy changes indicating bonds breaking, and Fast-Flo # 316® displays negative energy changes indicating bond formation. These materials also contain a plastic component and elastic component, respectively. At lower compaction forces, Fast-Flo # 316®'s plastic component produces additional bond formation (consolidation) during unloading which is indicated from the observed negative energies. Additional compaction was attributable to the limitations/artifact of the compaction simulator, as discussed previously in Section 3.1 of this report. Bond breaking appears constant for Starch 1500 below 30 kN, as seen from its constant internal energy change of approximately 1 J. Avicel® displays energies of approximately − 2 J, indicating bond formation as a result of plastic flow during unloading.

Above 35 kN compaction force, the energy rank order of the compacts are APAP > Emcompress® > Starch 1500 > Fast-Flo # 316® > Avicel®. APAP and Emcompress®, the most elastic materials, display the largest positive energies. These positive energies are a result of the net breaking of bonds during unloading. Starch 1500, which had little bond breakage below 30 kN, displays a significant increase in bonds being broken as compaction force increased. This may result from the inability of particles to flow sufficiently to fill voids effectively. Therefore, strained particles will recover elastically breaking bonds. Fast-Flo # 316®, which is known to have a minor plastic component in addition to its dominant brittle behavior, shows positive energies less than its purely brittle counterpart, Emcompress®. Avicel® also shows a transition from bond formation, i.e. negative energies, to the breaking of bonds, i.e. positive energies. In summary, APAP, the most elastic material, shows the most breaking of bonds, i.e. positive energies, over the compaction force range of 20–40 kN. Emcompress®, predominantly a brittle materials, displays elastic recovery during unloading, which results in bonds being broken. Emcompress® was second to APAP in positive internal energy changes.

The plotting of unloading internal energy change as a function of percentage compact solids content, Fig. 6, allows one to discern the compacts' behavior more easily than the use of Fig. 5. Typical percentage solids contents for commercial tablets are 85–95%. Compactions of some of the test materials were unable to reach these solids content due to the limitation of applied forces, and hence pressures, by the compaction simulator. Emcompress® produced compacts of 72–77% solids, which produced all positive internal energy changes, indicating the predominance of bonds being broken during unloading. Fast-Flo #316® showed bond formation (negative energies) below 77% solids with subsequent breaking of bonds (positive energies) above 82% solids. As discussed above, Fast-Flo #316®'s plastic component behavior may dominate at lower percentage solids levels, whereas its brittle behavior dominates at higher percentage solids. Starch 1500 displayed only positive energy values, which shows the prevalence of bonds breaking during unloading. Its constant energy of less than 1 J shows minimal breaking of bonds between 74 and 88% solids. However, above 88% solids, there is an increase in positive internal energy change, which indicates an increase in bonds being broken. This may imply that Starch 1500 provides a somewhat brittle behavior at percentage solids above 88%. It may also indicate that Starch 1500 may be unable to fill voids by plastic flow as efficiently as it did below 88%. Particles become strained, and upon the release of the applied load, bonds are broken during elastic recovery. Percentage solids content for APAP yielded a range of 85–88% solids with 22–42 kN applied compaction forces. It appears that APAP shows a dramatic elastic recovery above 85% solids, as indicated by large increases in energies with small increases in percentage solids. Below 85% solids, APAP does not have significant consolidation, and therefore, few bonds are broken. Avicel®, the most plastic material, displays negative energies below 89% solids. At 92% solids, Avicel® displays a relatively small positive energy of approximately 2 J. This indicates that only a small portion of the bonds formed during compaction are being broken.

3.4. Ejection work

The work required to eject a compact from a die is dependent upon the frictional forces within the compact and those with the die wall during the process. Ejection forces are derived from the

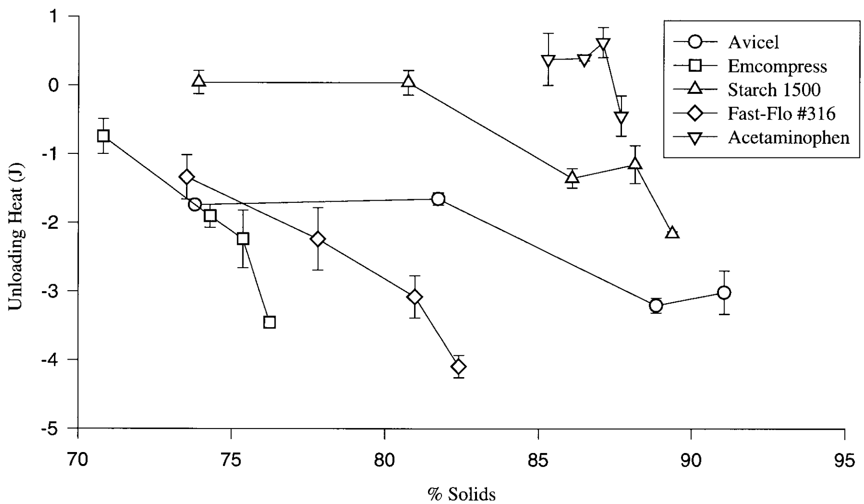

Fig. 4. Unloading heat vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

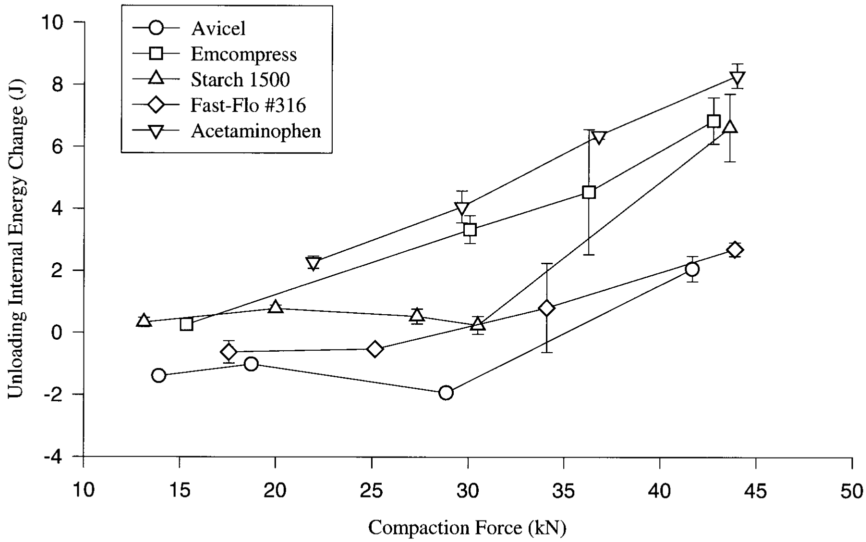

Fig. 5. Unloading internal energy change vs. maximum compaction force. (All points displayed are sample means of $n = 3$ with 2s error bars).

shear of the compact in contact with the die wall (Wray, 1992). During the process of ejection, if more particle surface is available for contact with the die wall, larger forces may be required to remove the compact. The tremendous shear that is present at the compact surface/die wall interface can achieve consolidation that the compaction event is incapable of achieving (Wray, 1992). Ejection can produce stresses that cause compacts to cap or laminate during the process or from radial expansion of the ejected compact.

Ketolainen et al. (1993) determined that increases in compaction force produce an increase in ejection work for both Avicel® pH102 and Emcompress®. In the present research, the punch tips and die wall were swabbed with a lubricant solution to reduce die-wall friction. However, the 'squeak' heard during ejection indicated that significant friction was present. Fig. 7 depicts Fast-Flo #316® and Emcompress® displaying larger ejection work values than the plastic materials and APAP. The work values increase proportionately with increase in compaction force from 15 to 35 kN. Above 35 kN, Emcompress® appears to reach maximal ejection work. Avicel® and Starch 1500 display constant work values over the range of 15–40 kN. This is most likely attributable to their characteristic to be 'self-lubricators'. Starch 1500, which is a better self-lubricator than Avicel®, shows a smaller work value. APAP, which is elastic, also displays constant work with increasing compaction force. However, this may be due to internal stresses that cause the compact to fracture and cap during ejection.

Fig. 8 mimics the results of Fig. 7 but plots work as a function of percentage solids content of the compacts. Ejection work is constant between 75 and 90% solids for Avicel® and Starch 1500, and between 85 and 88% solids for APAP. Emcompress® and Fast-Flo #316® display significant increases in work with increases in solids content. This is due to the increased die-wall friction of the materials and their lack of ability to be self-lubricators like Starch 1500 and Avicel®.

3.5. Ejection heat

As with unloading, investigators have not intimately studied the heat contribution of the tablet subprocess of ejection separately. One investigator used an infrared thermoviewer to determine the thermal energy as a result of friction during tableting on an eccentric press (Ketolainen et al., 1993). Compaction forces of 5 and 20 kN were used to determine the percentage thermal energy recovery from the combination of compression and ejection work. Percentage thermal energies for Avicel® pH 102 were 55.6 and 85.6% for 5 and 20 kN of compaction force, respectively. Emcompress® produced 18.7 and 46.2% for 5 and 20 kN of compaction force, respectively.

Heat generated during ejection can be the result of inter-particulate friction as well as friction from shear between the compact and the die wall. Absorption of heat during the process can result from bond formation. The shear forces can produce additional plastic flow and consolidation not encountered during the compaction event. As stated previously, lubrication of the punch tips and die wall was not sufficient to significantly reduce the die wall friction of the compact for the brittle materials. Lubrication assists in reducing ejection forces, but, as a detriment, the cohesion characteristics are reduced, resulting in a reduction in the compact strength. The unequal forces exerted on the compact during ejection can cause stress planes that break bonds and result in the compact capping or laminating. By incorporating a lubricant, stress patterns can be reduced and, thus, reduce the tendency for materials to cap or laminate. The particle size of the powdered starting material also has an effect on ejection forces and shear. As particle size decreases, more of its surface may be in contact with the die wall, or there may be an increase in shear strength (Wray, 1992). Both will add to increase friction forces and the generation of heat. In the present research, a common powder particle size of 150–212 μm was used to reduce the particle size effect (York, 1978; Boer et al., 1986; Roberts and Rowe, 1986b; Esezobo and Pilpel, 1987; Alderborn et al., 1988; Pesonen and Paronen, 1990b; Riepma et al., 1990, 1991; Celik and Driscoll, 1993) on the tableting sub-processes of compaction, unloading, and ejection.

Fig. 9 depicts ejection heat as a function of compaction force for the compacts of the test materials. All compacts displayed negative heats during ejection, indicating that interparticulate forces, particle/die wall friction, and/or bond formation dominate the process. By subsequently calculating the change in internal energy of the process (Figs. 11 and 12), negative energies will indicate bond formation, and positive energies will indicate friction and/or bonds being broken. Ejection heats for Avicel® and Starch 1500 were constant over the range of 15–40 kN and 22–43 kN for APAP. Avicel®, Starch 1500, and APAP showed heats of approximately −4, −2, and −2 J, respectively. These heat values were equivalent to the positive applied ejection work values (Fig. 8). The brittle materials, Emcompress® and

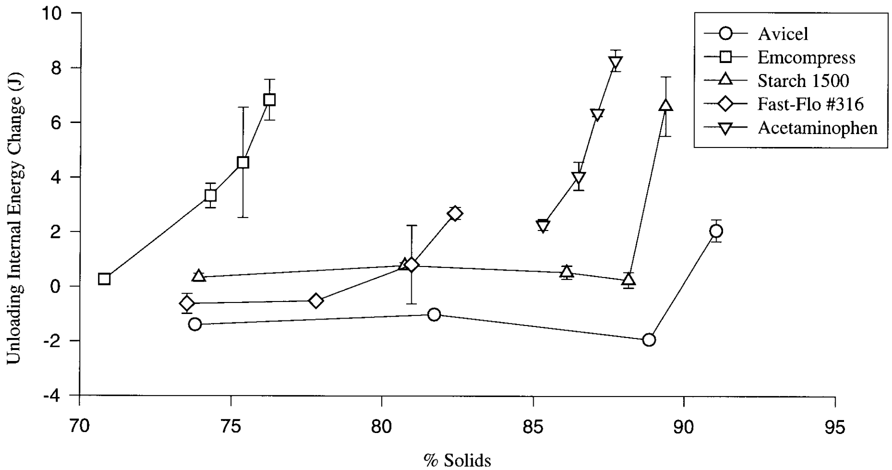

Fig. 6. Unloading internal energy change vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

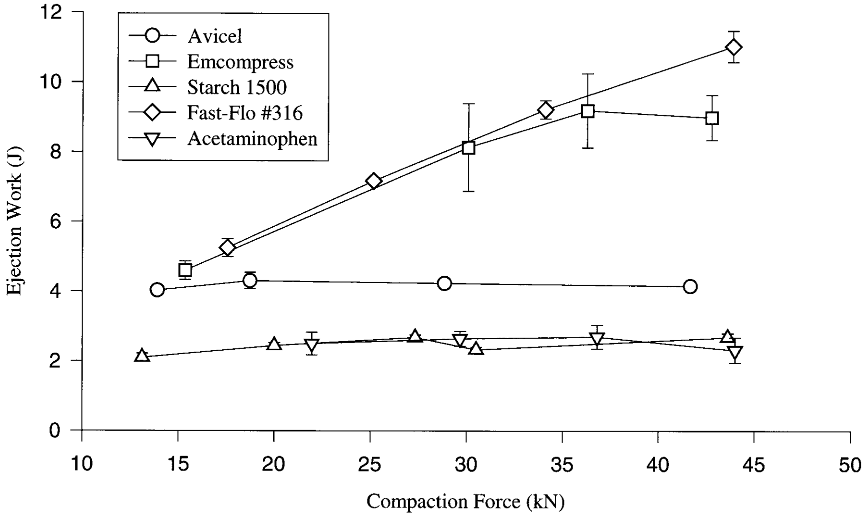

Fig. 7. Ejection work vs. maximum compaction force. (All points displayed are sample means of $n = 3$ with 2s error bars).

Fast-Flo #316®, show an increase in ejection heat, which corresponds to the increases in ejection work. However, one cannot distinguish between the dominance of heat generated by friction or bond formation. Only the calculation of the internal energy change, described later in this report, can provide the essential information.

Ejection heat plotted against percentage solids content, Fig. 10, discriminates the materials into two categories. The brittle materials, Emcompress® and Fast-Flo #316®, show heats significantly greater than the plastic, Avicel® and Starch 1500, and elastic, APAP, materials. The heat values increase for the brittle materials with increases in ejection force. Emcompress® appears to plateau at −12 J within the small range of 75–77% solids. Fast-Flo #316® displays significant heat increases between 75 and 82% solids. These brittle materials may generate more heat from friction or may form more bonds during the process than the other materials. Avicel® and Starch 1500 generate a constant quantity of heat, −2 and −4 J, respectively, between 75 and 90% solids. These materials are plastic and produce lower shear than the brittle materials, thereby generating less heat than the brittle materials. APAP shows decreasing heat values in the limited range of 85–88% solids tested. This decrease indicates the reduction in friction or breaking of bonds. Since APAP is known to cap, bond breaking is most likely the cause.

3.6. Ejection internal energy change

The change in internal energy of the ejection process yielded the largest negative values for Fast-Flo #316® and Emcompress® over the entire range of compaction forces tested (Fig. 11). Negative values indicate the net formation of bonds for the process. Starch 1500 and Avicel® displayed approximately zero energies, indicating neither the net forming nor net breaking of bonds during ejection. APAP showed small negative values (bond formation) at compaction forces less than 30 kN and small positive values (bond breaking) above 30 kN. As applied compaction force is increased, APAP's elasticity breaks bonds during ejection, but the net breaking of bonds during ejection is considerably less than during unloading. Fig. 12 displays ejection internal energy change as a function of percentage solids content of the compact. Avicel® and Starch 1500 show internal energy values of approximately zero for compacts of 75–90% solids. APAP, which produced compacts of 85–88% with 20–42 kN compaction forces, showed little bonding below 86% solids. Above 86% solids, bond breaking was minimal. Fast-Flo #316® displayed an increase in internal energy with increase in percentage solids over the range of 74–83%. Shear forces of the Fast-Flo #316® compacts with the die wall during ejection may reach sufficient temperatures for compacted particles to flow and, thereby, provide additional bonding. Fast-Flo #316® also has a plastic component in addition to its dominant brittle behavior. Emcompress® showed an increase in bonding from 71 to 74% solids (15–30 kN compaction force). Above 74% solids (30 kN compaction), Emcompress® displayed an increased net bonding.

In summary, the plastic materials, Avicel® and Starch 1500, displayed almost no net bond formation during ejection. The brittle materials, Emcompress® and Fast-Flo #316®, displayed negative internal energy changes indicating net bond formation as a result of compact ejection. APAP, an elastic material, displayed net bond formation below 30 kN (87% solids) and net breaking of bonds above 30 kN.

4. Conclusion

The evaluation of the thermal and mechanical energy of the unloading and ejection process was performed with the use of a constant strain (punch position) compact waveform only capable of a compaction simulator. Previous investigators have only evaluated the thermal effects of compaction or tableting process as a whole. The present report investigated the tablet subprocesses of unloading and ejection separately. Unloading work was found to be positive for all compacted materials indicating volume reduction and/or consolidation (Figs. 1 and 2). This was in contrast to the hypothesized negative work, i.e. compact expansion. Positive unloading work values in contrast to expected negative values were attributable to the limitation of the actuating valves and/or an artifact of the position transducers of the compaction simulator. Unloading heats (Figs. 3 and 4) were found to be negative for all materials, except APAP, indicating the forming of bonds and/or friction. APAP's positive heat values indicated the breaking of bonds during unloading. The change in internal energies for unloading of the compacts (Figs. 5 and 6) displayed predominantly positive values. These values indicated that the breaking of bonds dominates the unloading process. APAP displayed the largest positive energy values. These values indicate that unloading plays a major role in the known capping of this highly elastic material. Emcompress® gave the second largest positive energy values, which is indicative of its brittle/elastic behavior under load. Avicel® displayed slightly negative internal energy values, which showed the presence of bonding through additional compaction during

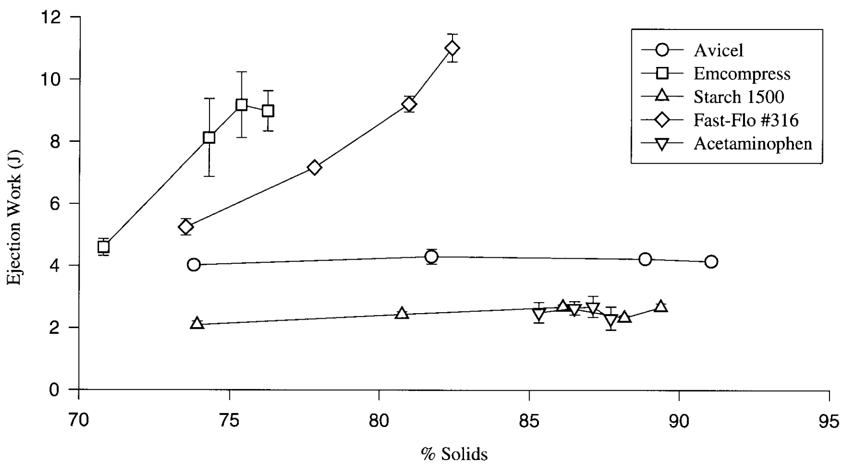

Fig. 8. Ejection work vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

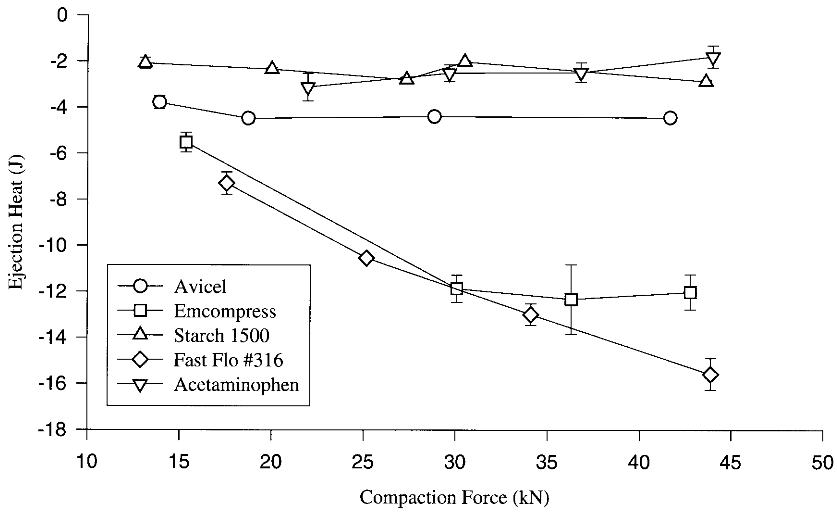

Fig. 9. Ejection heat vs. maximum compaction force. (All points displayed are sample means of $n=3$ with 2s error bars).

unloading. Fast-Flo #316® also displayed slightly negative energy values at lower forces from additional compaction as a result of its plastic component.

The work of ejection of the compacts (Figs. 7 and 8) was largest for the two brittle materials, Emcompress® and Fast-Flo #316®. Ejection work was found to increase with increasing compaction force for these materials. The plastic materials, Starch 1500 and Avicel®, displayed constant ejection work over the applied compaction forces of 15–49 kN. The self-lubricating nature of these materials provided the basis for constant ejection forces. APAP, which showed the breaking of bonds during unloading, also displayed constant ejection work. This approximate constant work is the result of the ejection of a fragmented compact. Ejection was found to be exothermic, i.e. negative heat, for all compacts. This exothermic process could be a result of either friction and/or bond formation. Larger negative heats (Figs. 9 and 10) were observed for Emcompress® and Fast-Flo #316® most likely attributable to their brittle behavior. Determination of ejection internal energy changes helped discern whether bonds were formed or broken during the process and whether the heats of ejection were a result of friction and/or bond formation. Both Avicel® and Starch 1500 displayed energy changes of approximately zero, i.e. -0.3 to $+0.3$ J, respectively. This indicated that neither bond formation nor the breaking of bonds dominates the ejection process. This may be attributable to their plastic/self-lubricating nature. APAP displayed slight bond formation, i.e. negative energies, at a compaction force of 22 kN, and slight bond breakage, i.e. positive energies, above 30 kN (Figs. 11 and 12). These positive values, at high compaction forces, were considerably less than the unloading internal energy changes, and therefore, ejection contributes only slightly to the capping of the material. Emcompress® and Fast-Flo #316® showed negative internal energy changes over the compaction force range of 20–40 kN. These values indicate bond formation. Consolidation occurs during ejection as result of high shear between the compact and die wall.

A novel technique of plotting both unloading and ejection work, heat, and change in internal energy as a function of percentage solids content of the compacts was more discriminating than plotting as a function of maximum compaction force. Both plotting techniques provided the same conclusions.

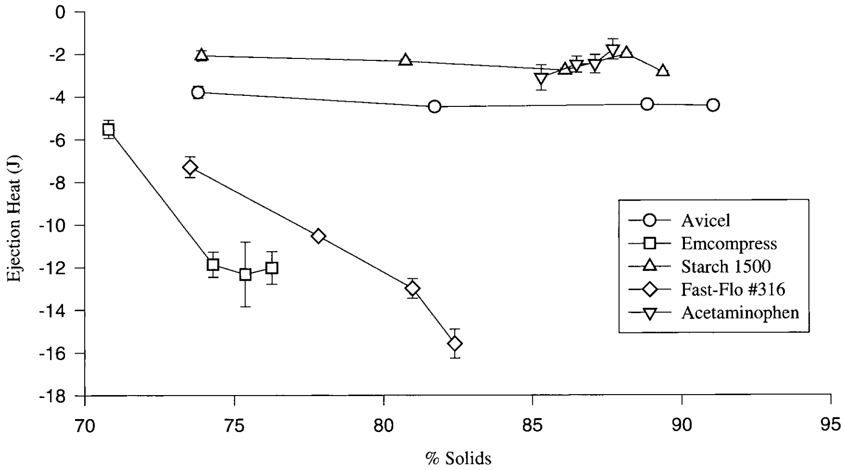

Fig. 10. Ejection heat vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

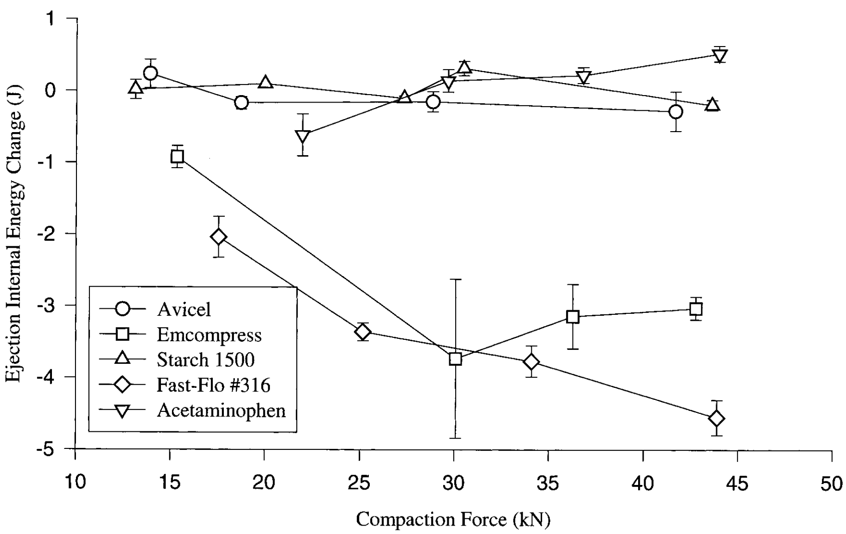

Fig. 11. Ejection internal energy change vs. maximum compaction force. (All points displayed are sample means of $n = 3$ with 2s error bars).

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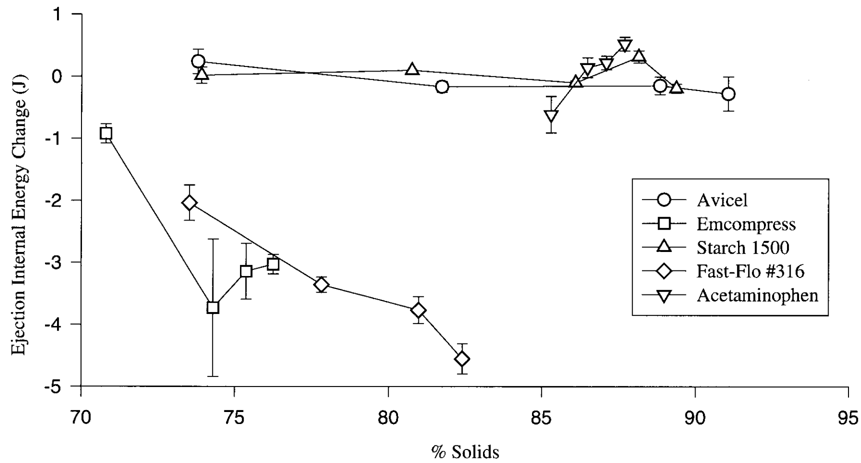

Fig. 12. Ejection internal energy change vs. % solids content of compact under load. (All points displayed are sample means of $n = 3$ with 2s error bars).

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