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# Using two scaling exponents to describe the mechanical properties of swollen elastomers

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ABSTRACT

We study the ability of two scaling exponents to describe the mechanical properties of swollen elastomers. Swelling effects on the Young's modulus and osmotic pressure of swollen elastomers at equilibrium swelling are investigated using literature data and the Flory–Rehner free energy function. An extended model is developed by introducing two scaling exponents into elastic strain energy functions that are separated into deviatoric and volumetric components. This extended model satisfactorily reproduces the two different swelling effects, and also predicts swelling-induced rupture. The predicted tendency readily explains experimental observations well, i.e., swelling-induced rupture occurs when small extensions are applied in good solvents, and elucidates the mechanism of swelling-induced rupture of elastomers.



## 1. Introduction

The Flory–Rehner (F–R) model (1943) is a well-known fundamental free energy function used to describe the mechanical and swelling behavior of elastomers (Flory, 1953; Treloar, 1975). The F–R model combines two free energies associated with polymer stretching and the mixing of polymer and solvent molecules that are derived from the Gaussian network theory (i.e., a neo-Hookean type model) and the Flory–Huggins solution theory, respectively. The interactions of elasticity and mixing are analyzed by examining the equilibrium states of stress and chemical potential. Flory and Rehner (1944), Gee (1946) and Treloar (1950) investigated the volume swelling ratio at equilibrium swelling in the stress-free state (i.e., free swelling) and in the presence of a homogeneous stress or strain; e.g., uniaxial tension and compression. They showed that the F–R model can satisfactorily describe homogeneous swelling of unstrained and strained rubbers.

Recently, Hong et al. (2009) and Kang and Huang (2010a) showed that the boundary value problem of swollen elastomers is equivalent to that of a hyperelastic solid. To analyze the inhomogeneous equilibrium swelling of elastomers subjected to mechanical loads and geometrical constraints, they implemented the F–R model into the finite element software Abaqus using the user-defined material subroutine UHYPER or UMAT. The UMAT subroutine was used to study swelling induced surface instability of hydrogel films (Kang and Huang, 2010b; Wu et al., 2013). The UHYPER subroutine was used to analyze swelling-induced buckling patterns in polymeric films with a square lattice of holes (Hong et al., 2009; Ding et al., 2013; Okumura et al., 2014), elucidating the mechanism of the homogeneous transformation into diamond plate patterns, and the effect of prestrains on the resulting buckling patterns (Okumura et al., 2015a, 2015b). Thus, the F–R model provides

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a basis to interpret the mechanical behavior of swollen elastomers, but it is not free from criticism, as detailed below.

When swollen elastomers are subjected to uniaxial loading, neo-Hookean type models predict that $E=E_d J^{-1/3}$ and $\sigma_r=E_d/3$, where $E_d$ and $E$ are the Young's moduli of the dry and swollen state, respectively, $J$ is the volume swelling ratio, and $\sigma_r$ is a transformed stress referred to as the swelling reduced stress (Han et al., 1999; Boyce and Arruda, 2001). For neo-Hookean type models, $E$ is proportional to $J^{-1/3}$ and $\sigma_r$ is a constant. However, as reported in the literature (Boyce and Arruda, 2001; McKenna et al., 1989; Bitoh et al., 2010), $E=E_d J^l$ has various values of $l$ depending on the elastomer, and $\sigma_r$ is not constant but a function of $J$, and, especially under tension, $\sigma_r$ is also affected by the stretch in the loading direction. To capture these features of the stress–stretch relation of dry and swollen elastomers, Flory and Erman (1982) proposed the constrained chain model in which a neo-Hookean model was modified by adding terms to describe constrained chains. Although these additional material parameters have a physical meaning in their study, McKenna and Hinkley (1986) reported that the values fitted based on experimental data are not physically rational. Drozdov and Christiansen (2013a, 2013b) derived an equivalent expression of the constrained chain model using stretch invariants, and developed extended models by including phenomenological parameters to correctly predict the mechanical response of hydrogels under multiaxial deformation. Generally, the advanced models involve complicated strain energy functions with additional phenomenological parameters. When the parameters are fitted to a particular set of mechanical responses, there may be no guarantee that other responses can also be successfully predicted using the same parameters.

McKenna and Hinkley (1986) used the Valanis–Landel strain energy function to demonstrate that the set of parameters determined from torsional tests of dry polybutadiene networks was not able to provide a sufficient elastic contribution to the chemical potential (called the osmotic pressure in the present study) under free swelling in benzene without inserting the volumetric term $a \log J$ into the energy function and using $a$ as a fitting parameter. To avoid adding a volumetric term, their group presumed that the Flory–Huggins interaction parameter is not just a constant associated with uncrosslinked polymer solutions, but is a linear function of the crosslink density (McKenna et al., 1990; Xu et al., 2013). Horkay et al. (1989) also reached a similar conclusion using the F–R model for swollen poly(vinyl acetate) networks in toluene or acetone. However, if it is generally assumed that the Flory–Huggins interaction parameter is independent of the crosslink density (Flory, 1953; Treloar, 1975), the strain energy function needs to be extended to solve the discrepancy between mechanical and swelling properties.

Bastide et al. (1981) and Durning and Morman (1993) developed a scaling approach to simply adjust the elastic contributions of swollen elastomers. Durning and Morman (1993) presumed that $E_d$ evolved in proportion to $J^m$ with a constant scaling exponent $m$ in the F–R model. This simple extension is effective to directly adjust the effect of swelling on elastic properties. In their scaling approach, one scaling exponent has to be used to scale different elastic contributions to swelling, such as the volume swelling ratio under free swelling and the Young's modulus at equilibrium swelling. In the former case, the scaling exponent scales the osmotic pressure at equilibrium swelling, i.e., the volumetric part of the strain energy function is scaled, while, in the latter, the deviatoric part is scaled. This scaling approach implicitly adjusts different elastic contributions using one scaling exponent. However, this may not be correct because such a scaling approach is phenomenological. Therefore, if two scaling exponents can be introduced to adjust both the volumetric and deviatoric elastic contributions, these exponents may successfully account for specific mechanisms that determine the mechanical behavior of swollen elastomers. It is therefore worthwhile to develop an extended model with two scaling exponents, and investigate how two scaling exponents influence the predicted mechanical and swelling behavior of elastomers.

In this study, we investigate the ability of two scaling exponents to describe the mechanical properties of swollen elastomers. Section 2 presents the fundamental relations derived from the F–R model, while Section 3 compares the F–R model with literature data and discusses the swelling dependence of the Young's modulus and osmotic pressure at equilibrium swelling. In Section 4, an extended model with two scaling exponents, which successfully predict the above-mentioned dependence, is developed. In Section 5, the effects of the two scaling exponents on the mechanical and swelling behavior of elastomers under uniaxial loading subsequent to free swelling are investigated. The extended model predicts that swelling-induced rupture can occur, which is experimentally observed when small extensions are applied in good solvents. Parametric studies are used to elucidate the mechanism of swelling-induced rupture. Finally, conclusions are presented in Section 6.

## 2. Relations derived from F–R model

Flory and Rehner (1943) presumed that to describe the mechanical and swelling behavior of elastomers, the free energy function is expressed as the sum of two free energies associated with polymer stretching and the mixing of polymer and solvent molecules, which are derived from the Gaussian network theory and the Flory–Huggins solution theory, respectively; i.e.,

$$W = W_e + W_m = \frac{E_d}{6}(I - 3 - a \log J) - \frac{kT}{\upsilon}\left\{ \upsilon C \log\left(1 + \frac{1}{\upsilon C}\right) + \frac{\chi}{1 + \upsilon C}\right\}. \tag{1}$$

Here, $W_e$ is the elastic strain energy and has a neo-Hookean form, where $I$ and $J$ are invariants, $I=F_{ij}F_{ij}$ and $J=\det \boldsymbol{F}$ with the deformation gradient $F_{ij}$, while $I=\lambda_1^2+\lambda_2^2+\lambda_3^2$ and $J=\lambda_1\lambda_2\lambda_3$ using the principal stretches $\lambda_i$. Moreover, $E_d$ is the Young's