Drug Development and Industrial Pharmacy, 24(3), 261–268 (1998)

RESEARCH PAPER

Influence of Plasticizers on Tableting Properties of Polymers

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ABSTRACT

This study relates tablet formation with relaxation properties of two polymers on the basis of the stress–deformation curve. The mechanical properties of the polymers were varied by changing tableting temperature, adding varying amounts of plasticizer, and incorporating a monomer with plasticizer effect on the polymer chain. The crucial parameter appeared to be the difference between the glass transition temperature and the tableting temperature. This temperature difference was found to determine the amount of energy stored during densification. The energy is manifested as the stress relaxation propensity of the material. Large stress relaxation yields porous and consequently weak tablets. At a low temperature difference (i.e., tableting temperature is much lower than the glass transition temperature), the amount of stored energy is large. An increase in tableting temperature, or a decrease in glass transition temperature, yields a decrease in stored energy as a result of a decrease in yield strength. Consequently, production of less porous and stronger tablet is possible. However, if the tableting temperature is higher than the glass transition temperature, the stress relaxation propensity of the deformed polymers is extremely high because the elastic modulus of the materials is low under these circumstances. This results in porous and even capped tablets. From the data it is concluded that, independent of the type of polymer and the method of plasticizing, compaction at a temperature of about 20 K under the glass transition temperature yields circumstances for which the amount of stored energy has a minimum. Consequently, tablet porosity has a minimum and

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tablet strength has a maximum. These circumstances are created by changing both the tableting temperature and the glass transition temperature of the powder.

INTRODUCTION

In tableting practice, polymers form an important group of excipients. This is partially because their bonding properties are generally good (1). However, one of the disadvantages of polymers is that there is a pronounced effect of compaction speed on tableting behavior. This has been attributed to the high elasticity of the excipients at high rates of strain (2). Another problem is that the compaction properties of many polymers used in tableting are strongly affected by environmental conditions such as relative humidity (3,4). It has been recognized that water added to the material at high relative humidities acts as a plasticizer.

Mechanical properties of amorphous and partially crystalline polymers are affected by plasticizers. These are products which affect the physical properties of polymers. Sorption of plasticizers has an effect on the mechanical properties (i.e., deformation characteristics) of the polymer. Addition of a plasticizer also influences the glass transition temperature, which is the temperature at which the material changes from rigid to easily deformable and plastic (5). An example is water that acts as a plasticizer in many polymers such as starches and celluloses.

A second approach to alter the physical properties of polymers is the incorporation of a monomer in the polymer chain with plasticizing effects on that chain. Strictly, the monomer is not a plasticizer. It has, however, a similar effect: it affects both the mechanical properties and the glass transition temperature of the material (6).

Although the two methods of changing properties of polymers are principally different, there are some similarities. The two methods affect both mechanical properties and glass transition temperature of the material. This paper is an extension of work reporting the effects of the two methods of plasticizing polymers. It attempts to develop a general relation between plasticizing agent added to the polymer and compaction properties of the materials. The tableting behavior of the materials is quantified on the basis of a previously developed model that describes the tableting process as an effect of mechanical properties.

THEORY

Deformation of Materials

In order to deform (strain) a body, a force (stress) is necessary. Figure 1 schematically depicts relations between stress and strain for several materials. For a plastic solid, stress (σ) is directly proportional to deformation (strain, γ):

$$\sigma = E \cdot \gamma \quad (1)$$

The proportionality constant (E) is the elastic or Young's modulus (7). It is a measure of the stiffness or resistance against deformation. The material behaves elastically up to the yield point (*P*), at which the stress is called yield stress (σ_c). Beyond that point the material behaves as a plastic, rather than as an elastic solid; it creeps under practically constant stress like a viscous liquid until the body breaks. An increase in rate of strain usually causes an increase in both Young's modulus and yield strength (Fig. 1).

Brittle materials can be distinguished from plastic materials by the absence of the yield point: stress increases proportionally with strain until the material breaks. Usually, the Young's modulus of these materials is almost independent of the rate of strain.

Rubbers have a low Young's modulus relative to other materials and a yield point is often not observed

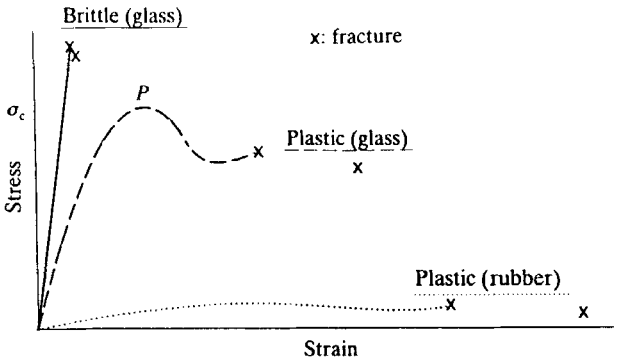

Figure 1. Stress–strain behavior of brittle and plastic materials, and rubbers at low (thin line) and high (bold line) rate of strain. The point *P* indicates the yield point with corresponding yield strength (σ_c).

(Fig. 1, rubber). These materials break at large deformations. An increase in strain rate changes the mechanical properties of these materials dramatically.

Plasticity of Materials

Deformation properties of many materials, especially amorphous and partially crystalline polymers, are strongly dependent on environmental conditions. At sufficiently low temperatures, an amorphous material is in the glassy state. The Young's modulus is high and the material is brittle (Fig. 1). A consequence of an increase in temperature of the material is that the rigidity of the material decreases and it is possible that the material yields without breakage: there is a gradual transition from the brittle to the plastic situation when the temperature of the amorphous polymer increases. At the glass transition temperature (T_g), the resistance against deformation decreases dramatically (transition from plastic to rubber in Fig. 1) and the amorphous material is then in the rubbery state. The glass transition temperature of a material depends on its chemical structure, the presence of a plasticizer and, in the case of polymers, on the molecular weight (8).

The previous paragraph indicates that the difference between temperature of measurement (T_m) and glass transition temperature (T_g), the temperature difference ΔT,

$$\Delta T = T_m - T_g \tag{2}$$

is a crucial parameter in relation to mechanical properties of noncrystalline materials. Evidently, temperature difference is affected by glass transition temperature and temperature of measurement. It is possible to vary the glass transition temperature of polymers by copolymerization of two monomers where one of the monomers has a plasticizing effect on chains of the other monomer. An example of this is the copolymerization of methyl methacrylate with lauryl methacrylate (6). It is also possible to decrease the glass transition temperature of a polymer by adding a plasticizer to that polymer. An example is water added to amorphous starch (9,10).

Energy Phenomena in Deformed Materials

The increase in stress with strain at small deformations is typically elastic, whereas the almost constant stress at larger deformations is a characteristic of viscous deformations. So, the stress–strain relation enables one to distinguish between small, elastic deformations and large, viscous deformations. This implies that a part of the energy that is necessary for deformation of the body is elastically stored and a part of the energy is dissipated and lost as heat. Consequently, it is principally possible to calculate stored or elastic energy (W_{rev} in Fig. 2). Because dissipated energy is lost as heat, it is not of interest here. Stored energy releases and forms the driving force for stress relaxation phenomena. For energy storage calculations, it is necessary to simplify the stress–strain relation (Fig. 2) (11). At small deformations (i.e., up to the yield strength), the materials behave in an elastic manner: stress is linearly proportional with strain. The proportionality constant is the elastic modulus. The area under the line with slope E up to a value of yield strength is an estimation of the amount of stored energy (shaded area in Fig. 2). Consequently, stored energy (W_{rev}) can be calculated by

$$W_{res} = \frac{1}{2} \cdot \frac{\sigma_c^2}{E} \tag{3}$$

with E the elastic modulus and σ_c the yield strength of the material. Deformations larger than the deformation at the yield point are then, by definition, viscous deformations (11).

Deformation of Particulate Matter in Tableting Processes

The description of deformation behavior of materials described so far applies for the characteristics of a

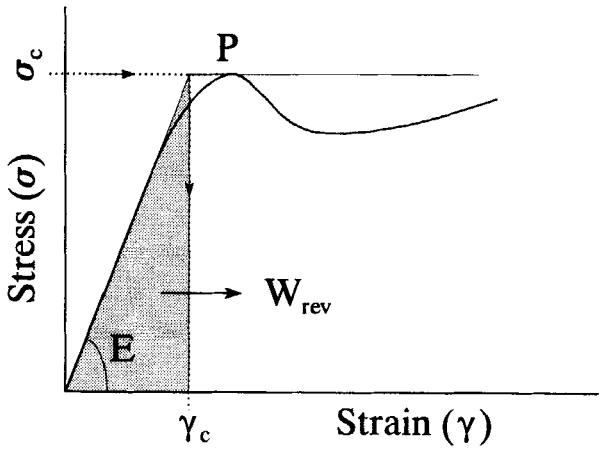

Figure 2. Stress–strain relation (bold line) and simplified stress–strain relation (thin line) with elastic modulus (E), yield strength (σ_c), critical deformation and stored energy (W_{rev}).

massive, nonporous body. However, powder consolidation deals with assemblies consisting of many small particles. Therefore, indirect methods are necessary to quantify the parameters described above. It is possible to distinguish different stages in the consolidation process of particulate matter. Initially, particle rearrangement takes place (12). When the particles reach a certain packing fraction, further rearrangement is not possible without deformation and particle deformation becomes the predominant characteristic of the densification of the powder bed. Energy storage as described in the previous section occurs in the stages where deformation takes place. At high compaction loads, compact porosity reaches zero. Further densification of the bed causes an increase in true density (13). The use of material density in porosity calculations results in negative porosity values under these circumstances (14,15). When the punch of the tablet press is released, the density of material decreases to its original value. Subsequently, the tablet creates a porous structure. Consequently, the final porosity of a compact produced at high loads is the result of relaxation rather than of compaction. Tablets compressed from materials that undergo material compression show values of porosity after relaxation that are independent of compaction pressure; this value is defined as the minimum attainable porosity (14).

Porous Structure as a Result of Stored Energy

Part of the particle deformation of plastic materials in the consolidation stage is elastic and the stress stored in this deformation will be relieved. The previous sections shows that the final porosity of a tablet compressed from plastic materials is often not directly the result of densification, but merely an effect of relaxation phenomena. A previous paper stated that there is a relation between the minimum attainable tablet porosity, or maximum attainable compact density ($\rho_{c,max}$), that can be reached (6). The minimum attainable porosity (ε_{min}) is related to the amount of stored energy by

$$\frac{\varepsilon_{min}}{1-\varepsilon_{min}} = \frac{\rho_t - \rho_{c,max}}{\rho_t} = \frac{1}{R} \cdot W_{rev} \qquad (4)$$

with W_{rev} the amount of stored energy, ρ_t true density of the material, and R the resistance to creation of a porous structure. The left-hand side of Eq. (4) is numerically equal to the minimum attainable void ratio. As a result of stress relaxation, a porous structure is created after compression. Consequently, the minimum attainable porosity is equal to the porosity expansion of the material (11). The resistance to porosity creation is determined by particle bonding and friction with the die wall. Particle bonding determines the resistance to porosity created in the tablet, whereas friction with the die determines the resistance to expansion of the tablet in the die (16). It is consequently possible to rewrite the resistance term R [Eq. (4)] as:

$$R = C \cdot k \cdot p_{ej} \qquad (5)$$

with k a quantification of particle bonding. The parameter p_{ej} represents the friction of the tablet with the die wall and is a direct function of the ejection pressure (16). The constant C is a fit constant.

The tensile strength (S) of a tablet is directly related to its porosity (ε) by (17)

$$S = S_0 \cdot e^{-k \cdot \varepsilon} \qquad (6)$$

with S_0 the calculated tensile strength of a massive tablet and k the quantification of particle bonding, consequently called bonding capacity.

This paper applies the concept described so far to two different polymers in which the plasticity was varied in different ways.

MATERIALS AND METHODS

The materials used were pregelatinized potato starch (Paselli® WA4, Avebe, Foxhol, The Netherlands) and poly(methyl methacrylate-*co*-lauryl methacrylate). The plasticizer of the starch product was water. Different amounts of water were added by storage of the dried pregelatinized starch under different climatic conditions for a period of at least a week at a temperature of 295 K (10). The method of synthesis of the copolymers was previously described in detail by Van der Voort Maarschalk et al. (6). The glass transition temperature of the pregelatinized starch was calculated as a function of water content with the Gordon-Taylor equation (5). The glass transition temperature of the methacrylate copolymers was measured with differential scanning calorimetry as previously described (6).

Viscoelastic properties were assessed by dynamic mechanical analysis (DMA) with a Rheometrics Solids Analyzer (Piscataway, NJ), using the dual cantilever method. The temperature of measurement was 295 K. Some methacrylate copolymers were also tested at temperatures of 353, 373, and 393 K. The method was described in detail in a previous paper (14).

Flat-faced compacts of 500 mg and a diameter of 13 mm were prepared on a high-speed compaction simulator (ESH, Brierley Hill, UK) at the same temperature as in DMA experiments. The maximum applied pressures varied between about 5 and 350 MPa. The upper punch displacement profiles were sine waves with different amplitudes in order to reach different maximum compression pressures. Because sinusoidal profiles were used, a complete profile involves π rad. If both the compression speed (v) and the penetration depth (A_{comp}) are known, it is possible to calculate the angular frequency of the compression (f):

$$f = \frac{\pi \cdot v}{2 \cdot A_{comp}} \tag{7}$$

which makes it possible to correlate DMA to compaction experiments. The average compaction speeds were 3, 30, and 300 mm·sec^{-1}, respectively. The lower punch was stationary during compression. The ejection time was always 10 sec. The ejection friction coefficient was calculated according to Van der Voort Maarschalk et al. (16). The resulting values are shown in Table 1. The yield stress of the test materials was measured according to Heckel (18,19). Linear interpolation was performed in the porosity range between 35 and 8%. After a relaxation period of at least 16 hr, tablet dimensions were measured with a micrometer and weighed on an analytical balance. The crushing strength of the tablets compressed at room temperature was measured at room temperature. The crushing strength of the starch tablets was measured with the compaction simulator. Profiles with a linear speed of 0.25 mm·sec^{-1} were created, and the maximum applied pressure was recorded on an XY-recorder (Kipp & Zonen, Delft, The Netherlands). Crushing strength of the methacrylate tablets was measured with a Schleuniger 4N strength tester (Dr. Schleuniger Productronic, Solothurn, Switzerland). There appeared to be no significant differences between the strength test methods. The tensile strength of the tablets was calculated according to Fell and Newton (20). The data were treated according to Eq. (6). The resulting values of k are depicted in Table 1.

RESULTS AND DISCUSSION

Mechanical Properties at Different Glass Transition Temperatures

Figure 3 shows the glass transition temperature of pregelatinized potato starch and of poly(methyl methacrylate-*co*-lauryl methacrylate) copolymers as a function of the amount of plasticizer. It shows decreasing glass transition temperatures with increasing amount of plasticizers, which clearly illustrates the plasticizing effect of water and lauryl methacrylate on polymer chains properties of pregelatinized starch and methyl methacrylate polymers, respectively.

Figure 4(a) shows the elastic modulus (measured by DMA) of the polymers as a function of the temperature difference. The figure shows decreasing elastic moduli when the tableting temperature approaches the glass transition temperature of the polymers. The dramatic decrease in elastic modulus at a temperature difference of around 0 K is a result of the glass-to-rubber transition of the material. Figure 4(a) also shows the effect of rate of strain on the elastic modulus. The elastic modulus increases with rate of strain, which is a result of decreasing relaxation during deformation of the material. When the strain rate is low, the material has the possibility to relieve stress during deformation. This is not possible at high strain rates (14).

Figure 4(b) depicts the relation between yield strength and temperature difference. The figure shows decreasing yield strengths with increasing temperature differences. In contrast with measurements of elastic moduli, the effect of glass transition temperature is not clearly visible here. This may be a result of spurious use

Table 1

Ejection Friction Coefficient, Bonding Capacity, and Constant C for Potato Starch and Methacrylate Copolymers

	Methacrylate Copolymers	Pregelatinized Starch
Average ejection friction coefficient (–)	$3.3 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
Average bonding capacity (–)	11.6	8.2
Constant C (J · m^{-3})	$2.7 \cdot 10^{7}$	$2.0 \cdot 10^{7}$

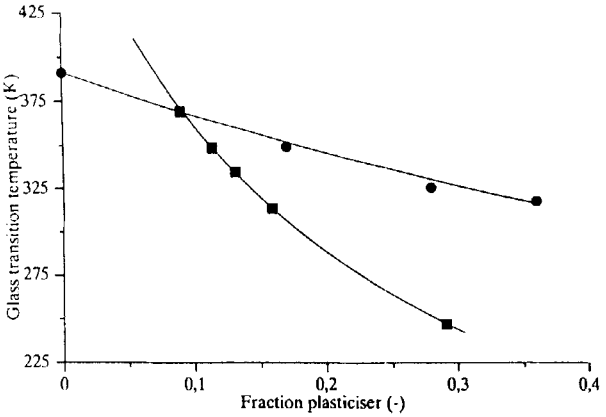

Figure 3. Glass transition temperature as a function of amount of plasticizer of pregelatinized starch (■) where water acts as a plasticizer and the methacrylate copolymers (●) are plasticized by incorporation of laurylmethacrylate in the polymer chain.

of Heckel's equation. Principally, it is impossible to calculate yield strengths of materials that do not yield (Fig. 1). Consequently, yield strength calculations under these circumstances may have limited relevance. The effect of compaction speed on yield strength is large, relative to its effect on elastic modulus.

Density Changes During Compression and Decompression

Figure 5 shows both the compact density under pressure and after ejection and relaxation of the tablets. It gives the results of measurements performed on pregelatinized starch with a glass transition temperature of 349 K (temperature difference -54 K). All other powders showed similar but numerically different profiles. The rearrangement stage is expressed by large densification at low pressures. Gradually, resistance to densification increases, indicating that deformation of the material takes place. When the density of the compact reaches values larger than true density of the material, further densification becomes extremely difficult. This shows that there is large resistance to uniform compression of the material. The decompression stage shows that the punch pressure decreases rapidly upon punch movement. The punch loses contact with the compact when the density of the compact is approximately equal to the true density of the material.

The density of the compact after 16 hr of relaxation differs significantly from the density of the compact after punch release: there is creation of a porous structure, expressed by a compact density lower than the true density of the material. Figure 5 shows a considerable effect of compaction speed on the final density of the tablets. In addition, tablets compacted at a fixed speed show values of compact density that become independent of compaction pressure. Maximum attainable compact density is reached when material compression has occurred.

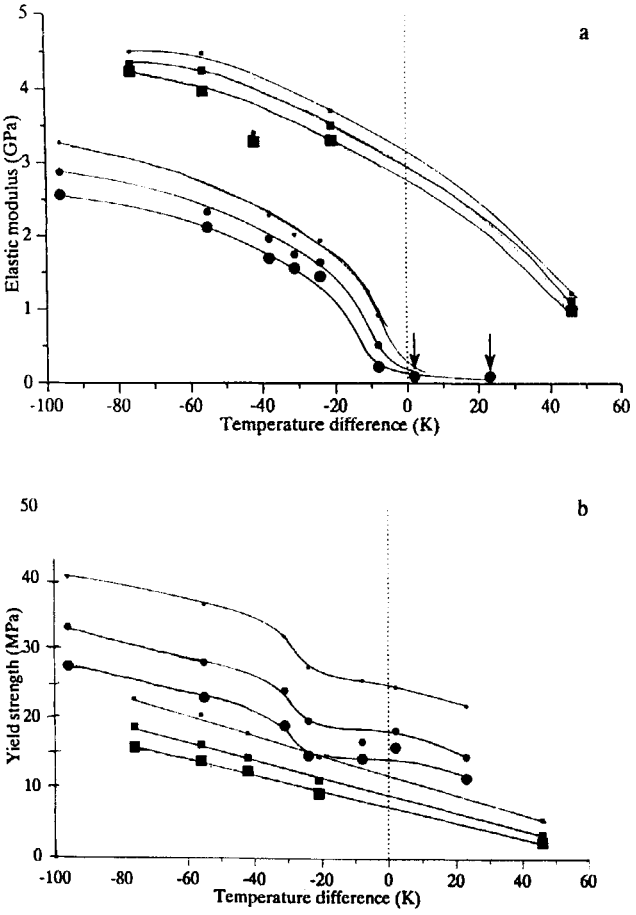

Figure 4. Elastic modulus (a) and yield strength (b) as a function of temperature difference [Eq. (2)] of pregelatinized starch (■) and the methacrylate copolymer (●) at rates of strain that correspond with compaction speeds of 3 (large symbols), 30 (medium-sized symbols), and 300 (small symbols) $mm \cdot sec^{-1}$. The arrows indicate that the elastic modulus is lower than about 0.1 GPa.

Tablet Porosity as a Result of Stress Relief

The fact that the final porosity of a tablet compressed from the materials used in this study is the result of

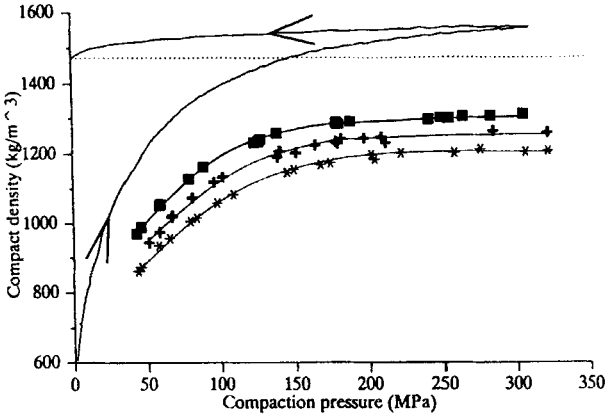

Figure 5. Compact density under pressure of pregelatinized potato starch with a glass transition temperature of 349 K (solid line) and the true density measured by pycnometry (dotted line). The symbols give the compact densities after relaxation compressed at speeds of 3 (■), 30 (+) and 300 (*) $mm \cdot sec^{-1}$.

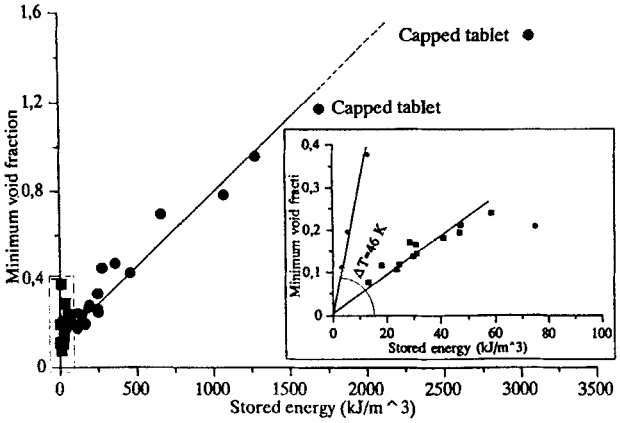

Figure 6. Minimum attainable porosity (expressed as void fraction) as a function of stored energy of pregelatinized potato starch (■ temperature difference equals 46 K; ■ all others) and the methacrylate copolymers (●). The box surrounded by dashed line indicates the part of the graph that is plotted in the inset.

relaxation phenomena implies that the minimum attainable porosity of tablets can very well be a quantification of the amount of stress relaxation. If both the elastic modulus [Fig. 4(a)] and the yield strength [Fig. 4(b)] as a function of temperature difference and rate of strain are known, it is possible to calculate stored energy under various circumstances [Eq. (3)].

The relation between minimum attainable porosity [Eq. (4)] and stored energy is presented in Fig. 6 for both materials. The amount of energy stored in the copolymer powder is much larger than in the case of compaction of pregelatinized potato starch. This is a result of both lower elastic moduli and higher yield strengths of the methacrylate copolymers than those of pregelatinized potato starch. The figure shows that both materials have their own more or less unique relation between stored energy and minimum attainable void fraction.

The different relations between minimum attainable porosity and stored energy of the two materials are found to be an effect of both different bonding capacities and ejection friction coefficients (16). According to Eq. (4), these parameters affect the resistance against porosity expansion (R). By means of the slopes of the lines in Fig. 6 and if the average bonding capacities and ejection friction coefficients (Table 1) of the materials are known, it is possible to calculate the value of the fit constant C, which has a value of $2 \cdot 10^7\ J \cdot m^{-3}$ for pregelatinized starch and $2.7 \cdot 10^7\ J \cdot m^3$ for the methacrylate copolymers. This value is in the same order of magnitude as in a previous paper (16). The starch with the highest moisture content was in the rubbery state; the glass transition temperature was 46 K (all other starches were in the glassy state). The relation between minimum attainable porosity and stored energy of this material follows another relation (Fig. 6). There may be two reasons for this anomalous behavior. First, it is possible that Heckel's equation is not applicable to rubbers, giving erroneous values of yield strength. Moreover, at high moisture contents, there is extensive adsorption of water on the surfaces of the particles. Adsorption of water affects the bonding capacity (k) of the material (10). This decrease in bonding capacity of the material has an effect on the resistance against tablet expansion (R).

Tablet Strength as a Result of Relaxation Phenomena

This paper indicates that the tablet porosity [and according to Eq. (6), tensile strength] is the final result of a relaxation propensity that creates a porous structure and a resistance against porosity creation, which is determined by particle bonding and the friction of the tablet with the die wall. This relation is mathematically described by Eq. (4). According to Eq. (5), the resistance against porosity creation is determined by particle bonding in the tablet and the friction of the tablet with the die wall. The two parameters appear to be independent on rate of strain and almost independent of the differ-

ence between the glass transition temperature of the material and the temperature of measurement when the materials are glasses. Stored energy, however, is strongly affected by both the rate of strain and temperature difference. Production of strong tablets requires creation of tablets with low porosity [Eq. (6)]. Since minimization of porosity implies minimization of stored energy [Eq. (4)], it is necessary to choose tableting circumstances for which yield strength of the material is low and elastic modulus is high [Eq. (3)]. A high elastic modulus implies that the material must be in the glassy state. Low values of yield strength, however, require that the material is a rubber. These two counteracting conditions force one to choose circumstances in which the elastic modulus is not too low and the yield strength is not too high. This means that the material must be a glass (high elastic modulus) and the tableting temperature should not differ too much from the glass transition temperature (low yield strength). Thus, it is necessary to choose circumstances in which the compaction temperature is not much lower than the glass transition temperature.

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