

Effects of mechanical softening and hardening of porous polymer films in solvents

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The Grosberg–Khokhlov theory was used to describe the mechanical properties of porous polymer films in good solvents. It is shown, as in the well-known Flory’s theory of polymer solutions, the swelling of films and the involvement of solvent in them makes it possible to detect effects of mechanical softening and hardening of films. In both theories, similar dependences of the Poisson’s ratio on the Flory–Huggins interaction parameter are obtained. These dependences make it possible to select an ideal (θ) solvent in which the Young’s modulus of the film is the same or greater than for a dry film.

Keywords: 2-nd virial approximation, polymer porous film, swelling, Young’s modulus, θ -solvent, poroelastic effect, lithium-ion batteries.

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The mechanical stability of polymer components can play an important role in the long-term performance of various devices [1], such as porous film separators in lithium-ion batteries (LIBs). In papers [2,3], experimental measurements of the thickness and modulus of elasticity of polypropylene (PP) separator films showed that a change in the Young’s modulus of the separator in good solvents can be associated with swelling of the films [2], and explained these results based on a careful analysis of the Hildebrand and Flory–Huggins parameters [3]. However, it was founded that on the one hand, certain solvents, such as dimethyl and diethyl carbonate and ethyl acetate, cause a noticeable decrease in the mechanical properties (i.e. softening) of the separator. On the other hand, the authors of the papers [2,3] can not explain why in other solvents, such as propylene carbonate and acetonitrile, the separator retained the mechanical properties of the dry film or even improved them, i.e. the so-called poroelastic effect occurred [4]. To explain these results, in this paper, in the 2nd virial approximation, a phenomenological theory of elasticity of porous polymer films in solvents will be developed.

The simplest physical model of swelling of non-porous polymers under the influence of solvents is the model of Gaussian subchains „beads on a string“ [5], which can be described by the Flory equation for the swelling coefficient $\alpha \equiv R/N^{0.5}a$, where N — the number of subchains in the chain, and the parameters a and R — the root-mean-square distances between adjacent beads and the ends of the chain. In this model, the free energy of swollen film containing n polymer chains (coils) characterized by root-mean-square sizes R has the form [5]:

$$F \equiv \frac{3kTn}{2} \left[\frac{R^2}{Na^2} + \frac{Na^2}{R^2} + \frac{BN^2}{2\pi R^3} \right]. \quad (1)$$

In formula (1) T — absolute temperature, B — second virial coefficient, the first and second terms characterize the entropy elasticity of the film during its tension and compression, respectively, and the third term is associated with a change in the concentration of chains in its volume.

We believe that for porous swollen polymer films, as well as for lattice systems, sufficiently large sections of chains (subchains) are deformed equally along with the film sample itself, i.e., if before deformation the distance vector between the ends of the chain is \mathbf{R}_1 has coordinates $\{R_{1x}, R_{1y}, R_{1z}\}$, then after deformation its coordinates are determined as

$$R_{2x} = \lambda_x R_{1x}, \quad R_{2y} = \lambda_y R_{1y}, \quad R_{2z} = \lambda_z R_{1z}, \quad (2)$$

where $\lambda_x, \lambda_y, \lambda_z$ — absolute film deformations in the directions x, y and z , respectively.

However, in contrast to lattice systems, during deformation of which their volume remains unchanged ($V_2 = V_1$) [5], when deforming samples of porous polymer films, it can change ($V_2 \neq V_1$). The anisotropy of relative deformations of the film in its various directions is characterized by Poisson’s ratio

$$\mu = -(\lambda_x - 1)/(\lambda_z - 1), \quad (0 \leq \mu \leq 0.5).$$

For uniaxial compression of a polymer film sample (along the axis z), the coefficients in relations (2) have the form: $\lambda_x = \lambda_y = 1 - \mu(\lambda - 1) > 1$, where $\lambda = \lambda_z < 1$. At such deformation change of its free energy $\Delta F \equiv F(R_2) - F(R_1)$ in Grosberg–Khokhlov theory [5] is defined as

$$\Delta F = \frac{3kTn}{2} \left[\frac{1}{Na^2} (R_2^2 - R_1^2) + \frac{Na^2}{R^2} \left(\frac{1}{R_2^2} - \frac{1}{R_1^2} \right) + \frac{BN^2}{2\pi} \left(\frac{1}{R_2^3} - \frac{1}{R_1^3} \right) \right]. \quad (3)$$

In formula (3) R_1 and R_2 — the dimensions of the chain before and after compression, respectively, and the number of subchains $n = \nu V$ in the film sample during its deformation is assumed to be an invariant quantity, i.e. $\nu_1 V_1 = \nu_2 V_2 = \nu_0 V_0$, where $\nu_0 = n/V_0$ — number of chains per unit volume of dry, unswollen film, $V_1 = \alpha^3 V_0$ and V_0 — volumes of swollen and dry film, respectively.

The change in free energy (3) and the equation of state in the Grosberg–Khokhlov theory [5] for the film swelling coefficient α allow us to calculate the dependence of the strain σ on strain ε of the swollen film (along the axis z) according to the formula $\sigma = (1/V_1)\partial\Delta F/\partial\varepsilon$. We obtain

$$\sigma = \frac{\sigma_0}{\alpha^3} A(\varepsilon, \mu) \left[\alpha^2 \left(1 - \frac{1}{C^{2.5}(\varepsilon, \mu)} \right) - \frac{1}{\alpha^2} \left(\frac{1}{C^2(\varepsilon\mu)} - \frac{1}{C^{2.5}(\varepsilon, \mu)} \right) \right], \quad (4)$$

where functions

$$C(\varepsilon, \mu) = [(1 + \varepsilon)^2 + 2(1 - \mu\varepsilon)^2]/3 \\ = 1 + [2\varepsilon(1 - 2\mu) + \varepsilon^2(1 + 2\mu^2)]/3$$

$$A(\varepsilon, \mu) = \frac{3}{2} \frac{dC(\varepsilon, \mu)}{d\varepsilon} = 1 - 2\mu + \varepsilon(1 + 2\mu^2),$$

and the parameter $\sigma_0 = kT\nu_0$.

So, Young’s modulus of the film in the solvent is permanent, and it is equal to

$$E(\alpha) = \frac{E_0(\mu)}{\alpha^3} \left(5\alpha^2 - \frac{1}{\alpha^2} \right), \quad \alpha \geq 1/\sqrt[4]{5} \approx 0.669. \quad (5)$$

In formula (5) function $E_0(\mu) = \frac{5}{3}\sigma_0(1 - 2\mu)^2$. For dry, non-porous PP film with polycrystalline structure $\mu = 0.3$, the swelling coefficient $\alpha = 1$, and the Young’s modulus $E(1) = 4E_0(\mu)$, which leads to the value $\sigma_0 = 3E_0/8 = 92.63$ MPa. Maximum value of Young’s modulus

$$E_m = 0.8E_0 \approx 1.33\sigma_0(1 - 2\mu)^2$$

is realized at $\alpha = 1$ (Figure 1), which corresponds to dry film or film in θ -solvent. The value E_m decreases monotonically with increase in Poisson’s ratio μ from the values $E_0 = 1.33\sigma_0$ (at $\mu = 0$) respectively to zero (at $\mu = 0.5$).

In the region $\alpha > \alpha_{m1}$ in both theories, the Young’s modulus E monotonically decreases to zero with increase in degree of swelling α (Figure 1) according to the same asymptotic law $5\sigma_0(1 - 2\mu)^2/3\alpha$, i.e. the sample softens, which qualitatively confirms the experimental data [2,3]. In Grosberg–Khokhlov theory the Young’s modulus of swollen film ($\alpha > 1$) is always less than the Young’s modulus of dry film ($\alpha = 1$), and the effect of hardening of porous polymer films (poroelastic effect) is not possible in any good solvents.

However, in Flory’s theory in the region $1 < \alpha < \alpha_{m1}$, i.e. for solvents close to Θ -solvents, Young’s modulus

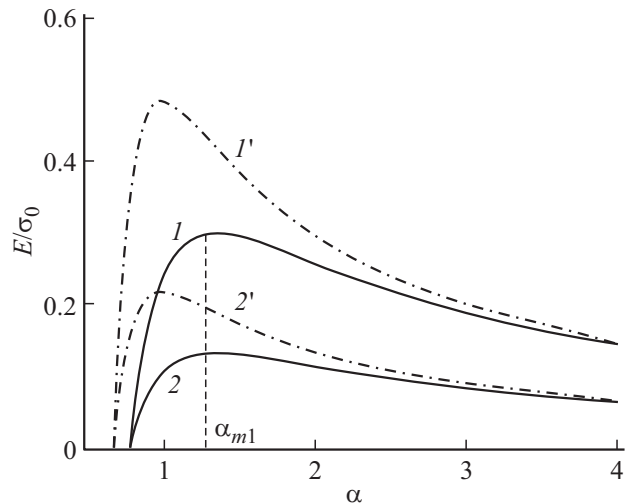


Figure 1. Shown Young’s modulus E/σ_0 vs. swelling coefficient α in theory of Flory (1, 2) and Grosberg–Khokhlov (1', 2') at $\mu = 0.2$ (1, 1'), 0.3 (2, 2'). In the region ($1 < \alpha < \alpha_{m1}$) in Flory theory, a poroelastic effect is possible ($\alpha_{m1} \sim 1.342$).

even increases, i.e. there is poroelastic effect predicted by modeling [4], in which in some solvents (propylene carbonate and acetonitrile) the same separator retains or even improves its mechanical properties due to the displacement of the solvent from the porous polymer film.

The dependences of the Young’s modulus in the Grosberg–Khokhlov and Flory theories slowly decrease with swelling increasing, and therefore do not quantitatively explain the experimental values of the Young’s modulus measured in papers [2,3], where it is shown that even a slight swelling (within the limits 1.04) of porous PP films in most good solvents leads to a noticeable change, a decrease (by 50%) in the Young’s modulus and a noticeable softening.

Therefore, the authors assume that swelling of the film leads to change in its structure, which means that the Poisson’s ratio μ of the film in both theories depends on the Flory–Huggins interaction parameter χ . These dependences can be obtained semi-empirically by substituting into the left side of equation (5) the experimental values of the Young’s modulus measured for solvents with a known value of the parameter χ , and from the right side — calculating the values μ . Dependences $\mu(\chi)$ obtained in this way are presented in Figure 2.

It can be seen that at small values of $\chi < 0.6$ the Poisson’s ratio μ of the film increases monotonically. This means that the proportion of solvent involved in the film also increases, which leads to its noticeable „softening“. And only starting from pentane (at $\chi > 0.6$) the dependences $\mu(\chi)$ decrease monotonically. For an ideal (θ -) solvent, in which there is no swelling ($\alpha = 1$), the values are $\chi_\theta = 2.25$ (in the Flory theory [6]) and $\chi_\theta = 2.39$ (in the Grosberg–Khokhlov theory [7]). Therefore, the intersection point of the dependence $\mu(\chi)$ with the vertical line $\chi = \chi_\theta$

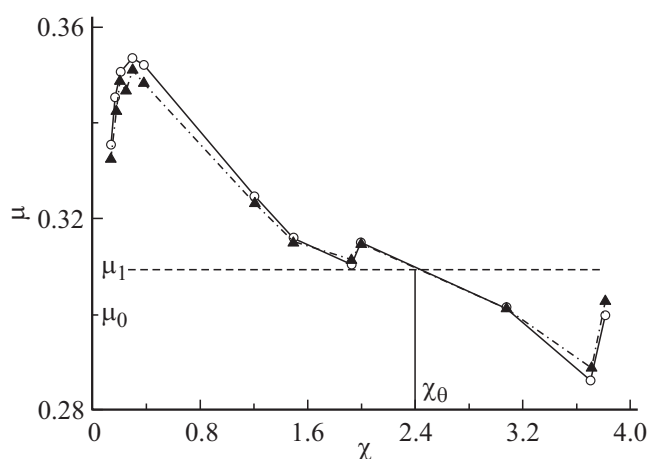


Figure 2. Semi-empirical dependences of Poisson's ratio on the Flory–Huggins interaction parameter χ ; in the Flory (\circ) and Grosberg–Khokhlova (\blacktriangle) theories.

makes it possible to clarify the value of Poisson's ratio, already for dry porous PP film: $\mu_1 = 0.31$ (remember that for dry non-porous PP film $\mu_0 = 0.3$). The values range of parameter χ for solvents in which poroelastic effect is possible, and film hardening occurs corresponds to points that lie below the straight line $\mu = 0.31$. For PP films, these solvents are acetonitrile ($\chi = 3.07$) and propylene carbonate ($\chi = 3.7$).

The results confirm the weak correlation between the swelling of PP separator films and the decrease in their modulus of elasticity in most good solvents, which was discovered experimentally [2,3]. It was shown that the main reason for film softening is not the film swelling, but the solvent entrainment into the separator. Joint consideration of these effects made it possible to agree the experimental values of the Young's modulus with theoretical calculations, both in the Grosberg–Khokhlov theory and in Flory theory, and to propose the method for selecting an ideal solvent in which its Young's modulus is the same or greater than for dry film.

Conflict of interest

The authors declare that they have no conflict of interest.

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