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Fracture in disordered media and tensile strength of microcrystalline cellulose tablets at low relative densities

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Abstract

The purpose of this study is to establish a theoretical basis for the tensile strength of low density tablets. In a first step, a lattice model based on percolation theory is presented. As a theoretical result, a power law is obtained for the lattice strength. The exponent in this law is expected to be universal and as a numerical value $T_f \cong 2.7$ is proposed. The result is identical with an earlier theoretical finding from an alternative approach proposed by Guyon et al. (1987). In a second step, the new model equation is applied to the tensile strength of low density tablets. The compacts were manufactured and tested with an universal testing instrument Zwick® UPM 1478 (Zwick–Roell). Different types of microcrystalline cellulose Emcocel® 50M, Emcocel® 90M, Avicel® PH101 and Avicel® PH102 were assayed as model excipients because of their ability to form tablets at comparatively low relative densities (ρ_r). For determination of the tensile strength, two different strain rates 0.5 and 25 mm min^{-1} were examined. All experimentally determined exponents were in the same range with an average of $\bar{T}_f = 3.2 \pm 0.1$ and the critical solid fractions (ρ_{rc}), yielded values close the relative bulk densities. In a third step, the new model is compared to the Ryshkewitch–Duckworth equation. This exponential relationship of the tensile strength and porosity was found to have an inferior fitting adequacy than the new power law. As a conclusion, the lattice model presented is able to explain the power law behaviour of the tensile strength as a function of the relative density with an exponent close to three. The expected universal character of this exponent was supported by the results of the assayed substances at two different strain rates. Plus, in the case of the tested substances, the new relationship between the tensile strength and the relative density should be preferred to the often used exponential function. However, further studies have to be conducted to know more about the validity of the new model.

Keywords: Tensile strength; Polymer tablets; Lattice model; Percolation theory

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1. Introduction

1.1. Mechanical strength in a disordered medium

Tablet strength is an important property for safe transportation and handling by patients as well as for finishing the compacts in a coating machine. Mechanical strength is also measured for quality assurance during pharmaceutical production. In addition, this property helps in elucidating the physics of compression.

Many test methods for mechanical strength have been established, ranging from direct tensile testing over flexural tests to the most widespread diametral compression tests (radial tensile strength measurements).

There exist attempts to describe tensile strength as a function of the relative density (Ryshkewitch, 1953; Leuenberger, 1980; Hiestand and Smith, 1984). Such approaches are empirical or contain at least some *heuristic* elements, as it is difficult to develop a straightforward theoretical description. The simplest theoretical procedure is to assume equal volume elements within a compact. This view of tablets as a homogenous medium can be very successful (Leuenberger, 1980), especially in the case of dense compacts close to a solid continuum. However, powders or granules compressed at low pressures will form particle assemblies rather than a solid continuum, especially particles, being polydisperse and showing some asperity form heterogeneous compacts at low pressures. The consequence is a disordered structure. This disorder can be present as a disorder of particles or as a disorder of contact points. In the latter case, the disorder can also be understood in terms of the absent bonding points which is highly of interest regarding the fact that the flaws in a material lead to crack propagation. If the disorder takes place on comparatively large length scales, a theoretical problem is raised by the fact that the tablet can not be divided into mechanically equal volume elements, i.e. homogenisation is invalidated. For this type of physical problem, usually concepts of fractal geometry are used. Especially the theory of *percolation* (Flory, 1941; Stockmayer, 1943; Broadbent and Hammersley, 1957; Stauffer and Aharony, 1992) can be successfully applied to disordered media.

1.2. Percolation theory and critical mechanical behaviour

In the field of pharmaceutical powder technology, percolation theory was introduced by Leuenberger et al. (1987). Emphasising mechanical properties of tablets, it was important to discover that the model Leuenberger and Leu (1992) is consistent with an *effective medium approximation* (EMA) (Kuentz and Leuenberger, 1998). The latter concept is a linear approximation of the measured property far away from the percolation threshold. The challenge was therefore given to elucidate the mechanics of tablets also at comparatively low relative densities. Thus, the modified Young's modulus of microcrystalline cellulose tablets was analysed in vicinity of the percolation threshold and a non-linear behaviour with an exponent close to four was observed (Kuentz and Leuenberger, 1998). This exponent was explained on behalf of a mechanical percolation model. In this version of the percolation process, springs are imagined to be placed on a lattice with a given occupation probability p. Above a critical concentration p_c two arbitrary sides of a system are connected by a coherent cluster of springs. Thus, any mechanical property (X) becomes non-zero above this threshold (p_c). In vicinity of p_c, a power law exhibiting a critical exponent q can be proposed (Stauffer and Aharony, 1992):

$$X \propto (p - p_c)^q \tag{1}$$

The mechanical percolation problem can also be formulated, starting from a description above the percolation threshold. Hence, an elastic network can alternatively undergo a dilution process where springs are removed with a probability $r = 1 - p$. The critical value r_c names again the threshold concentration where a given mechanical property (X) vanishes. This is the original formulation of the *central-force percolation* (Feng and Sen, 1984). It is interesting to know that the threshold in a central-force problem appears to be higher than expected for ordinary percolation. Fig. 1 shows a small part of a triangular lattice where the sites are occupied with springs. It has to be kept in mind that the rigidity of the system is given by the springs in the occupied sites. It is now imagined that for every

individual site we have a certain probability p that the site is occupied with a spring or that it is removed by the probability r. After removal of the springs, a new structure is given by the occupied sites that is statistically determined by the probability $p = 1 - r$. As long as the probability r is smaller than the critical value r_c, the entire lattice exhibits a rigidity.

It should be added that Eq. (1) is only valuable as long as disorder is predominant. In this range, the exponent is expected to be universal. This assumption is based on the theoretical fact that critical exponents are as a rule independent of the lattice type used (Stauffer and Aharony, 1992). Thus, a macroscopic critical behaviour is not affected by the local details of a system.

Coming to the experimental situation of porous bodies like tablets, the relative density holds for a corresponding parameter to the occupation probability p of percolation theory (Ehrburger and Lahaye, 1989; Leuenberger and Leu, 1992). Only low density tablets of different types of microcrystalline cellulose (MCC) were used in the present study. The excellent compaction properties of MCC permit to manufacture tablets at very low relative densities. This can be of importance, considering the lack of knowledge on how broad the range is where the fundamental power law of percolation theory Eq. (1) can be applied accurately.

It should be mentioned as well that the tensile strength is a very suitable property to study percolation effects, because mechanical breakage is known to be extremely sensitive to local disorder (Duxbury, 1990).

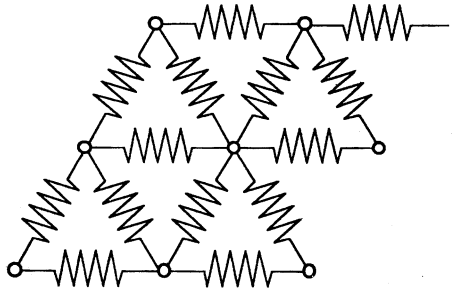

Fig. 1. A small part of a triangular lattice is shown where all sites are occupied by springs. In a classical central-force model, individual springs will be removed with a given probability r. If this probability is large enough, i.e. r equals or exceed r_c, the lattice looses the macroscopic rigidity (Roux et al., 1993).

1.3. Fracture in central-force networks

The fracture problem has already been theoretically studied in elastic networks. The dilution process in central-force percolation, i.e. the removing of springs, leads to a mechanical breakdown at the threshold $p_c = 1 - r_c$. The simplest models consider only stretching forces along the springs. This leads to a similar problem as in the well known analogous electrical case where the breakdown of fuses is emphasised (Kahng et al., 1988). However, for a realistic mechanical model, the existence of torques needs to be taken into account. Such bond bending forces lead to a new class of exponent universality, violating the analogy to the electrical problem (Kantor and Webman, 1984).

As a conclusion, the breakdown behaviour of a central-force network allowing bending forces is of special interest. The tensile strength of such a network (σ_{lattice}) can be expected to scale close to p_c with a fracture exponent T_f:

$$\sigma_{\text{lattice}} \propto (p - p_c)^{T_f} \tag{2}$$

Guyon et al. (1987) proposed an analytic expression for T_f as given below:

$$T_f = \nu \cdot d \tag{3}$$

where ν is the critical exponent of a characteristic length ξ (*correlation length*) and d is the space dimension (Euclidean dimension). The arguments leading to this result started from a balance of forces and torques whereas this study follows an alternative approach.

2. Theoretical development

2.1. The mechanical strength of a theoretical lattice

The critical strength (σ_k) of a crystal lattice can be calculated if the elastically stored energy per

volume element is balanced with the energy of creating a new breakage surface δS (Gregg, 1965):

$$\Gamma_s \cdot \delta S \cong \frac{1}{2}\frac{\sigma_k^2}{E} \cdot c \cdot \delta S \quad (4)$$

where Γ_s is the surface energy, E is the elastic modulus and c stands for the atomic distance in the crystal lattice. Accordingly, one finds for σ_k at constant stress:

$$\sigma_k \cong \sqrt{\frac{2E \cdot \Gamma_s}{c}} \quad (5)$$

In a real material, the strength will be much smaller than predicted by the above equation, as stress concentrations are produced by flaws or voids (Griffith, 1921). Thus, the meaning of E, Γ_s or c depends on the properties of the system, i.e. the vacancies of the crystal lattice. To model such effects, Eq. (5) can be adapted to a theoretical lattice model of percolation theory:

$$\sigma_{lattice}(p) \propto \sqrt{\frac{E(p)\cdot\Gamma_s(p)}{c(p)}} \quad (6)$$

The elasticity, the surface energy as well as the characteristic length $c(p)$ in the lattice are here functions of the occupation probability p. This probability denotes the chance to introduce a mechanical element to an arbitrary lattice site. Such elements are imagined to produce brittle fracture if their elastic limit is exceeded. In addition, occurrence of torques shall be allowed in this virtual lattice. To achieve a final expression for the lattice strength, the functions of the parameters $E(p)$, $\Gamma_s(p)$ and $c(p)$ need to be evaluated, raising three individual theoretical problems:

Emphasising first the elastic problem, Kantor and Webman (1984) provided a solution for the elasticity of a bond bending network:

$$E(p) \propto (p - p_c)^{\tau} \quad \text{with} \quad \tau = \nu \cdot d + 1 \quad (7)$$

where τ is the exponent of elasticity, ν is the critical exponent of a characteristic length ξ (*correlation length*), and d is the space dimension (Euclidean dimension). This result is based on the assumption that not all mechanical elements within the lattice contribute to overall elasticity. Only elements, building the backbone of the percolating cluster can take part of the stress transmission. This backbone can be divided into further substructures. Dense regions of multiple connecting elements (*blobs*) can be distinguished from connections, established only by single elements (*single connecting elements*). This hierarchical view of the backbone is well known as the *node-link and blob model* (Fig. 2). In the Cantor and Webman result, only the single elements were imagined to respond to an applied force. *Blobs* were treated as entirely rigid and were consequently neglected. Yet, it can be argued that this simplified view on elasticity can only give a lower border for the exponent τ (Bunde and Havlin, 1996). In the context of the fracture problem however, focusing on single connecting elements seems justified as they hold for the weakest links in the entire lattice.

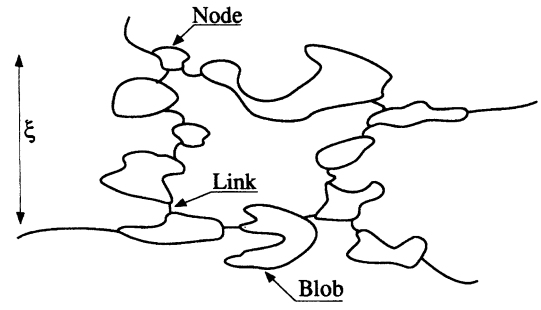

Fig. 2. A view from far on a detail of the backbone of the percolating structure is illustrated (*node-link and blob picture*). The correlation length ξ provides a length scale in this hierarchical lattice (Hansen, 1990).

Coming to the second part of the theoretical problem, we propose the following function for $\Gamma_s(p)$:

$$\Gamma_s(p) \equiv k \cdot N_s \cdot \Pi(p) \propto \Pi(p) \quad (8)$$

where k is a proportionality constant, N_s a constant number of sites belonging to a unit cross sectional area in the lattice, and $\Pi(p)$ is the probability that an arbitrary site contains a *relevant* element. Again the term *relevant* stresses the fact that not all elements contribute to a macroscopic property like $\Gamma_s(p)$. Close to the percolation threshold, a power law can be proposed for the surface energy with a critical exponent φ as given below:

$$\Gamma_s(p) \propto \Pi(p) \propto (p - p_c)^{\varphi} \quad (9)$$

In vicinity of the percolation threshold ($p > p_c$), the percolating cluster has a fractal dimension $D_f \cong 2.5$ for $d = 3$ (Stauffer and Aharony, 1992). If only the backbone of this structure is taken into account, a fractal dimension of $D_{BB} \cong 1.7$ ($d = 3$) (Stauffer and Aharony, 1992) results. This backbone is the force transmitting part of the percolating structure. It should be kept in mind that mechanical strength is determined by the weakest link in the structure that are given by the *single connecting* elements. The sum of these *single connecting* links, i.e. *relevant* mechanical elements within an arbitrary radius R is proportional to $R^{D_{sc}}$ with $D_{sc} \cong 1.1$ ($d = 3$) (Stauffer and Aharony, 1992). To obtain the probability $\Pi(p)$, i.e. the probability that an arbitrary site contains a *relevant* element, a normalisation by R^2 ($d = 3$) is needed, or more general in d dimensions $\Pi(p)$ reads:

$$\Pi(p) \propto \frac{R^{D_{SC}}}{R^{d-1}} \quad (10)$$

The fractal aspect is not present on all length scales. There exists a characteristic length ξ (*correlation length*) below which the fractal structure of a system becomes visible. The radius R is as a measure of length proportional to ξ. Therefore expression (10) becomes:

$$\Pi(p) \propto \frac{\xi^{D_{SC}}}{\xi^{d-1}} \propto \xi^{D_{SC} - (d-1)} \quad (11)$$

In percolation theory, the following power law (12) is well known:

$$\xi \propto (p - p_c)^{-\nu} \quad (12)$$

Using this proportionality in combination with expression (11) one finds:

$$\Pi(p) \propto (p - p)^{-\nu D_{SC} + \nu(d-1)} \quad (13)$$

The exponent φ in expression (9) is therefore given by:

$$\varphi = -\nu D_{SC} + \nu(d-1) \quad (14)$$

According to Coniglio (1982), the fractal dimension D_{sc} can be expressed by

$$D_{SC} = \frac{1}{\nu} \quad (15)$$

Therefore, the exponent φ reads:

$$\varphi = \nu(d-1) - 1 \quad (16)$$

The third problem that was initially formulated, is given by the characteristic length $c(p)$ in the lattice. So far, a hierarchical view of the lattice (*node-link and blob picture*) (Fig. 2) was used to find expressions for $E(p)$ and $\Gamma_s(p)$. If again only the *single connecting* elements are considered, the average spacing between these weakest links in the lattice corresponds to ξ. For the length $c(p)$ with its exponent α, the expression below is proposed:

$$c(p) \propto \xi \propto (p - p_c)^{\alpha} \quad \text{with } \alpha = -\nu \quad (17)$$

Thus, from the formulae (2), (6), (7), (9), (17) the fracture strength of the lattice can be calculated:

$$\sigma_{lattice} \propto (p - p_c)^{T_f}, \quad \sigma_{lattice} \propto \sqrt{\frac{(p - p_c)^{\tau} \cdot (p - p_c)^{\varphi}}{(p - p_c)^{\alpha}}} \quad (18)$$

$$T_f = \frac{1}{2} \cdot [\tau + \varphi - \alpha] \quad (19)$$

In the case that only *single connecting* elements are *relevant* for breakage, formulae (7), (16), (17) and (19) can be combined to:

$$T_f = \frac{1}{2}[\nu d + 1 + \nu(d-1) - 1 + \nu] = \nu \cdot d \quad (20)$$

The result obtained just agrees with Eq. (3) and can be linked to the elastic exponent τ of the Kantor and Webman Eq. (7):

$$T_f = \tau - 1 \quad (21)$$

The numerical value for T_f can be approximated in three dimensions ($d = 3$) using Eq. (20) with $\nu \cong 0.9$ (Stauffer and Aharony, 1992) resulting in $T_f \cong 2.7$. This value is in excellent agreement with computer simulations of critical fracture behaviour on a cubic lattice, obtained from Sahimi and Ararabi (1992).

2.2. Tensile strength of tablets

As mentioned in the introduction, the percolation probability has a corresponding parameter in

tableting technology that is given by the relative density. Thus, ρ_r is expected to exhibit the same critical exponent T_f as theoretically predicted for p. There exist also the analogous proportionality between the probability r and the porosity ε (bearing in mind that $r = 1 - p$ and $\varepsilon = 1 - \rho_r$). Taking into account expression (20), the proportionality (22) is conjectured:

$$\sigma_t \propto (\varepsilon_c - \varepsilon)^{T_f} \propto (\rho_r - \rho_{rc})^{T_f} \quad (22)$$

The value $T_f = 3\nu \cong 2.7$ is expected to hold close to the threshold density.

3. Materials and methods

Tablets (round, flat, 11 mm diameter, 400 ± 1 mg weight) for the subsequent determination of the tensile strength using the Zwick® 1478 Universal Testing Instrument (Zwick® GmbH, Ulm, Germany) were prepared. As starting material four types of microcrystalline cellulose were used: Emcocel® 50M (Mendell), batch No.1333, Emcocel® 90M (Mendell) batch No.6011, Avicel® PH101(FMC) batch No.6918 and Avicel® PH102 (FMC) batch No.7539 (Table 1).

The true density was determined with a Beckman Air Comparison Pycnometer® Model 930 and the particle size assayed with a Malvern® Mastersizer X.

For each powder system, five tablets were compressed at different pressure levels ranging from 1.05 up to 105.23 MPa at a relative humidity of $45 \pm 10\%$. The compression speed was 10 mm min^{-1} and the die wall was lubricated with magnesium stearate before every cycle. Forthy-eight hours after manufacture, the radial tensile strength of the compacts was tested. The preforce was 0.3 N and the testing speed 0.5 and 25 mm min^{-1}, respectively. The radial tensile strength was calculated according to Newton et al. (1971):

$$\sigma_t = \frac{2F}{\pi \cdot D \cdot h} \quad (23)$$

where F is the maximal force recorded, D the tablet diameter and h its thickness. Only compacts, showing an ideal fracture were taken into account for the subsequent statistical evaluation.

For presentation of data, the radial tensile strength was normalised by the maximal values (σ_{tmax}) obtained from linear extrapolation (EMA) of the relative density $\rho_r \to 1$, using only data from the highest four pressure levels.

Tablets compressed at 78.920 and 105.226 MPa were used for determination of σ_{tmax} but omitted for evaluation of the new model.

In order to take care of the existing flip-flop effect in the simultaneously determination of the critical exponent and percolation threshold, and to examine the range of validity of the power law, the exponents were determined in the logarithmic space according to Eq. (24). In a second step the exponents were averaged and a non-linear regression of Eq. (25) conducted. This method is described in detail by Kuentz and Leuenberger, (1998).

$$\ln\left(\frac{\sigma_t}{\sigma_{tmax}}\right) = \ln(S) + T_f \cdot \ln(\rho_r - \rho_{rc}) \quad (24)$$

$$\frac{\sigma_t}{\sigma_{tmax}} = S \cdot (\rho_r - \rho_{rc})^{\bar{T}_f} \quad (25)$$

All statistical evaluations were conducted with the program: SYSTAT® for Windows Version 7.0 (SPSS, Evanston, IL).

Table 1
Physical characterisation of the different types of microcrystalline cellulose

	Emcocel® 50M	Emcocel® 90M	Avicel® PH101	Avicel® PH102
True density (g cm^{-3})	1.57	1.56	1.57	1.56
Relative bulk density	0.207	0.236	0.205	0.213
Relative tapped density	0.250	0.271	0.260	0.258
Mean particle size (*Sauter*) (μm)	54.0	83.5	48.1	81.2

Table 2
Linear extrapolated values σ_{tmax} from highest compression pressures (EMA) and critical fracture exponents T_f determined according to Eq. (24)

	Testing speed (25 mm min^{-1})		Testing speed (0.5 mm min^{-1})	
	σ_{tmax}(MPa)	T_f	σ_{tmax}(MPa)	T_f
Emcocel® 50M	12.38 ± 0.17	3.17 ± 0.15	11.76 ± 0.71	3.14 ± 0.24
Emcocel® 90M	11.12 ± 0.91	3.30 ± 0.16	10.42 ± 0.86	3.25 ± 0.16
Avicel® PH101	12.27 ± 1.03	3.27 ± 0.16	10.48 ± 0.62	3.30 ± 0.14
Avicel® PH102	12.31 ± 1.14	3.14 ± 0.22	10.39 ± 0.59	3.15 ± 0.16

4. Results and discussion

4.1. The new model for the tensile strength of tablets and its limitations

Statistical analysis according to Eq. (24) yielded r^2(corrected) values of 0.999 and even higher, indicating the adequacy of the proposed model equation. (Table 2). Comparing the results for the two different strain rates, the fracture exponents were very similar. Thus, critical fracture behaviour seemed not to be affected by testing speed. However, the absolute values of the tablet strength were sensitive to strain rate. (Fig. 3). This trend was also supported by the small differences of the extrapolated maximal values between the two groups tested (Table 2). The curvature of σ_t as a function of ρ_r produced exponents ranging from 3.1 to 3.3. This result is little higher than the theoretically predicted value of 2.7.

So far the question can be asked, to what extent theoretical predictions can match experimental results? How similar is the structure of the bonding links within the tablet, as compared to the corresponding percolation structure in theory? It may also be questioned, if it is correct to focus on bonding elements, since the absent contacts appear to be more important, regarding the fact that crack propagation is a result of stress concentrations originated by the voids. The latter question can be answered directly. Introducing mechanical elements in a lattice and removing such elements from the lattice are inverse formulations of a percolation process having the same critical fracture exponent. In tablets, the porosity and relative density must exhibit the same critical behaviour, as the two parameters are linearly related (proportionality (22)).

The first question is more difficult to answer. The structure in tablets that is *relevant* for mechanical strength can unfortunately not be studied directly. Therefore one has to resort to a theoretical argumentation. A percolation structure should in general provide a good model for a heterogeneous physical structure unless no *long range correlations* occur. That is, the distribution of contacts and voids in the tablet should practically be random. A general application of percolation concepts to particle packing is therefore still a debated subject (Guyon et al., 1990). Yet, accepting a percolation like structure in tablets, it is especially of interest to ask for the physical mean-

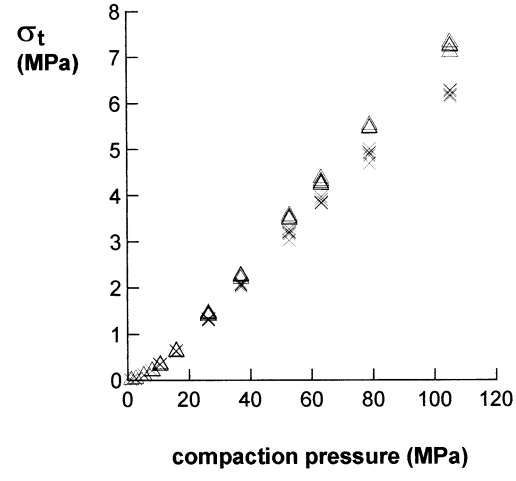

Fig. 3. Tensile strength (σ_t) (MPa) of Avicel® PH101 along the compaction pressure (MPa) for two different testing speeds. Δ: 25 mm min^{-1}, ×: 0.5 mm min^{-1}

ing of the *single connecting* elements. In the lattice model, these weakest elements are assumed to dominate mechanical behaviour. Thinking of tablets, the spots where stress concentrations occur are in the first place *relevant* for breakage and therefore the fractal dimension D_{sc} becomes important. In a first approximation one can assume that the trace of the crack that occurs during testing exhibits a fractal dimension that equals roughly D_{sc}. An experimental analysis of cracks from different metals was performed by Mandelbrot et al. (1984). Their results showed that cracks indeed can exhibit a fractal dimension. This is in agreement with our theoretical expectations but for quantitative statements, studies of crack patterns from tablets are certainly needed.

Two further aspects have to be mentioned if percolation theory is applied. First, the tablet has a limited specimen size as opposed to the theoretical lattices being infinite in extension. Small corrections of an assessed exponent can therefore account for such *finite size effects* (Stauffer and Aharony, 1992). Second, the range of validity of a percolation power law is a priori restricted. In a broad range of the order parameter, a power series would most accurately describe an arbitrary macroscopic property. The fundamental power law (1) names therefore only the most important term in this series and provides only in vicinity of the threshold an exact result. In a broader range however, the unknown terms of the series can gain increasingly weight and can possibly influence best fitted parameters in the model.

Besides these general limitations of a percolation approach there are additional issues to be discussed for the special case in this study. The lattice model proposed for simplicity completely brittle elements. This is surely justified thinking of the fact that tablets are composites of particles and therefore essentially brittle if subjected to diametral compression. Still, on the microscopic scale dissipative processes can also take place. The term of the surface energy should better be replaced by a *fracture surface energy*, also involving energy dissipation (Stokes and Evans, 1997). Note further that the applied load may not be entirely converted to tension. Compressive stresses or shear stresses can additionally occur in the specimen. Such effects possibly influence the determined exponent. If they dominate Eq. (23) is even invalidated.

So far, a number of reasons were given to explain the difference between observed exponents and the theoretical prediction. In this list, the aspect of anisotropy within the compacts should not be left out. The derivation of Eq. (5) assumes a constant stress, but in case of a constant strain an additional factor of the Poisson ratio would have to be introduced. If this factor is a constant with respect to ρ_r, the proportionality (6) is still correct. The aspect of changing anisotropy was not included in the present isotropic lattice model and may be part of further theoretical developments.

As mentioned in the introduction, a critical exponent shows in general universality. Despite this fundamental principle of percolation theory, differences between experimental and theoretically predicted values for a critical exponent can occur due to the already mentioned effects. Also on a theoretical level there is a possible source of non-universality, originated by a broad distribution of the microscopic property (Kogut and Straley, 1979). However, the practical relevance of this theoretical argument is still unclear. The existence of a narrow strength distribution however, will not violate the concept of universality. Accordingly, the universality of the critical fracture exponent was postulated. The averaging over all experimentally determined values yields $\bar{T}_f = 3.2 \pm 0.1$. In the subsequently performed non-linear regressions of Eq. (25), the best r^2 values were found in the range between 0.999 and 1.000 (Table 3 Figs. 4 and 5).

4.2. Discussion of the parameters

Considering the thresholds ρ_{rc} (Table 3), it is apparent that the values were close to the interval of the relative bulk density and tapped density for individual substances. It is interesting to notice that in a preceding study of elasticity (Kuentz and Leuenberger, 1998), the thresholds ρ_{rc} were smaller. This led to the assumption that the relative density can be regarded as a critical volume fraction in a *continuum percolation* (Stauffer and

Table 3
Comparison of the new model with the former Ryshkewitch–Duckworth approach

	Power law according to Eq. (25) with $T_f = 3.2 \pm 0.1$						Exponential law according to Eq. (27)					
	Testing speed (25 mm min^{-1})			Testing speed (0.5 mm min^{-1})			Testing speed (25 mm min^{-1})			Testing speed (0.5 mm min^{-1})		
	S	ρ_{rc}	r^2	S	ρ_{rc}	r^2	σ_0 (MPa)	b	r^2	σ_0 (MPa)	b	r^2
Emcocel® 50M	2.28	0.204	1.000	2.30	0.193	1.000	20.77	6.69	0.997	21.35	6.66	0.996
Emcocel® 90 M	2.93	0.247	0.999	2.38	0.214	1.000	18.03	6.70	0.996	16.96	6.66	0.997
Avicel® PH101	2.62	0.213	1.000	2.76	0.217	0.999	23.03	6.80	0.996	19.33	6.64	0.994
Avicel® PH102	2.50	0.211	0.999	2.52	0.211	0.999	22.74	6.84	0.997	17.84	6.58	0.996

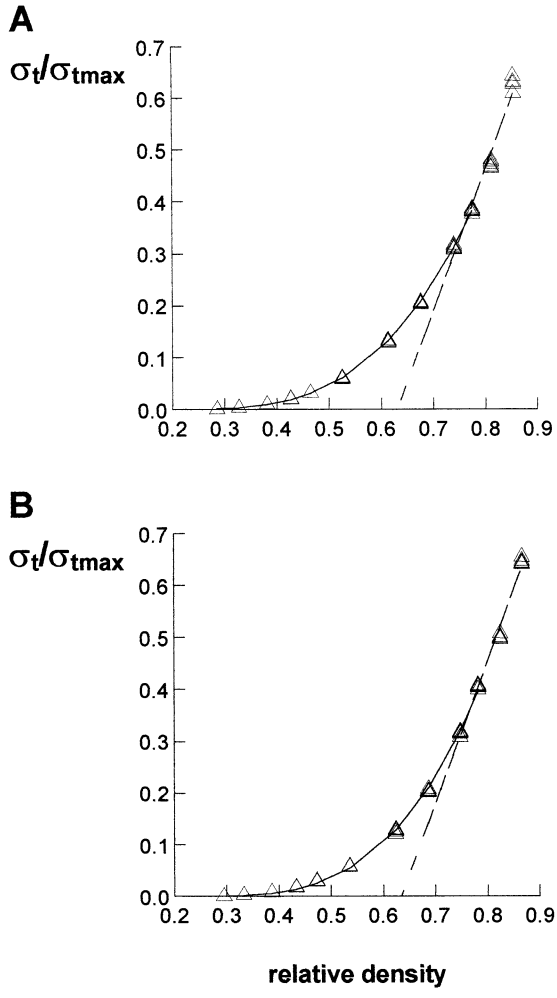

Fig. 4. Normalised tensile strength (σ_t/σ_{tmax}) (25mm min^{-1} testing speed) of A-Emcocel® 50M and B-Emcocel® 90M. Δ: experimental data, the line shows calculated values according to Eq. (25) and the dashed line holds for the linear approximation (EMA) far away from the threshold ρ_{rc}.

Aharony, 1992) model. This view provided an explanation for a threshold value, being lower than the relative bulk density. Yet, the present study shows that to ensure mechanical strength, higher values of ρ_{rc} are needed than in case of elasticity. Thus, the threshold where a mechanical property becomes zero can experimentally vary for different properties studied. The elastic modulus for example refers to the rigidity of a tablet. In case of the tablets strength however, the contacts for rigidity might not be enough. Adjacent particles need to share a certain minimal surface bonding area to form a *relevant* bonding strength. Thus, a minimum local force is required for particle adhering and therefore the threshold can not be below the relative bulk density.

It is important to know that the scaling factor S can not be calculated theoretically, except for very defined cases. Yet, it can be stated that S will strongly depend on individual system characteristics and on the fact whether the given property, such as σ_t is normalised by its maximal value

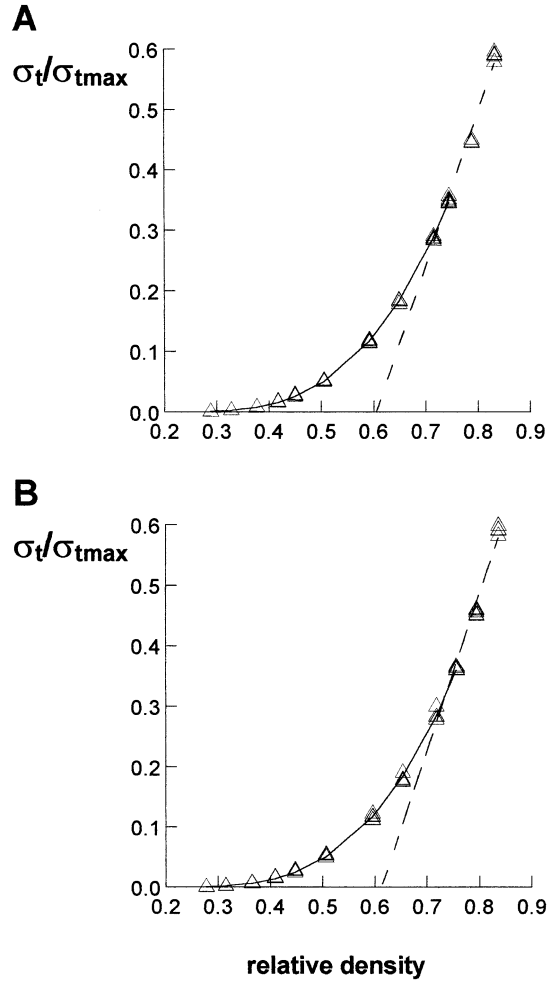

Fig. 5. Normalised tensile strength (σ_t/σ_{tmax}) (25mm min^{-1} testing speed) of A-Avicel® PH101 and B-Avicel® PH102. Δ: experimental data, the line shows calculated values according to Eq. (25) and the dashed line holds for the linear approximation (EMA) far away from the threshold ρ_{rc}.

σ_{tmax}. In the case of the normalised σ_t/σ_{tmax}-values, S is related to the specific microstructure of the compacts. Factors of the shape or size of the pores may be included in this constant. To know more about the physical meaning of this constant, further experimental studies will have to be conducted.

4.3. Comparison of the new model equation with an exponential relationship of the tensile strength and porosity

In the field of pharmaceutics or material sciences an exponential function is commonly proposed for the tensile strength of tablets in relation to their porosity. This goes back to a study of Ryshkewitch (1953) for ceramic materials which was later discussed by Duckworth (1953):

$$\sigma_t = \sigma_0 \cdot e^{-b \cdot \varepsilon} \quad (26)$$

The parameter σ_0 holds for the zero porosity strength, b is a material depending constant and ε denotes the porosity. The latter parameter can be replaced by the relative density resulting to Eq. (27):

$$\sigma_t = \sigma_0 \cdot e^{b \cdot (\rho_r - 1)} \quad (27)$$

Applying this exponential function to the tensile strength measured, adequate models result (Table 3). An analysis of the residuals (Fig. 6) indicates the superiority of the new model. Yet, it has to be kept in mind that the present study is restricted to low density tablets of polymers.

The fitting of Eq. (27) also reveals another interesting fact. The σ_0 values (Table 3) were clearly higher than the extrapolated parameter σ_{tmax} (Table 2). Note that in this study the tensile strength at zero porosity was linearly extrapolated, using only the highest density values. This is theoretically based on the *effective medium approximation* (Kuentz and Leuenberger, 1998). The alternative method of an exponential extrapolation has the drawback of a lacking theoretical background. So far, it should be added that the maximal strength was understood as a maximal value attached to a material for given experimental conditions and it was in the first place used to normalise σ_t. This seems meaningful since absolute strength values appear to be determined by individual factors of the tableting material as well as by process parameters. In addition only the use of relative strength values enable the scaling factor to be obtained. Note, that the constant S is only affected by the estimated value σ_{tmax}. The threshold ρ_{rc} that marks the onset of strength, and the exponent T_f, describing the power of the

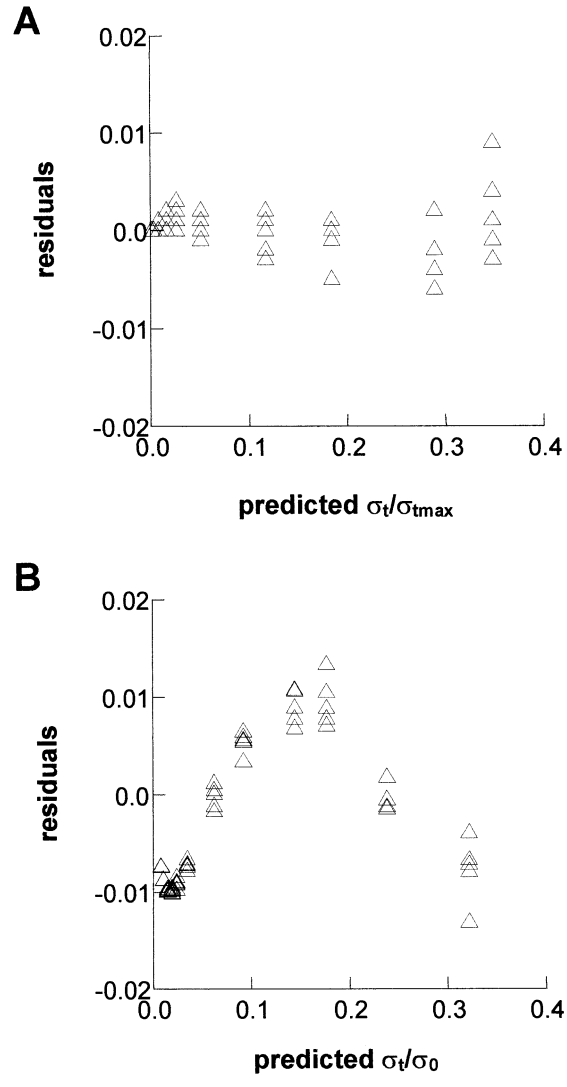

Fig. 6. Residuals of the model: (A) Eq. (25) and (B) Eq. (27) using data of Avicel® PH101 (25mm min^{-1} testing speed). The abscissa displays the predicted values of (A) the normalised tensile strength (σ_t/σ_{tmax}) and (B) the tensile strength divided by the estimate of the zero porosity strength (σ_t/σ_0).

tensile strength curve, should both not be influenced by the normalisation.

5. Conclusions

The disordered (micro)structure of tablets at comparatively low densities seems to be a key factor in understanding their mechanical behaviour. With concepts of percolation theory an explanation can be given for the non-linear behaviour of the tensile strength in relation to the relative density. A power law holds in the proximity of a critical relative density with a fracture exponent close to three. The experimentally determined exponent was slightly higher than its theoretical prediction and further research work is necessary to show whether this difference is significant. A comparison of the new model with the often used Ryshkewitch–Duckworth equation showed a better fitting capacity in favour of the power law presented. Additional studies are of interest to apply the new model to other substances than microcrystalline cellulose.

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Appendix A. List of symbols

b	dimensionless fitting constant in the exponent of the Ryshkewitch–Duckworth equation
c, $c(p)$	atomic spacing in a crystal lattice and the corresponding characteristic length of the theoretical lattice as a function of the occupation probability p
d	dimension of space (Euclidean dimension)
D	tablet diameter
D_{BB}	fractal dimension of the backbone of the percolating cluster
D_f	fractal dimension of the percolating cluster
D_{sc}	fractal dimension of the *single connecting* elements in the percolating cluster
E, $E(p)$	elastic Young's modulus of a crystal lattice and the corresponding Young's modulus of the lattice model as a function of the occupation probability p
F	maximal force recorded in the diametral compression test
h	thickness of the tablet
k	constant in the dimension of a surface energy
N_s	number of sites in a unit cross sectional area of the theoretical lattice
p, p_c	occupation probability of a site in the lattice and its critical value (percolation threshold)
q	universal exponent in the fundamental power law of percolation theory
r, r_c	probability to remove a mechanical element from a lattice site and its critical threshold value (percolation threshold)
R	arbitrary radius that is spanned in a unit cross sectional area of the theoretical lattice
S	dimensionless proportionality constant (scaling factor) in the power law of the normalised tensile strength
T_f, $\bar{T}_f$	fracture exponent in theory and the experimental average value
X	arbitrary mechanical property of a disordered medium
α	critical exponent of the characteristic length $c(p)$
Γ_s, $\Gamma_s(p)$	surface energy of a crystal lattice and the corresponding property of the lattice model as a function of the occupation probability p
δS	breakage surface in a crystal lattice
ε, ε_c	porosity and the critical threshold value

ν	critical exponent of the correlation length
$\Pi(p)$	probability that an arbitrary site in unit cross sectional area contains a *relevant* mechanical element
ρ_r, ρ_{rc}	relative density of a tablet and its critical threshold value
σ_0	fitting constant of the Ryshkewitch–Duckworth equation which holds for the zero porosity strength
σ_k	critical strength in a crystal lattice
$\sigma_{lattice}(p)$	tensile strength of the theoretical lattice as a function of the occupation probability
σ_t, σ_{tmax}	tensile strength of a tablet and the extrapolated maximal value
τ	critical exponent of the elastic Young's modulus
φ	critical exponent of the surface energy

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