Estimation of Mechanical Stability and Resistance of Microporous Materials Prepared by Pyrolysis

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A theoretical method for the estimation of mechanical stability and resistance of microporous materials is proposed. The method is based on the combined fractal/thermodynamic model of microporous media. The proposed method is utilized for the evaluation of parameters of mechanical resistance of microporous materials prepared by pyrolysis, using the thermodynamic theory of pyrolytical microporous structure. An engineering method for the evaluation of mechanical resistance of microporous materials is derived. © 2001 Academic Press

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INTRODUCTION

The evaluation of the mechanical resistance of microporous materials is very important for the machinery and building industries. Most existing construction materials (except for metals, alloys, and some special ceramics) are microporous, and the evaluation of their mechanical characteristics is extremely important for their practical use. Moreover, forecasting of the properties of new materials (on the threshold of their elaboration) would seriously reduce the costs of experimental studies and tests due to the preliminary evaluation of mechanical characteristics of the projected microporous material, based on the relationship between its preparation conditions, structure, and properties (1).

In the present paper, we propose a theoretical method for the evaluation of mechanical characteristics of microporous materials prepared by pyrolysis, first of all their mechanical stability and resistance, and we propose a related engineering method for forecasting the mechanical resistance of a microporous material, based on the conditions of its preparation.

MICROPOROUS STRUCTURES

Porous structure is characterized by the following parameters: volume of porous space, internal surface area, pore distribution in size (or energy), and percolation/nonpercolation (closed/open) type.

According to IUPAC classification, pores are divided into three types: macropores having a large radius (> 500 Å), mesopores having a middle radius (from 20 to 500 Å), and micropores with a small radius (less 20 Å) (2). Dubinin sub-divided micropores into ultramicropores (less than 7 Å) and supermicropores (2, 3).

The principal physical difference between various types of pores is the large divergence in their energetic potentials. More surface area per volume unit means higher energy potential and corresponds to more striking adsorptive and catalytic properties.

Microporous structures can be regular or random. Regularity of a structure means that (1) the structure is composed of the same fragments and (2) the orientation of these fragments follows several strict limitations.

Microporous structure is defined as homogeneous if all structural elements having the same volume and porosity have the same values of characteristic parameters.

Numerous homogeneous structures exhibit fractal properties, meaning that the same fragment of structure is reproduced in all volumes, while realization of various orientations has the same probability. As a result, there

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is no preferred direction; the difference in form between the entire structure and the elements is negligible.

MODELS OF MICROPOROUS MEDIA

According to the technique used, models of microporous structure can be divided into numerical and analytical models. According to physical assumptions, models of microporous structures can be divided into models related to the preparation process and those not related to the preparation process (1). Models not related to the preparation process assume several distributions of micropores according to their size, shape, or energy (3) or their fractal properties (4, 5).

Models based on the micropore formation process allow evaluation of structural parameters and technical characteristics of microporous materials from the conditions of their preparation (1, 6–8). In most cases, preparation-related models are preferred for engineering applications.

Most existing microporous materials are prepared by pyrolysis of organic materials or polymerization/aggregation. The present paper considers pyrolytically prepared materials. The corresponding models of microporous structure were developed in Refs. (1, 6–8). It was shown that most microporous materials used in real practice are well described by a steady-state model, in which the energy distribution of pores has the Gibbs form

$$f(\varepsilon) = q_e \exp[-\varepsilon/(R_g T)], \qquad [1]$$

where ε is the micropore energy per volume unit (the volume unit contains 1 mol of ideal gas under 1 atm and 298°K) and q_e is the normalizing coefficient.

EXISTING METHODS OF DESCRIPTION OF MECHANICAL PROPERTIES OF MATERIALS

Existing theoretical methods for the study of mechanical stability/resistance of materials are based on traditional theories of the solid state. The approaches employed include

— statistical mechanics and thermodynamics (9–11),
— perturbation methods (12, 13),
— interface and colloid theory (14, 15),
— phonon theory (16), and
— cumulative damage theory (17).

All of these methods can be used in an analytical or a numerical form.

Some of these methods (e.g., Refs. (9–11, 14, 15)) are similar to the technique used in the preparation-related theory of microporous media considered above. However, these methods do not account for the structural features of microporous materials, and the mathematical technique for the description of mechanical properties of microporous mater-

ials should be derived on the basis of thermodynamic theory (1, 6–8).

DEFINITION OF PROBLEM

Let us consider a homogeneous random microporous material prepared by pyrolysis. Its structure is characterized by porosity x and the pore distribution (in energy) $f(\varepsilon)$ or (in pore size) $\phi(r)$, where ε is the pore energy (per volume unit) and r is the characteristic size of a pore (e.g., radius for a cylindrical pore). The function $f(\varepsilon)$ is evaluated as described in Refs. (6–9). Mechanical stability is determined by elements of continuous solid phase (fibers). The fiber substructure is considered as a fractal having dimensionality f_c. Let us assume that all fragments of the continuous solid phase (fibers) are fixed in the solid structure. Instead of being characterized by the pore distribution in energy/size, the material can be characterized by an analogous distribution of fibers: energy distribution $F(E)$ or size distribution $\Phi(\rho)$, respectively.

From the material considered, a cubic sample is taken so carefully that the border effects can be neglected. The size of the sample is H; its volume is $V_0 = H^3$. The sample is placed under a press exerting pressure P onto all sides. Because of the homogeneity of the sample, its deformation (h) is the same at all coordinates, and the mechanical resistance is characterized by a function $P(h)$. All changes in the sample are irreversible. At the beginning of the process, $h = 0$ and $P(h = 0) = 0$. The process is finished when all pores are destroyed: $h(\text{finish}) = h' = Hx^{(1/3)}$; $P(h = h') = P'$ is the pressure determined by the compressibility of the continuous solid phase. Every increase in the pressure causes destruction of several elements of the continuous solid phase. Such destruction depends on the thickness of these elements. Fiber having size ρ is destroyed into fractal cubes, each of which has dimensionality f_c and size ρ; such destruction needs energy $Q_c \sigma_c \rho^{f_c - 1} \Phi(\rho)$, where σ_c is the cohesion tension, Q_c is a normalizing coefficient, and f_c is the fractal dimensionality of the fiber.

For the evaluation of mechanical stability and resistance of a microporous structure, the following subproblems need solutions:

(1) correlation among the different kinds of distribution functions found for the system,
(2) thermodynamic functions of structural elements, and
(3) volume and energy balances regarding distribution functions.

SOLUTIONS

Single Pore–Single Fiber Formation

Let us consider the process of formation of a single pore coexisting with a single fiber—fractal with dimensionality f_c

in a cubic initial volume $\omega_0 = h_0^3$, the porosity obtained is x_0, and the size of the fiber is ρ. Such a system is described by the equations [6–9]

$$\omega_p = x\omega_0 = r^{fp} \tag{2}$$

$$\omega_c = (1 - x_0)\omega_0 = \rho^{fc} \tag{3}$$

$$A_p = x_0 A_e + A_i = 2f_p r^{(fp-1)} \tag{4}$$

$$A_c = (1 - x_0)A_e + A_i = 2f_c \rho^{(fc-1)} \tag{5}$$

$$A_i = A_0 x_0(1 - x_0), \tag{6}$$

where A_0 is the initial total surface area, f_p is the fractal dimensionality of pores, A_i is the internal surface area, A_c and A_p are the surface areas of the fiber and the pore, respectively, and $A_e = 6h_0^2$ is the exterior surface area of the initial cube.

The combinatorial entropy is found from

$$\Delta S = R_g \omega_0 [-\ln(x_0) - \ln(1 - x_0)]. \tag{7}$$

The free energy is

$$\Delta G = \sigma_c A_e - T\Delta S. \tag{8}$$

The chemical potential of the continuous solid phase is

$$\mu_c = \Delta G / V_c, \tag{9}$$

where V_c is the volume of the continuous solid (fibers) phase.

Thus, we get a sequence of parameters available for evaluation: $\varepsilon - r - \rho$. Hence, knowing the function $f(\varepsilon)$, we get all necessary forms of distributions.

Breaking-Up of Fibers

A fiber having characteristic size ρ has a cohesive bond with the solid structure, the bond strength being $\sigma_c \rho^{(fc-1)}$. The volume of such fibers is proportional to their volume fraction $Q_c \Phi(\rho)d\rho$, while their number is the same divided by the fiber volume: $Q_c \Phi(\rho)d\rho / \rho^{fc}$. Hence, the total strength of the cohesive bond of these fibers to the solid structure is $\sigma_c Q_c \Phi(\rho)d\rho / \rho$. The work performed by the exterior force destroying the fibers is found from

$$3P(h)(H - h)^2 dh = Q_c \sigma_c \Phi(\rho)d\rho / \rho. \tag{10}$$

On the other hand, the volume change is related to the reduction of the porous volume,

$$3(H - h)^2 dh = q_p f(\varepsilon)d\varepsilon = Q_p \phi(r)dr, \tag{11}$$

where ε and r are, respectively, the energy (per volume unit) and the size of the pores coexisting with the broken fibers, and Q_p is a normalizing coefficient.

Size/Energy Distribution in the Continuous Solid Phase

Previous publications (1, 6–8) give the correlation between $f(\varepsilon)$ and the conditions of preparation of the microporous material. Evaluations of other distributions (pores in size and fibers in energy and size) are not performed. However, it was shown in Ref. (8) that geometric properties of porous and continuous phases are similar, and these substructures differ in fractal dimensionality only. Considering them as cubes having different fractal dimensionalities, we may write the equations

$$V_p = xV_0 = (L_p)^{fp} \tag{12}$$

$$V_c = (1 - x)V_0 = (L_c)^{fc} \tag{13}$$

$$A_p = 2f_p(L_p)^{(fp-1)}, \quad A_c = 2f_c(L_c)^{(fc-1)}, \tag{14}$$

where L_p and L_c are the formal linear sizes of the porous and continuous-solid clusters (fractals), respectively:

$$V_p = \int_{r_{min}}^{r_{max}} Q_p \phi(r)dr \tag{15}$$

$$V_c = \int_{R_{min}}^{R_{max}} Q_c \phi(\rho)d\rho \tag{16}$$

$$U_p = \int_{r_{min}}^{r_{max}} Q_p \varepsilon(r)\phi(r)dr \tag{17}$$

$$U_c = \int_{R_{min}}^{R_{max}} Q_c E(\rho)\Phi(\rho)d\rho. \tag{18}$$

On the other hand, the total pore volume and energy are found from the following equations, respectively:

$$V_p = \int_{\varepsilon_{min}}^{\varepsilon_{max}} q_e f(\varepsilon)d\varepsilon \tag{19}$$

$$U_p = \int_{\varepsilon_{min}}^{\varepsilon_{max}} q_e \varepsilon f(\varepsilon)d\varepsilon. \tag{20}$$

There are two balances: volume and energy.
Volume balance is

$$dV = -q_e f(\varepsilon)d\varepsilon \tag{21}$$

or

$$dV = -Q_c \Phi(\rho) d\rho, \quad [22]$$

where ρ is the size of a continuous solid substructure (fibers), Q_c, q_e and Q_ρ are normalizing coefficients, and Φ is the function of distribution of fibers by size.

Energy balance is

$$P(V)dV := Q_c \sigma_c \rho^{f_c - 1} \Phi(\rho) d\rho \quad [23]$$

Equations [22] and [23] provide the correlation between V and P; hence, the system of Eqs. [2]–[23] gives complete information about such mechanical properties of the considered microporous system as stability and resistance.

ENGINEERING METHOD OF CALCULATION

Now, let us consider the engineering application of the above proposed method to the following example.

Let us consider a porous material characterized by a Gibbs distribution of micropores in energy. The calculations include the following stages:

(1) Initial stages. The initial parameters needed for calculations are porosity ε (or fractal dimensionality of the porous cluster f_p or that of the continuous solid phase f_c, as follows from Refs. (4, 8); of these parameters only one is independent), energy distribution of micropores (that is estimated as described in Refs. (6–8)), cohesive tension σ_c, and temperature T.

(2) For each value of ρ we evaluate ε from Eqs. [10] and [11], so we have the size distribution of fibers.

(3) Then, from Eq. [23] we find the function $P(V)$ that is the solution (see Fig. 1 for typical mechanical behavior of a pyrolytically prepared microporous material, $\sigma_c/(R_gT) = 0.4, f_c = 2.95$; this value of f_c corresponds to a moderate porosity that is normal for such types of structures).

We note, based on the graph presented in Fig. 1, that the mechanical resistance function gets a minimum. In the initial part of the argument, the resistance is high because of large fraction of micropores of small size, while the end part of the graph rises because of the high resistance of bigger fibers.

The axis label "deformation/porosity" means that only the volume of the porous phase changes under deformation, and only its relative change needs to be accounted for (without relation to the continuous phase).
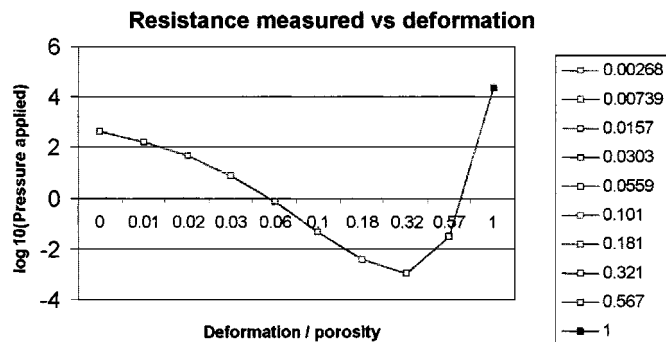

FIG. 1. Mechanical behavior of a microporous material. $\sigma_c/(R_gT) = 0.4$ (R_g is the gas constant); $f_c = 2.95$.

CONCLUSIONS

A theoretical method for the estimation of mechanical stability and resistance of microporous materials has been proposed. The method has been based on the combined fractal/thermodynamic model of microporous media. The proposed method has been utilized for the evaluation of parameters of mechanical resistance of microporous materials prepared by pyrolysis, using the thermodynamic theory of pyrolytical microporous structure. An engineering method for the evaluation of mechanical resistance of microporous materials has been derived.

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