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Mechanical Behaviors of Mechanochemical Materials*

(Part 2, Mechanical Outputs in an Equilibrium State)

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Mechanical properties of mechanochemical materials have been scarcely investigated.

This paper deals with the theoretical and experimental studies on the mechanical behaviors of mechanochemical materials in an equilibrium state. That is, the degree of swelling under external forces and the works developed during the swelling of mechanochemical materials in forms of a particle, a film and particles in a rigid cylinder are treated from the engineering point of view.

The expressions of the mechanical works are derived. Several other mechanical characteristics such as the degree of swelling, the restriction of energy conversion due to an external force, the work efficiency and the swelling pressure are also quantitatively explained. Comparison of the present materials with the muscle is made.

1. Introduction

From the engineering point of view, a polymer called a mechanochemical material^{(1)~(5)} has the following interesting characteristics: (1) It converts directly the chemical energy into the mechanical energy like the muscle; (2) it is soft; and (3) chemical solutions which are used as an energy source are safe and convenient for storage. Moreover, even if the microscopic mechanism of contraction is different from that in the muscle, it has the possibility of working as a kind of an artificial muscle, because the material can perform the above-mentioned energy conversion. At the same time, it has the merit of serving as a simulator of mechanical properties of muscle.

The mechanical properties of the material have been scarcely known. The present paper discusses theoretically and experimentally the mechanical properties such as the forces, the pressure and the mechanical work developed by the material and the efficiency of the work.

At first, the results obtained in the previous paper⁽³⁾ are briefly introduced.

The entropy change ΔS involved in the deformation of a cross-linked polymer is expressed as follows

$$\Delta S = -(k\nu_e/2) \{ \alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - 2 \ln(\alpha_x \alpha_y \alpha_z) \} \quad (1)$$

where k is the Boltzmann's constant, ν_e is the effective number of chains in a real network, and α_x , α_y and α_z the factors characterizing a general homogeneous deformation with reference to a Cartesian coordinate. From Eq. (1) we obtain the force-strain relation of elastic body as

$$f = -T \left(\frac{\partial \Delta S}{\partial l} \right)_{T, V, n_i} = \frac{RT\nu_e}{l_0} \left(\alpha - \frac{1}{\alpha^2} \right) \quad (2)$$

$$p = T \left(\frac{\partial \Delta S}{\partial V} \right)_{T, V, n_i} = -\frac{RT\nu_e}{V_0} \left(\frac{1}{\alpha} - \frac{1}{\alpha^3} \right) \quad (3)$$

where f is a force, p is a pressure, T is the absolute temperature, l_0 is the length of a gel without external force, V_0 is the volume of the gel without an external pressure and α is a factor of the linear deformation of the gel (the network structure).

The equation of equilibrium swelling for mechanochemical materials is

$$\alpha^2 = 1 + \frac{gn}{\nu_e} \quad (4)$$

where α is a factor expressing the linear deformation of the network structure by isotropic swelling and g is n^*/n , where n is the total number of fixed ions in the polymer and n^* is the total number of the effective gegen-ions.

2. The relationship between the swelling and the force subjected to a mechanochemical material

Let's investigate the degree of swelling under an external force.

The thermodynamic framework required for the treatment of a mechanochemical material is

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given by the following fundamental equation^{(6) (7)}

$$dF = -SdT - p dV + f dl + \sum_i \mu_i dn_i \quad \dots\dots\dots (5)$$

where dF is the change of Helmholtz's energy, dV is the volume change of a material under an external pressure p , dl is the displacement change in the material under an external force f , dn_i is the number of the ions introduced into the material from the reservoir at chemical potential μ_i of the i -th component.

2.1 The theoretical study on the deswelling in a filament under an external force

Thermodynamical cycle (mechanochemical cycle)^{(4) (7)} can be carried out in a filmlike or filament-like mechanochemical material. The cycles consist of the following processes: ①→②: swelling due to NaOH solution, ②→③: elongation due to an external force f in the solution, ③→④: deswelling due to HCl solution under the constant force f and ④→①: compression due to the removal of the force f (Fig. 1).

Applying Eq. (5) to each step of the cycle in Fig. 1, we have

$$\left. \begin{aligned} [dF]_{① \rightarrow ②} &= [\mu_{\text{NaOH}} dn_{\text{NaOH}}]_{① \rightarrow ②}, \\ [dF]_{② \rightarrow ③} &= [f dl]_{② \rightarrow ③} + [\mu_{\text{NaOH}} dn_{\text{NaOH}}]_{② \rightarrow ③}, \\ [dF]_{③ \rightarrow ④} &= [f dl]_{③ \rightarrow ④} + [\mu_{\text{HCl}} dn_{\text{HCl}}]_{③ \rightarrow ④}, \\ [dF]_{④ \rightarrow ①} &= [f dl]_{④ \rightarrow ①} + [\mu_{\text{HCl}} dn_{\text{HCl}}]_{④ \rightarrow ①} \end{aligned} \right\} \quad \dots\dots\dots (6)$$

at constant temperature without an external pressure.

It is difficult to obtain an accurate value of the deswelling $[dl]_{③ \rightarrow ④}$ simply by the use of Eq. (6), because dF , dl and dn respectively must change in each process. However, if we can assume that the conditional change of the solution in a gel is negligibly small for the small load f , that is, if the following relation is satisfied

$$[dn_{\text{NaOH}}]_{② \rightarrow ③} \cong 0, \quad [dn_{\text{HCl}}]_{④ \rightarrow ①} \cong 0 \quad \dots\dots\dots (7)$$

we have

Fig. 1 Mechanochemical cycles

$$\left. \begin{aligned} [dF]_{② \rightarrow ③} &= [f dl]_{② \rightarrow ③}, \\ [dF]_{④ \rightarrow ①} &= [f dl]_{④ \rightarrow ①} \end{aligned} \right\} \quad \dots\dots\dots (8)$$

Considering that the change of the internal energy (dU) in the gel is negligibly small, we have

$$\begin{aligned} [dF]_{② \rightarrow ③} &= [dU - SdT - TdS]_{② \rightarrow ③} \\ &\cong -[TdS]_{② \rightarrow ③} \quad \dots\dots\dots (9) \end{aligned}$$

Here, dF of Eq. (8) is the Helmholtz's energy change due to an external force and dS of Eq. (9) is the elastic entropy change due to the force. Thus, substituting Eq. (1) into Eq. (9), we obtain the following relations*

$$f = -T \left(\frac{\partial (dS)}{\partial (dl)} \right)_{n_i, T} = \frac{RT \nu_e}{l_m} \left(\beta - \frac{1}{\beta^2} \right) \quad \dots\dots\dots (10)$$

$$f = -T \left(\frac{\partial (dS)}{\partial (dl)} \right)_{n_i, T} = \frac{RT \nu_e}{l_m} \alpha \left(\gamma - \frac{1}{\gamma^2} \right) \quad \dots\dots\dots (11)$$

where α , β and $\gamma > 1$. Hence, the degree of deswelling α_D in the step ③→④ can be calculated from the following Eq. (12)

(a) External force and the degree of swelling for filmlike mechanochemical material (calculated)

(b) External force and the degree of swelling for filmlike mechanochemical materials (set) (calculated)

Fig. 2

* Equation (11) is derived by substituting $\alpha_x = \alpha$, $\alpha_y = \alpha_z = \alpha/\sqrt{\gamma}$ and $dl = \alpha l_m d\gamma$ into Eqs. (1) and (2). The tensile force of a filament (or a film) is observed to be larger in the swollen state than in the contracted one.

$$\alpha_p = \beta/\alpha\gamma \dots\dots\dots (12)$$

Figure 2 shows the calculated values of the degree of swelling in a filament with a weight. The calculation was performed on an OKITAC 5090 H computer by the use of Eqs. (4), (10), (11) and (12) where $l_m=4.5$ cm, $V_m=0.054$ cm³, $g=0.1$ and $n=4.5 \times 10^{-5}$ mol are employed.

Remarks :

(1) The curves in Fig. 2 (a) show the relation between isotonic tension and the degree of swelling of a filmlike mechanochemical material. The degree of swelling decreases with an increase of the external force.

(2) In the case of a highly cross-linked material, the swelling is almost independent of the external force.

(3) Swelling and deswelling phenomena in a filament under a large force are hardly observed in spite of the addition of a chemical solution. If the maximum force which the filament can generate is defined as the force by which the swelling reaches 20 % of the swelling when no force is applied, it would be about 140 gr from curve III of Fig. 2 (a). This definition is considered because in the present theory, an infinite force is required for the perfect restriction of swelling. This force can correspond to the isometric tension of muscle in tetanus.

(4) From Eq. (10) or (11), the (isotonic) tension is found to be proportional to the number of cross-linkages in the initial unit volume and the initial cross-sectional area of the gel. Hence, short filaments in parallel are advantageous in order to generate a larger force.

2.2 The theoretical study on the swelling of a particle under an external pressure

Figure 3 shows the mechanochemical cycle of a particle of mechanochemical material under a constant external pressure. Substituting $dT=0$ and $f=0$ into Eq. (5) and assuming that $[dn_{HCl}]_{2 \rightarrow 3}=0$ and $[dn_{H_2O}]_{4 \rightarrow 1}=0$, in the steps $2 \rightarrow 3$ and $4 \rightarrow 1$, we have

Fig. 3 Mechanochemical cycles (external pressure)

$$p = T[\partial(\Delta S)/\partial(\Delta V)]_{n_i, T} \dots\dots\dots (13)$$

In the step ①→④, by using Eqs. (13) and (1), we have

$$p = -(RT\nu_e/V_m)(1/\beta - 1/\beta^3) \dots\dots\dots (14)$$

where β is a linear compressive factor of volume change due to external pressure p . In the process ②→③, we also have

$$p = -(RT\nu_e/\alpha^3 V_m)(1/\gamma - 1/\gamma^3) \dots\dots\dots (15)$$

Now, we return to the original state, ①. Thus, solving Eqs. (14) and (15) with respect to β and γ for p and α given, we have the degree of swelling α_s as

$$\alpha_s = \beta/\alpha\gamma \dots\dots\dots (16)$$

Figure 4 shows the calculated values based on Eqs. (4), (14), (15) and (16) where $RT=24.6162 \times 10^3$ kg-cm/mol, $g=0.05\sqrt{C}$ and $n=7.14 \times 10^{-9}$ mol. C is the concentration of the external solution in mol/l and ν_e is reasonably assumed.

Remarks :

(1) The degree of swelling decreases with the increase of the external pressure. In addition, Fig. 4 shows that swelling phenomena are hardly observed at high pressures when a chemical solution is added.

(2) The degree of swelling due to the pressure is smaller with the materials of higher cross-linking. Hence, the number of cross-linkages in the initial unit volume, ν_e/V_m , can be used as a parameter of mechanical strength. In order to make the larger swelling, it is advantageous to use particles with large values of n/V_m and ν_e/V_m and also to use a solution of high concentration.

(3) From Fig. 4, the pressure to be sustained by a particle is about 70 atms~200 atms (20 % of the swelling is considered for the former as the definition and 10 % for the latter), at $\nu_e=1.05 \times 10^{-9}$ mol (1 % crosslinkage), or about 200 atms~1000 atms at $\nu_e=2.10 \times 10^{-9}$ mol (2 % crosslinkage). The pressures obtained are higher than expected.

Fig. 4 The degree of swelling for a spherical mechanochemical material undergoing external pressure (calculated)

On the other hand, the force caused in a filmlike gel is rather small. The reason is considered to lie in the difference of ν_e/V_m for the two cases ($\nu_e/V_m = 0.50 \times 10^{-3} \text{ mol/cm}^3$ for a particle, while $\nu_e/V_m = 1.85 \times 10^{-4} \text{ mol/cm}^3$ for a filament). It is found that particles of mechanochemical materials for a pressure-generating device are more effective than filaments (or films).

2.3 Experiments

The method used for the experiment of a filmlike gel is the same as described in the previous paper (part 1). Comparison between the experimental and the calculated results is made, which is shown in Figs. 5 and 7. The curves in Fig. 5 are found to be similar to those of the load-elongation

Fig. 5 Load-extension curve of filmlike mechanochemical material (experimental)

Fig. 6 Load-extension curve of frog's muscle

Fig. 7 The decrease in degree of swelling for filmlike mechanochemical material due to force (calculated and experimental)

relation of resting muscle as shown in Fig. 6, which was demonstrated by O. Meyerhof et al.⁽⁵⁾, while the former not to similar to the latter of contracted muscle. In Fig. 7, the calculated values (solid line) agree quantitatively with the experimental ones (circles). Figure 8 shows comparison between the theoretical (solid lines) and the experimental values with respect to elongation of a filament. A similar tendency is seen with vulcanized rubber⁽⁶⁾.

Figures 5 and 7 show that the contractile length decreases with the increase of a load. On the other hand, in the initial twitch in muscle, its contractile length does not change even if a load increases. This is known through physiological experiments. In this macroscopic respect, the present mechanochemical material is also different from a muscle.

3. On the mechanical works

3.1 A filament

A mechanochemical work in a filament is easy to determine when it contracts like the muscle. Effective mechanical work E can be calculated by the following set of equations.

$$\left. \begin{aligned} E &= f \left(\frac{1}{\alpha_D} - 1 \right) l_{HCl}, \quad \alpha_D = \frac{\beta}{\alpha r}, \quad \alpha^2 = 1 + \frac{gn}{\nu_e} \\ f &= \left(\frac{RT\nu_e}{l_m} \right) \left(\beta - \frac{1}{\beta^2} \right) = \left(\frac{RT\nu_e \alpha}{l_m} \right) \left(r - \frac{1}{r^2} \right) \end{aligned} \right\} \dots \dots \dots (17)$$

Figures 9 and 10 show the calculated values. Figure 11 shows comparison with the experiments (circles).

Remarks:

(1) From Eq. (17), we can see that the increase in the volume of a specimen (V_m), the

Fig. 8 Load-strain relations of filmlike mechanochemical material (calculated and experimental)

number of the fixed ions in unit volume (n/V_m) and the number of cross-linkages in unit volume (ν_e/V_m) are effective for the mechanical work developed by the contraction of a filament. The solution of the concentration of 0.05 to 0.1 mol/l is also effective for the mechanical work.

(2) The work increases linearly with the length of a filament, while the force does not change. Heavier load can be sustained by the use of filaments in parallel than in series.

(3) From Fig. 11 the maximum value of the work done is 23 gcm (theoretical) while it is 16 gcm (experimental). We have 30 g-cm (theoretical) from Fig. 9. The last value is equal to 1.3×10^{-2} cal/g, which is lower than $15 \sim 20 \times 10^{-2}$ cal/g in muscle.

3.2 A particle

The mechanical work in a particle when it swells is easy to determine. From the following set of equations we have the effective mechanical work E developed by a gel

$$\left. \begin{aligned} E &= p\alpha^3\gamma^3V_m(\alpha_s^3-1), \quad \alpha_s = \beta/\alpha\gamma, \\ \alpha^2 &= 1(1+gn/\nu_e), \\ p &= -(RT\nu_e/V_m)(1/\beta-1/\beta^3) \\ &= -(RT\nu_e/\alpha^3V_m)(1/\gamma-1/\gamma^3) \end{aligned} \right\} \dots\dots(18)$$

The calculated results are shown in Fig. 12.

Remarks :

Fig. 9 The mechanical work occurring in a filmlike mechanochemical material (calculated) ($g=0.1$)

Fig. 10 The mechanical works occurring filaments connected as parallel (calculated) ($g=0.1$)

(1) The effective work is proportional to V_m and ν_e/V_m . The work increases when a solution of high concentration and a material with high density of the fixed ions n/V_m are used.

(2) From Fig. 12, the maximum value of the work done is 5.5×10^{-6} kgcm at about 20 atms. This value is equal to $3 \sim 6 \times 10^{-2}$ cal/g, which is lower than $15 \sim 20 \times 10^{-2}$ cal/g in muscle. However, theoretically the work should be possible even under the external pressure more than 1000 atms.

4. The studies on energy transformation

4.1 Reversible transformation

The energy transformation in a mechanochemical material is sometimes cited as an example of irreversible process. That is, it is regarded impossible to convert the mechanical energy into the chemical energy. The aim of the present section is to study on these questions, based on the mechanochemical cycle.

In Fig. 1, if the concentration of the solution surrounding a gel is assumed to be low, the processes $[dl]_{1 \rightarrow 2}$ and $[dl]_{4 \rightarrow 3}$ correspond to $[dn]_{1 \rightarrow 2}$ and $[dn]_{3 \rightarrow 4}$ respectively.

Fig. 11 The mechanical works occurring in a filament (calculated and experimental)

Density of crosslinking ν_e/V_m mol/cc

I 0.125×10^{-3}

II 0.25

III 0.5

The present degree of crosslinking % shows as follows

$\nu_e = 2.10 \times 10^{-3}$ mol (2%)

$\nu_e = 1.05 \times$ " (1%)

Fig. 12 The mechanical work occurring in a spherical mechanochemical material (calculated)

That is,

$$[dl]_{1 \rightarrow 2} \geq [dl]_{4 \rightarrow 3} \quad \text{---} \\ [dn]_{1 \rightarrow 2} \geq [dn]_{3 \rightarrow 4}$$

That $[dl]_{1 \rightarrow 2} > [dl]_{4 \rightarrow 3}$ must be established because the area within the closed curves of mechanochemical cycle expresses the work done by a cycle. Thus,

$$[dn]_{1 \rightarrow 2} > [dn]_{3 \rightarrow 4} \dots \dots \dots (19)$$

is obtained. Equation (19) shows a decrease in the number of ions which are designated for exchange. That is, the conversion of the chemical energy into the mechanical one is restricted under the external load. In addition, dn_{NaOH} and dn_{HCl} which have been consumed in a cycle must be equal. Thus, we have

$$[dn_{\text{NaOH}}]_{2 \rightarrow 3} < 0, [dn_{\text{HCl}}]_{4 \rightarrow 1} > 0 \dots \dots \dots (20)$$

Equation (20) shows the conversion of the mechanical energy into the chemical one. The step $2 \rightarrow 3$ is the loading process while the step $4 \rightarrow 1$ is the unloading process.

Now, let's consider the inverse cycle. In Fig. 13, it is clear that $[dl]_{1 \rightarrow 2} = [dl]_{1' \rightarrow 4'}$. That $[dl]_{4 \rightarrow 3} = [dl]_{2' \rightarrow 3'}$ is obtained by the one-to-one mapping of the ions designated for exchange to the external force. In addition, from the relations with $dn < 0$ (loading of the external force) and $dn > 0$ (unloading), we obtain

$$[dl]_{4 \rightarrow 1} = -[dl]_{1' \rightarrow 2'},$$

$$[dl]_{2 \rightarrow 3} = -[dl]_{3' \rightarrow 4'}.$$

Hence, the mechanochemical cycle is reversible.

Moreover, in Fig. 1, it is found that the mutual transformation between the chemical and the mechanical energy can be realized in the steps $2 \rightarrow 3$ and $4 \rightarrow 1$. However, the transformation of the mechanical energy into the chemical one can not in the strict sense be realized in the process of $3 \rightarrow 4$ where chemical reactions exist.

In summary, a mechanochemical material can perform thermodynamically reversible transformation. The conversion of the chemical energy into the mechanical one can be restricted by a force (a load), when the load exists. The inverse conversion from the mechanical energy to the chemical energy can not always be realized in any process.

Fig. 13

4.2 Analogy of the mechanochemical engine with a heat engine

Here, we regard the motion of a mechanochemical material as a kind of reciprocal engine. The work E that the working substance of a heat engine performs on the external system is $(T_1 - T_2)\Delta S$ as shown in Fig. 14 (a). In the case of the mechanochemical material, as shown in Fig. 14 (b), an increase in the number of the effective gegen-ions, dn , is caused by the chemical potential difference $|\mu_1 - \mu_2|$. The increased ions generate a swelling pressure (the steps $1 \rightarrow 2 \rightarrow 3$). Therefore, analogy can be made between the two engines. That is: the temperature difference (in a heat engine) $\leftrightarrow$ the chemical potential difference (in a mechanochemical engine), entropy change of the steam molecules $\leftrightarrow$ entropy change of the gegen-ions, the steam pressure $\leftrightarrow$ the swelling pressure (origin of mechanical energy), and the steam $\leftrightarrow$ the polymer (the working substance). In addition, the conversion of the chemical energy (movements of the gegen-ions, etc) into the mechanical one (the material expansion due to the swelling pressure) is as direct as the conversion of the thermal energy into the steam pressure.

4.3 The study on the work efficiency

The absolute work E developed by a mechanochemical material is

$$E = \int \Delta \mu dn \dots \dots \dots (21)$$

where $\Delta \mu$ is the chemical potential change in the solution outside the gel before and after swelling.

The effective mechanical work E_1 developed

(a)

(b)

Fig. 14

by the material is given as $E_1 = -\int f dl = f \Delta l$ or $E_1 = \int p dV = p \Delta V$, where Δl is the contractile length of the material, and ΔV is the increase of its volume. Thus, the work efficiency of the mechanochemical material is given as

$$\eta = E_1/E = -\int f dl / \int \Delta \mu dn,$$

or

$$\eta = \int p dV / \int \Delta \mu dn \dots\dots\dots (22)$$

$$\Delta \mu = -(\mu_i - \mu_i^0) = -RT \ln C_i \dots\dots\dots (23)$$

where C_i is the concentration (mol/cm³) of the i -th component, μ_i^0 is the chemical potential of the i -th component in the standard state, and Δn is the increasing number of the effective gegen-ions which is approximately equal to gn .

If we deal with a hypothetical case, for simplicity, that the solution used would become a pure water, we have

$$\begin{aligned} \text{Chemical energy} &= \text{absolute work } E, \\ E &= -RTgn \ln C_i \dots\dots\dots (24) \end{aligned}$$

On the other hand, though the concentration may decrease, the solution used contains still chemical energy. Therefore, we can improve the efficiency by re-using the solution used for swelling or deswelling. There are two values of the chemical potentials μ_1 and μ_2 , that is, before and after the solution is mixed with gel respectively. The difference is equivalent to the potential term of the absolute work. Now, the solution of the volume v_i with the concentration C_i is mixed with gel of the volume v_i' with the concentration C_i' . Then, the decrease in the chemical potential $\Delta \mu_i$ in the volume $(v_i + v_i')$ is expressed as

$$\begin{aligned} \mu_1 &\equiv \mu_i = \mu_i^0 + RT \ln C_i \\ \mu_2 &\equiv \mu_i - \Delta \mu_i = \mu_i^0 + RT \ln \left(\frac{C_i v_i + C_i' v_i'}{v_i + v_i'} \right) \end{aligned} \dots\dots\dots (25)$$

$$\Delta \mu = \mu_1 - \mu_2 = \Delta \mu_i = RT \ln \left\{ \frac{C_i (v_i + v_i')}{C_i v_i + C_i' v_i'} \right\} \dots\dots\dots (25)'$$

If $v_i > v_i'$, excess ions designated for exchange will pass through without ionization, and the number of the gegen-ions is supposed to be proportional to the ratio of the volume v_i/v_i' . Therefore, Δn is equal to $gn(v_i/v_i')$. Thus, we obtain

$$\begin{aligned} \text{Chemical energy} &= \text{absolute work } E, \\ E &= RTgn(v_i/v_i') \times \ln \left\{ \frac{C_i (v_i + v_i')}{C_i v_i + C_i' v_i'} \right\} \dots\dots\dots (26) \end{aligned}$$

Assuming that $v_i \approx v_i'$ and $C_i' = 0$, we obtain

$$\text{chemical energy} = gnRT \ln 2 \dots\dots\dots (27)$$

Examples of numerical calculation:

(i) PMAA-PVA system

Cross-linking ratio 1:5, gel volume $4.5 \times 1.5 \times 0.008$ cm³ wet, we have $0.1 \text{ N HCl} \rightleftharpoons 0.1 \text{ N NaOH}$.

According to Eq. (27).

$E = 76.78$ g-cm. E_1 is given in Fig. 11.

(ii) H-form ion exchanger

$E = 8.4 \times 10^{-3}$ g-cm. E_1 is given in Fig. 12.

Figures 15 and 16 show the efficiency of above two examples.

5. The theoretical studies on the mechanical work developed by swelling of granulated materials

The swelling of particles (not a particle) can be utilized for purposes such as the waterproofing of a vessel bottom. The theory in the present section deals with the mechanical outputs of granulated mechanochemical materials (the equilibrium swelling, the mechanical work, etc). A supposed sphere in the materials swells isotropically under a constant external pressure keeping its spherical form.

Let's discuss the mechanical outputs based upon the following assumptions:

Fig. 15 The work efficiency for a filmlike mechanochemical material (calculated and experimental)

Fig. 16 The work efficiency for a spherical mechanochemical material (calculated)

Assumption (A)—Each particle is assumed to be of the same size and keep its spherical shape. A change in relative position of each particle is assumed not to occur.

As the configurations of particles before swelling are assumed to be similar to those after swelling, the equilibrium swelling of granule is also α' if that of each particle is α' . Hence, the equilibrium swelling x in the granule and the mechanical work E are

$$x = \alpha', \quad E = \frac{4}{3} \pi R^3 (\alpha'^3 - 1) p \quad (28)$$

where R is the radius of a spherical granule and p is an external constant pressure. In addition, the packing factor ϕ is given as $\phi = Nr^3/R^3$, where r is the radius of each particle before swelling and N is the number of particles. Substituting this relation into Eq. (28), we have

$$E = p \cdot \frac{4}{3} \pi r_m^3 N \alpha^3 \gamma^3 (\alpha'^3 - 1) / \phi \quad (29)$$

where α and γ are the same as defined in the mechanochemical cycle (in Fig. 3) and r_m denotes the radius of a particle in the equilibrium swelling without external pressure. Under this assumption, particles of the same size are regularly arranged and have no frictions among them.

Assumption (B)—Each particle is assumed to be of the same size and of a spherical shape. Energy conservation law which holds when the chemical energy is converted into the mechanical one is applied to each particle and its group.

With respect to a particle, assuming that the energy loss within a particle is negligible, we obtain from the energy conservation law

$$\int p' dv = \int \mu dn' \quad (30)$$

where dn' is the number of the exchanged ions under an external pressure p , p' the swelling pressure exerted by a particle and dv its volume change. Therefore, the chemical energy which the particles of the number of N receive is $N \int \mu dn'$. This is all consumed to generate the mechanical work including the swelling of each particle and friction loss. The absolute work done by the granule is expressed by $\int PdV$ (where P is the swelling pressure exerted by the granule). Friction loss A between the particles is regarded to be proportional to the absolute work developed by the granule. If we define a probability in which any movement of a particle is restricted by the friction, it is expressed as $\tan^{-1} \kappa / (\pi/2)$.

Thus we obtain

$$A = \tan^{-1} \kappa / (\pi/2) \times \int PdV \quad (31)$$

where κ is the coefficient of the friction. Hence, from the energy conservation law in the granule, we have

$$N \int \mu dn' = N \int p' dv = \left(1 + \frac{2 \tan^{-1} \kappa}{\pi} \right) \int PdV \quad (32)$$

Under the assumption that $p' = P = \text{constant}$, we can easily carry out the integration in Eq. (32). Then, we obtain

$$x^3 - 1 = \phi (\alpha'^3 - 1) / (1 + 2 \tan^{-1} \kappa / \pi) \quad (33)$$

It is clear from Eq. (33) that we have $x = \alpha'$ in the case of $\kappa = 0$ and $\phi = 1$ (that is, a single spherical gel) and $x < \alpha'$ in the case of $\kappa > 0$ and $\phi < 1$ (granulated). We have the effective mechanical work E as

$$E = p \cdot \frac{4}{3} \pi r_m^3 N \alpha^3 \gamma^3 (\alpha'^3 - 1) \left(1 + \frac{2 \tan^{-1} \kappa}{\pi} \right) \quad (34)$$

If we assume that p' is related to the volume change of a particle and that the cycle ①→②→③→④ is replaced by another cycle ①→②→③'→④ in Fig. 17, we have the formulation for p'

$$\begin{aligned} -p &= \frac{RT\nu_e}{V_m} (1/\beta - 1/\beta^3) \\ &= \frac{RT\nu_e}{V_m} \left\{ \left(\frac{\alpha}{\alpha'} \right) - \left(\frac{\alpha}{\alpha'} \right)^3 \right\} \quad (35) \end{aligned}$$

The absolute work $\int p' dv$ developed by a particle is

$$\begin{aligned} \int p' dv &= \int_1^{\alpha^3} \left[\frac{RT\nu_e}{V_m} \left\{ \left(\frac{\alpha}{\alpha'} \right)^3 - \left(\frac{\alpha}{\alpha'} \right) \right\} \right] V_m d\alpha'^3 \\ &= 3RT\nu_e \left\{ \alpha^3 \ln \alpha - \frac{1}{2} \alpha (\alpha^2 - 1) \right\} \quad (36) \end{aligned}$$

In addition, we assume the following approximation

$$\Delta n' = \Delta n (1 - p/p_\infty) \quad (37)$$

where p_∞ is defined as the external pressure to balance the swelling.

Then, we have

$$\begin{aligned} 3\nu_e \left\{ \alpha^3 \ln \alpha - \frac{1}{2} \alpha (\alpha^2 - 1) \right\} &= -gn \ln C_i, \\ 3\nu_e \left\{ \alpha^3 \ln \alpha' - \frac{1}{2} \alpha (\alpha'^2 - 1) \right\} \\ &= -gn \ln C_i \times \left(1 - \frac{p}{p_\infty} \right) \quad (38) \end{aligned}$$

Using Eq. (38), we can calculate the equilibrium

Fig. 17

swelling α' under the external pressure p .

Figures 18 and 19 show two calculated mechanical works. One (solid line) is obtained from the mechanochemical cycle in which α' is α_1' , while another (dotted line) is calculated based on Eq. (38) in which α' is α_2' . The work E calculated from Eq. (29) is E_1 , and that from Eq. (34) is E_2 , where $N=10^6$, $r_m=0.01$ cm and $\phi=65\%$.

Remarks:

(1) The real mechanical work must lie between the values corresponding to α_1' and α_2' because the former overestimates the degree of swelling while the latter may underestimate it under a large external pressure.

(2) E_2 may be closer to the real work in an actual system than E_1 . The particle movement and the frictional loss are included in E_2 .

(3) The possible maximum pressure to be generated would be larger than 1000 atms.

(4) The maximum work is found to be about 6 kgcm in the case of 6N HCl for $N=10^6$ and at 5~10 atms.

6. The studies on the mechanical work developed by the granuls in a cylinder

A piston motion due to the swelling of the granule can possibly be utilized as an artificial muscle with one freedom, a press, a jack or process control elements with both a detector and an

Fig. 18 The mechanical work and pressure occurring in spherical granule mechanochemical materials (calculated)

Fig. 19 The mechanical works and pressures occurring in spherical granule mechanochemical materials (calculated)

operator such as the PH meter. Here, we present the theoretical and experimental treatments of the mechanical behaviors (elongation, work, etc) of a piston, which is to be called "a granule mechanochemical piston"⁽⁸⁾.

6.1 Theory

By the energy conservation law we have the following relation for the granule mechanochemical piston.

$$\begin{aligned} & \text{(The absolute work developed} \\ & \quad \text{by all the particles)} \\ & = \text{(the work consumed for the swelling} \\ & \quad \text{of particles)} \\ & + \text{(the effective mechanical work)} \\ & + \text{(the friction loss)} \dots\dots\dots (39) \end{aligned}$$

Each work and loss in Eq. (39) are denoted by E_1 , E_2 , E_3 and E_4 in order. Then, we have

$$E_1 = E_2 + E_3 + E_4 \dots\dots\dots (39)'$$

We define D =the diameter of a rigid cylinder with a bottom, r =radius of a particle before swelling, N =the number of particles, W =a, load, L =the height of the stacked granule in the cylinder before swelling and xL =the height of the granule after swelling. We also define that the granule consists of m layers perpendicular to the axis of the cylinder and that the initial thickness of each layer is dZ_k ($k=0, 1, 2, \dots, m$) and $\beta_k dZ_k$ after swelling. We denote p as the swelling pressure of the k -th layer in the axial direction and Δn_k as the number of effective gegen-ions which a particle receives from the external solution. As in the previous section, we have p_k and Δn_k

$$p_k = \frac{RT\nu_e}{V_m} \left\{ \left(\frac{\alpha}{\alpha_k'} \right)^3 - \left(\frac{\alpha}{\alpha_k'} \right) \right\},$$

$$\Delta n_k = n(1 - p/p_k).$$

From Eqs. (38) and (39), we obtain

$$\begin{aligned} E_1 &= \mu \sum_{k=0}^{m-1} \frac{N}{m} \Delta n_k \\ &= 3RT\nu_e \sum_{k=0}^{m-1} \frac{N}{m} \left[\alpha^3 \ln \alpha - \frac{\alpha}{2} (\alpha^2 - 1) \right] \\ & \quad \times (1 - p_k/p_\infty) \dots\dots\dots (40) \end{aligned}$$

We also obtain E_2 and E_3 as

$$\begin{aligned} E_2 &= \frac{N}{m} \sum_{k=0}^{m-1} \int p_k dV_k = \frac{NRT\nu_e}{m} \sum_{k=0}^{m-1} \left[\alpha^3 \ln \alpha_k'^3 \right. \\ & \quad \left. - \frac{3}{2} \alpha (\alpha_k'^2 - 1) \right] \dots\dots\dots (41) \end{aligned}$$

$$E_3 = W(x-1)L \dots\dots\dots (42)$$

where dV_k is the volume change of the k -th layer.

To obtain E_4 , we divide the friction losses into two parts, the friction loss ($E_{4,1}$) among the particles and the wall friction loss ($E_{4,2}$) between the cylinder wall and the particles. We obtain from Eq. (31),

$$\begin{aligned}
 E_{4,1} &= \frac{2 \tan^{-1} \kappa}{\pi} \frac{N}{m} \sum_{k=0}^{m-1} \int p_k dV_k \\
 &= \frac{2 \tan^{-1} \kappa}{\pi} \frac{NRT\nu_e}{m} \sum_{k=0}^{m-1} \left[\alpha^3 \ln \alpha_k'^3 - \frac{3}{2} \alpha (\alpha_k'^2 - 1) \right] \dots \dots \dots (43)
 \end{aligned}$$

The force tangential to the side wall (that is, $\mu \kappa p_k$ per unit area) must oppose the upward movement of the granule and $E_{4,2}$ must be proportional to the increasing wall area which contacts with the granule. Thus, we obtain $E_{4,2}$ as

$$\begin{aligned}
 E_{4,2} &= \mu \kappa \sum_{k=0}^{m-1} \int p_k dV_k' \\
 &= \mu \kappa \sum_{k=0}^{m-1} \int_1^{\beta_k'} \int_0^L \int_0^{Z_k/m} dZ_k' dZ_k \cdot \pi D p_k \cdot d\beta_k \\
 &= \frac{1}{2} \mu \kappa \pi D L (L/m) \sum_{k=0}^{m-1} \int_1^{\beta_k'} p_k d\beta_k \dots \dots \dots (44)
 \end{aligned}$$

where μ is the coefficient of friction between the particles and the cylinder wall.

Assuming that the packing factor ϕ is constant throughout swelling, we have $\beta_k = \alpha_k'^3$. Substituting it into Eq. (44), we obtain

$$\begin{aligned}
 E_{4,2} &= \frac{\pi}{2} \mu \kappa D L (L/m) \frac{RT\nu_e}{V_m} \sum_{k=0}^{m-1} \left[\alpha^3 \ln \alpha_k'^3 - \frac{3}{2} \alpha (\alpha_k'^2 - 1) \right] \dots \dots \dots (45)
 \end{aligned}$$

Arranging the relations described above, we have

$$\begin{aligned}
 &\frac{N}{m} RT\nu_e \left\{ \alpha^3 \ln \alpha^3 - \frac{3}{2} \alpha (\alpha^2 - 1) \right\} \sum_{k=0}^{m-1} \left[1 - \frac{RT\nu_e}{p_\infty V_m} \right. \\
 &\quad \times \left. \left\{ \left(\frac{\alpha}{\alpha_k'} \right)^3 - \frac{3}{2} \alpha (\alpha_k'^2 - 1) \right\} \right] \\
 &= W(x-1)L + \frac{N}{m} RT\nu_e \\
 &\quad \times \left\{ 1 + \frac{2 \tan^{-1} \kappa}{\pi} + 2\mu \kappa \left(\frac{L}{D} \right) \frac{1}{\phi} \right\} \\
 &\quad \times \sum_{k=0}^{m-1} \left\{ \alpha^3 \ln \alpha_k'^3 - \frac{3}{2} \alpha (\alpha_k'^2 - 1) \right\} \dots \dots \dots (46)
 \end{aligned}$$

There are m variables of α_k' in Eq. (46), which can not be solved with respect to α_k' . Assuming that $\alpha_k' = \alpha'$, we obtain

$$\begin{aligned}
 &\left\{ \alpha^3 \ln \alpha - \frac{1}{2} \alpha (\alpha^2 - 1) \right\} \left[1 - \frac{RT\nu_e}{p_\infty V_m} \right. \\
 &\quad \times \left. \left\{ \left(\frac{\alpha}{\alpha'} \right)^3 - \left(\frac{\alpha}{\alpha'} \right) \right\} \right] = \frac{W}{3NRT\nu_e} (\alpha'^3 - 1)L
 \end{aligned}$$

Fig. 20

(a) Equilibrium elongating for granule mechanochemical piston (calculated and experimental)

(b) Equilibrium elongating for granule mechanochemical piston (calculated and experimental)

(c) The mechanical work occurring granule mechanochemical piston (calculated and experimental)

Fig. 21

$$+ \left\{ 1 + \frac{2 \tan^{-1} \kappa}{\pi} + 2\mu\kappa \left(\frac{L}{D} \right) \frac{1}{\phi} \right\} \times \left\{ \alpha^3 \ln \alpha' - \frac{1}{2} \alpha (\alpha'^2 - 1) \right\} \dots \dots \dots (47)$$

Equation (47) is the expression which makes it possible to explain the behaviors of the piston. If we substitute the parameters W , L , D , N , ν_e and α into Eq. (47), we obtain the value of α' . The equilibrium elongation $x = \alpha'^3$, the displacement of the piston $\Delta L = (\alpha'^3 - 1)L$, the mechanical work $E = W(\alpha'^3 - 1)L$, and the averaged pressure in the axial direction $\bar{p} = \left(\frac{RT\nu_e}{V_m} \right) \left\{ \left(\frac{\alpha}{\alpha'} \right)^3 - \left(\frac{\alpha}{\alpha'} \right) \right\}$ are computed from the value of α' .

We define the height L of the swollen granule in the cylinder as the standard one. By substituting L/α'^3 for L into Eq. (47), we have

$$\left\{ \alpha^3 \ln \alpha' - \frac{1}{2} \alpha (\alpha'^2 - 1) \right\} \left[1 - \frac{RT\nu_e}{p_\infty V_m} \times \left\{ \left(\frac{\alpha}{\alpha'} \right)^3 - \left(\frac{\alpha}{\alpha'} \right) \right\} \right] = \frac{W}{3NRT\nu_e} \left(1 - \frac{1}{\alpha'^3} \right) L + \left\{ 1 + \frac{2 \tan^{-1} \kappa}{\pi} + 2\mu\kappa \left(\frac{L}{D} \right) \frac{1}{\alpha'^3} \frac{1}{\phi} \right\} \times \left\{ \alpha^3 \ln \alpha' - \frac{1}{2} \alpha (\alpha'^2 - 1) \right\} \dots \dots \dots (48)$$

$$x = \alpha'^3, \quad \Delta L = (1 - 1/\alpha'^3)L, \quad E = W \left(1 - \frac{1}{\alpha'^3} \right) L \dots \dots \dots (48)'$$

In the derivation of Eq. (47) or (48), the strain of the cylinder, the variation of the swelling pressure along the axis of the cylinder and the static compression of the granule due to the load are not considered.

6.2 Calculations and comparison with the experiments

Figures 21 (a), (b) and (c) show comparisons between the theoretical (solid line) based on Eqs. (48) and (48)' and the experimental results. The data employed are as follows: $D = L = 5$ cm, $N = 1.5 \times 10^7$, $\nu_e = 2.1 \times 10^{-9}$ mol, $V_m = 4.2 \times 10^{-6}$ cm³, $\phi = 65\%$, $\kappa = \mu = 0.1$, $RT = 24.6162 \times 10^3$ cm³ atm/mol and $p_\infty = 10^3$ atm. In the experiment, the cylinder is made of acrylic resin and its diameter D is 5 cm. Particles are nominal Dowex 50 W- $\times 2$, 80 gr (wet). The relation of α to the concentration of the solution used for calculation is given from the experimental results reported in Part 1⁽³⁾. The calculated values (solid line) fairly agree with the experimental (circles, etc).

Figures 22, 23 and 24 show the values calculated from Eqs. (48) and (48)'. The values of the parameters in the figures are the same as mentioned above. The calculations were performed by a digital computer.

Theoretical conclusions are as follows:

(1) The number of particles: Both the displacement and the work vary linearly with the number of particles (or exchanger quantity).

(2) The absolute temperature: The displacement and the work are proportional to the absolute temperature.

(3) α : Both the displacement and the work become larger with the value of α . The maximum value of α is 1.43 for Dowex 50 w- $\times 2$ with HCl (12 N).

(4) Coefficient of friction: The displacement increases as the coefficients of the inner and the surface friction of the granule are smaller.

(5) L/D : Larger values of L/D make the equilibrium elongation smaller, and when do the displacement and the work larger [at $L/D = 10 \sim 20$, both the displacement and the work show maximum values, as shown in Figs. 23 (b), (c)].

(6) ν_e : The lower degree of crosslinking is realized to make the equilibrium elongation, the displacement and the work larger as shown in Fig. 24 (a). The calculated (solid line) results agree with the experimental (circles) ones in Fig. 24 (b).

(7) ϕ : Both the equilibrium elongation and the displacement and the work are larger as the packing factor is larger.

(8) W : Both the equilibrium elongation and the displacement become smaller as the load W is larger. The value of the work reaches maximum under a much heavier load. The relation $W \propto NT\nu_e$ is established from Eq. (48).

(9) About the size and shape of the cylinder: From Eq. (48) we have the following relation.

Fig. 22 Elongation for granule mechanochemical piston (calculated)

That is, when other conditions are constant, the equilibrium elongation in the piston of diameter aD , with the particles of the number a^3N and with a load a^2W is equal to that in the piston of D , N and W .

(a) Equilibrium elongating and L/D for granule mechanochemical piston (calculated)

(b) Elongation and L/D for granule mechanochemical piston (calculated)

(c) The occurred work and L/D for granule mechanochemical piston (calculated)

Fig. 23

(10) Radius of particles: This is theoretically of no concern with elongation. An experimental result shown in Fig. 25 agrees nearly with the theoretical one.

Figure 26 shows comparisons of the calculated

(a) Elongation of the piston and degrees of crosslinking of particles (calculated)

(b) Equilibrium elongating for the piston and degrees of crosslinking for a particle (calculated and experimental)

Dowex 1 (80 g, 50~100 mesh)
 $D=5$ cm, $W=1.63$ kg

Fig. 24

Dowex 50W- $\times 4,160$ g
 $D=5$ cm, $W=0.9$ kg, HCl 3N

Fig. 25 Equilibrium elongating for the piston and the radius of particle (experimental)

Table 1

	Natural muscle ⁽⁷⁾	Filament	Particle	Spherical granule	Grannule mechanochemical piston
The converted force(maximum), divided by weight of substance* in each cm of filament [The converted pressure (maximum), divided by weight of substance each cm ³ of substance]	15~60 × 10 ³	12 × 10 ³ (Fig. 2. III) (6 × 10 ³) (Fig. 7)	200 × 10 ³ (Fig. 4)	200 × 10 ³	200 × 10 ³ More than 12 × 10 ³
The converted work per each g of substance (cal/g)*	45~20 × 10 ⁻²	1.3 × 10 ⁻² (Fig. 9) (0.7 × 10 ⁻²) (Fig. 11)	3~6 × 10 ⁻² (Fig. 12)	2~3 × 10 ⁻² (Fig. 19)	15.6 × 10 ⁻² [Fig. 23 (c)] More than 5 × 10 ⁻²

Fig. 26 The swelling pressures averaged about axis-direction (calculated and experimental)

Fig. 27 The variation of the swelling pressures with respect to axis-direction (calculated and experimental)

values (solid line) with the experimental ones about the mean swelling pressure $\bar{p}$ where the values of N and L are twice those as mentioned above. The experimental data ($\circ$ and $\times$ in Fig. 26) are obtained from the multiplication $1/\kappa$ of the values measured by a pressure detector set on the cylinder wall. Figure 27 shows comparison between the calculated (solid line) and the experimental (circles) results with respect to variation of the swelling pressure along the axis of the cylinder. Formula

* The linguistic expression in the table is partly rewritten as suggested by Dr. Yoji Umetani.

of $p(z)$ is obtained from the force balance in a layer after swelling as

$$p(z) = \frac{4\mu\kappa x L R T \nu_e}{V_m D} \left\{ \left(\frac{\alpha}{\alpha'} \right)^3 - \left(\frac{\alpha}{\alpha'} \right) \right\} \times \exp\left(\frac{4\mu\kappa z}{D}\right) / \left\{ \exp\left(\frac{4\mu\kappa}{D} x L\right) - 1 \right\} \\ = \frac{R T \nu_e}{V_m} \left\{ \left(\frac{\alpha}{\alpha_k'} \right)^3 - \left(\frac{\alpha}{\alpha_k'} \right) \right\} \quad \dots\dots\dots (49)$$

$$x = \frac{1}{m} \sum_{k=0}^{m-1} \alpha_k'^3 \quad \dots\dots\dots (50)$$

7. Conclusions

The displacement, the force (or the pressure) and the mechanical work developed by mechanochemical materials are now clear from this work. Several mechanical properties such as the decrease in swelling (or the contraction) due to an external force, energy transformation between the chemical energy and the mechanical energy, the efficiency of the work, the swelling pressure and the behaviors of the swelling particles are discussed here.

Table 1 shows comparison of the performances between the muscle and the mechanochemical materials (data in bracket are experimental results).

References

- (1) Mori, M., *Trans. Japan Soc. Mech. Engrs.* (in Japanese), Vol. 65, No. 517 (1962-2), p. 275.
- (2) Kuhn, W., et al, *Nature*, Vol. 65, No. 4 (1950-4), p. 514; Katchalsky, A., *Progress in Biophysics and Biophysical Chem*, Vol. 4 (1954), p. 1.
- (3) Tatara, Y., *Trans. Japan Soc. Mech. Engrs.* (in Japanese), Vol. 37, No. 297 (1970-5), p. 908.
- (4) Katchalsky, A. and Zwick, M., *Jour. Polymer Sci.*, Vol. 16 (1955), p. 221.
- (5) Tani, H., *Kohbunshi* (in Japanese), Vol. 1, No. 2 (1952), p. 16.
- (6) Treloar, L. R. G., *Trans. Faraday Soc.*, Vol. 39 (1943), p. 36; *ibid*, p. 241; Flory, P. J., *Principles of Polymer Chemistry*, (1967), Cornell Univ. Press, Ithaca, N. Y.
- (7) Wassermann, A., *Size and Shape Changes of Contractile Polymers*, (1960), Pergamon Press.
- (8) Matushima, S. and Mori, M., *Seisankenkyu*, (in Japanese), Vol. 15, No. 4 (1963), p. 96.

Discussions

T. NAGAO (University of Tokyo):

(1) Explain clearly about the physical meaning of equilibrium swelling α .

(2) It is written in 6 lines of left column p. 926 that the static compression of the granule due to the load is not considered. However, does this assumption become somewhat different from the actual system if a mechanochemical material changes its volume involved in the external pressure?

(3) In 3 lines of right column in p. 923, the probability that the movement of a particle is restricted owing to inner friction is expressed as $\tan^{-1}\kappa/(\pi/2)$. What consideration is this expression based on, especially isn't it necessary to use a solid angle about the problem?

Y. UMETANI (Tokyo Institute of Technology):

(4) In section 4.1, the conclusion that "The inverse conversion from the mechanical to the chemical energy can not always be realized in any process" is presented. Tell whether or not the inverse conversion is absolutely impossible, and in what cases, it is possible.

According to the thermodynamics of the irreversible process, it is true that the conjugate coupling between mechanical energy and chemical one can be realized; Moreover, there surely exists a process of the inverse conversion of chemical into mechanical energy under existence of the conversion of mechanical into chemical energy.

M. SENO (University of Tokyo):

(5) The free energy change based on a chemical reaction is given by $\sum \mu_i dn_i$ as shown in the present report, and the chemical potential can be divided into the enthalpy and the entropy term. Which term do you consider may be converted into the mechanical energy in the present system?

(6) I consider that the existence of a mechanism is necessary in order to convert the chemical energy into the mechanical energy. Show in general your consideration with respect to the mechanism for the present system, if any.

(7) Show what value has the efficiency of the energy conversion in the present system and what are the factors to control the efficiency.

Author's closure

(1) Equilibrium swelling α means a factor expressing the linear deformation of a gel by isotropic swelling or deswelling, i.e., $\alpha = (V/V_0)^{1/3}$

where V_0 and V are the volume of the gel before and after swelling respectively. That is, α is equal to $1+\epsilon$, where ϵ is strain. $0 < \alpha < 1$ means the contraction and $\alpha > 1$ means the swelling.

(2) The present experiments were carried out under a small load: In Fig. 21, $W=1\sim 2\text{kg}$, $D=5\text{cm}$, that is, $p_0=0.05\sim 0.1\text{kg/cm}^2$. In general, the pressure p decreases exponentially with an increase in the depth of the granule. Moreover, the volume change of a particle involved in the external pressure is comparatively small [from Eq. (14), $\beta=0.96$ under the external pressure 1kg/cm^2]. Thus, this assumption is not considered inappropriate. However, it is certain that the static compression can not ignored in the case of a heavy load.

The strain ϵ of the height L of the granule due to a load W is discussed as follows. We assume that a mere volume change in each particle is caused by a load, that the granule consists of k layers perpendicular to the axis of the cylinder and that k -th layer is dZ_k in thickness. Denoting by β_k the degree of the deswelling of each particle in k -th layer, applying the Janssen's equation to variation of the static pressure of the granule along the axial direction and using Eq. (3), we obtain

$$p(Z_k) = p_\infty + (p_0 - p_\infty) \exp\left(-\frac{4\mu\kappa}{D} Z_k\right),$$

$$p(Z_k) = -\left(\frac{RT\nu_c}{V_m}\right) \left(\frac{1}{\beta_k} - \frac{1}{\beta_k^3}\right)$$

where $p_0 = W / \left(\frac{\pi}{4} D^2\right)$, $p_\infty = D\gamma / 4\mu\kappa$, γ is the specific weight of granule, and V_m is the initial volume of a particle. Solving above equations and using the following relations

$$L = \sum dZ_k, \quad L' = (1-\epsilon)L = \sum \beta_k dZ_k$$

we have L' by substituting L' for L into Eq. (48).

(3) As shown in Append.-Fig. 1, with respect to two particles which contact each other, if we select a plane to contain both one direction where the swelling pressure acts and another one where a particle moves, representing $\pi/2 - \theta$ as the internal angle between the above two directions on the plane and assuming the specific weight of a particle negligibly small, we find that a sliding between the two particles does not occur, if $p \sin \theta \leq \kappa p \cos \theta$. On the other hand, assuming that θ is uniformly distributed between 0 and $\pi/2$ and defining $0 \leq \theta \leq \pi/2$ and $\theta_c = \tan^{-1}\kappa$, we find that a sliding between the two particles of $0 \leq \theta \leq \theta_c$ does not occur. Thus, we consider that

Append. Fig. 1

the probability in which the sliding between the two particles does not occur is $\tan^{-1} \kappa / (\pi/2)$.

(4) In Fig. 1, in the step ②→③ (or the step ④→①), Na ions (or H ions in the latter step) inside a gel can be turned out of the gel by application of the external force. The gel can contain a greater amount of Na ions through unloading. Thus, the conversion of the mechanical energy into the chemical one is realized in the above processes. However, in the step ③→④, it is impossible to receive Na ions again which have turned out of the gel and have been consumed to neutralize H ions. Therefore, we have made such conclusion.

The conjugate coupling (that is, $J_i = \sum L_{ij} X_j$, where X_j is force, J_i is flow and L_{ij} is phenomenological coefficient) is considered to be a hypothesis whereas it agrees well with many experiences. Though we can not know whether or not it may be applied to the material having the strong nonlinearity such as rubber or a mechanochemical material, it may be dangerous to judge the energy conversion of the present material from the theory.

(5) The logarithm term of the chemical potential is converted into the potential term of the mechanical energy. The osmotic pressure due to gegen-ions or others promotes the swelling. Thus, the entropy term contributes to the energy conversion to the mechanical energy.

(6) There have been found no materials which have the ability of direct conversion of the chemical energy into the mechanical one other than the muscle and mechanochemical materials. On the mechanism of the energy conversion of the former, there are the sources of occurrence of tension in the parts where a myosin filament and an actin one overlap, and the actin filament slides past the myosin one. This is well-known, but we have little idea what happens when the muscle develops a tension. On the mechanism of the latter, we understand it is the variation of the statistical distribution

of polymeric chains having the fixed ions. Judging the general mechanism from the above two examples, there must exist filaments or bridges having active sites where locking and unlocking are reversibly done (the fixed ions along the chains and gegen-ions are an example which we can now cite). However, we feel an essential gap between muscle and mechanochemical materials because the former has regular structures and chemical reactions with automatic mechanism while the latter has irregular structures and diffusion phenomena without automatic mechanism.

(7) Judging the general behaviors from mechanochemical material, as there is the chemical energy left or turned out without expenditure of the energy conversion, a kind of mechanical energy consumed in the size and shape changes of the material itself and heat loss, chemical energy subtracted from the above three energies are considered to be converted into the effective mechanical work. The efficiency of the work is 80 % at most, judging from Figs. 15 and 16.

The conditions to rule the efficiency are drawn as follows.

(i) The value of load (external force): A value of the load makes the efficiency the highest, from Figs. 15 and 16. The chemical energy is, in the case of low efficiency, spent on the volume change of the material.

(ii) The types of the molecular movements: The efficiency is influenced by the problems whether or not the direction in which each molecule moves agree with the direction of macroscopic material movement. On the mechanochemical materials, the reason why the efficiency is found from Figs. 15 and 16 to be better in a particle than in a film is as shown in the above-mentioned discussion.

(iii) The recovery of the used solution: In the case of the present material, from Eq. (24), the efficiency becomes about 10 % of the data in Fig. 15. The re-use of the used solution is not done in the real experiments shown in Fig. 15. In the muscle, there is expected an ingenious mechanism where the re-use of the solution or ions is realized.

(iv) The quantity of solution or ions, the concentration of solution, the number of the fixed ionic groups and temperature may be expected to be the factors of the efficiency.