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Elasticity of Swollen Polyvinyl Alcohol and Poly(Vinyl Acetate) Networks

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SUMMARY

In this paper we report on a series of unidirectional compression measurements carried out on chemically cross-linked polyvinyl alcohol (PVA) and poly(vinyl acetate) (PVAc) networks. The influence of the molecular mass and the molecular mass distribution of the primary chains on the mechanical properties has been studied. The PVAc gels were prepared by total acetylation of the PVA gels without producing changes in the network topology (topo-analogous transformation) (NAGY et al. 1978) . The comparison between the mechanical behaviour of PVA and PVAc gels enables us to make a more detailed analysis of the molecular parameters relevant to the network structure.

INTRODUCTION

The aim of the present paper is to discuss the effects of different factors (e.g. the molecular mass and molecular mass distribution of the primary chains, the swelling ratio, the topo-analogous transformation) on the mechanical properties of swollen PVA and PVAc gels.

EXPERIMENTAL

Materials and methods

PVA samples I to V with narrow molecular mass distribution were prepared by fractionation of a hydrolised Poval 420 (Kuraray Co., Japan) product. Polydisperse samples were prepared by mixing different amount of fractions I and V. Cylindrical network specimens of equal height and diameter were obtained at 298 K. Crosslinking was performed in PVA solutions (9.0 w%, pH=1.5) with different quantities of glutaric aldehyde (GDA). The gel specimens were dialysed in order to remove traces of ions. Finally the PVA gels were swollen in destilled water to the equilibrium state at 298 K. Some characteristics of the fractionated polymer samples, the mixtures and the gels prepared from them are summarized in Table 1 and 2, respectively.

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TABLE 1

Properties of the fractionated PVA samples

Sample	$\bar{M}_w$	$[\eta]_{303\,K}$	DC			
I	22300	0.26	50	100	200	
II	52600	0.45	50	100	200	
III	102700	0.70	50	100	200	400
IV	139600	0.84	50	100	200	400
V	345500	1.50	50	100	200	400

DC means the moles of monomer units per one mole of cross-linking agent.

TABLE 2

Properties of the polydisperse PVA samples

Sample	$\bar{M}_n$	$\bar{M}_w$	$\left(\bar{M}_w/\bar{M}_n\right)-1$	DC			
PD I	25800	69500	1.69	50	100	200	
PD II	41900	184000	3.39	50	100	200	400
PD III	110900	298300	1.69	50	100	200	400

Both fractionated and polydisperse PVA samples were subjected to acetylation in a mixture of pyridine-acetic acid-acetic anhydride, at 363 K 8 hours through. After this procedure the acetate content was 98-99 percent of the theoretical value. Preceding the experiments the PVAc networks were swollen in acetone and in toluene, respectively.

Unidirectional compression

Unidirectional compression measurements were carried out at 298 K, by means of an apparatus which allowed to measure stress-strain relations over a wide range of force and deformation (from 0.0001 N to 2.0 N and from 0.006 mm to 3.333 mm) with high accuracy (±0.0001 N and ±0.006 mm) (HORKAY et al. 1980).

Force-deformation functions were determined at the state of equilibrium swelling in the pure solvent and at different solvent activities. The solvent activity in the gel was decreased by a modified deswelling method developed by us (NAGY and HORKAY 1980).

The absence of volume changes and barrel-distortion phenomena was checked by studying the shape of the deformed gel cylinders.

RESULTS AND DISCUSSION

For evaluation of the compression measurements we applied the

$$f = 2C_1\left(\Lambda_x - \Lambda_x^{-2}\right) + 2C_2\left(\Lambda_x - \Lambda_x^{-2}\right)\Lambda_x^{-1} \qquad (1)$$

relationship, where f is the force of retraction at compression ratio $\Lambda_x = L_x/L_{ox}$, C_1 and C_2 are constants. Under the experimental conditions used here, we found the term C_2 equal to zero.

Based on statistical thermodynamical calculations, the force is also related to the corresponding deformation ratio by the following equation

$$f = \frac{RTA\nu_{el}^{*}\, q_o^{-2/3}\; q_i^{2/3}\; V_d}{L_{ox}} \left[\Lambda_x - \frac{q}{q_i} \Lambda_x^{-2} \right] \qquad (2)$$

where A is the front factor, ν_{el}^{*} the moles of the elastically effective chains in unit volume of the dry gel, V_d the volume of the dry gel and L_{ox} the initial length of the sample. q_i and q symbols the equilibrium swelling degree before and after the deformation, respectively. q_o is the so-called reference degree of swelling defined by the equation $q_o^{2/3} = \langle r^2 \rangle_{os} / \langle r^2 \rangle_d$, where $\langle r^2 \rangle_{os}$ and $\langle r^2 \rangle_d$ are the mean square end-to-end distances of the elastic chains in the swollen reference state and in the dry network, respectively (DUŠEK and PRINS 1969).

In the case of deformation at constant volume ($q=q_i$) the $2C_1$ term of Eq.(1) equals to $RTA\nu_{el}^{*}\, q_o^{-2/3}\, q_i^{2/3}\, V_d\, L_{ox}^{-1}$.

The influence of the average molecular mass of the primary polymer chains

In order to study the effect of the average molecular mass of the chains on the mechanical properties a series of gels were prepared at the same fraction of GDA.

Figure 1 shows a noticeable increase of the cross-linking efficiency ($2C_1/c_{GDA}$) with the rising molecular mass of the primary chains. The smaller the molecular mass, the effect is more pronounced. (The c_{GDA} values were calculated by substracting the quantity of the cross-linking agent used below the gel point from the total amount added to the system.)

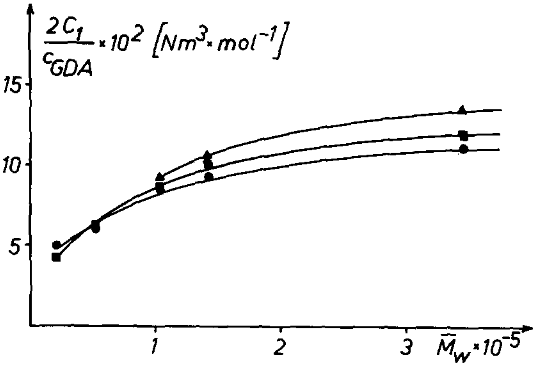

Fig. 1. The effect of the primary molecular mass on the efficiency of the cross-linking process.
DC: 100 ●, 200 ■, 400 ▲

To interpret this finding it is to be supposed that with increasing molecular mass the distribution of the segments becomes more homogenous throughout the system. It is well-known that the crystallinity of a PVA sample depends on many factors, including the degree of polymerization. In the solutions of low molecular mass samples the non-random segment density distribution may cause the decreasing of the efficiency of the cross-linking process.

The effect of the swelling ratio on the elastic modulus

An attempt has been made to check the constancy of the term $A\nu_{el}^{*} q_o^{-2/3}$ of Eq.(2) through a wide range of polymer concentration. By means of the ideal network theory $A\nu_{el}^{*} q_o^{-2/3}$ can be treated as a constant. In Fig. 2 the $A\nu_{el}^{*} q_o^{-2/3}$ values for PVA and PVAc gels are plotted against the volume fraction of the polymer ($v_2 = q_i^{-1}$).

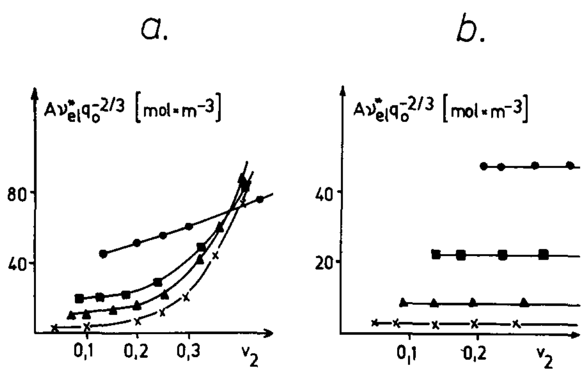

Fig. 2. $A\nu_{el}^{*} q_o^{-2/3}$ - v_2 functions
a. PVA in water, b. PVAc in toluene
DC: 50 ●, 100 ■, 200 ▲, 400 ×

In the case of PVA-water systems a very significant increase of $A\nu_{el}^{*} q_o^{-2/3}$ can be detected when the volume fraction increases. This phenomenon, not observed previously, may be assigned to crystallization induced by deswelling of the gels. Decreasing the swelling ratio X-ray diffraction measurements show (Fig. 3) the increasing crystallinity of the gels.

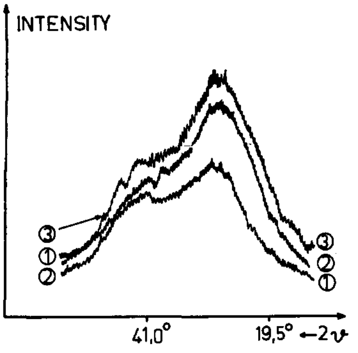

Fig. 3. X-ray diffractometer scans for PVA gels.
1. $v_2=0.065$, 2. $v_2=0.190$, 3. $v_2=0.273$

In order to eliminate the effect of crystallization the $A\nu_{el}^{*}q_{o}^{-2/3}$ values for the PVA gels were determined by extrapolating the curves to $v_2=0$.

In the case of PVAc gels the $A\nu_{el}^{*}q_{o}^{-2/3}$ values do not change in the whole concentration renge studied.

Molecular parameters of the network structure

In Fig. 4 the $A\nu_{el}^{*}q_{o}^{-2/3}$ values for the PVA gels are plotted against the concentration of the elastically active network chains calculated on the basis of Flory's equation

$$\nu_{el}^{*} = \nu^{*}\left[1 - \frac{2\,d_2}{\nu^{*}\bar{M}_n}\right] \qquad (3)$$

where ν^{*} is the concentration of network chains per unit dry volume of the gel, $\bar{M}_n$ is the number average molecular mass of the polymer chains in the solution and d_2 is the density of the dry polymer.

The straight lines found lead to the conclusion that the topological factor, $Aq_o^{-2/3}$, does not depend on the cross-linking density. The $Aq_o^{-2/3}$ values, determined from the slope of these lines, are summarized in Table 3.

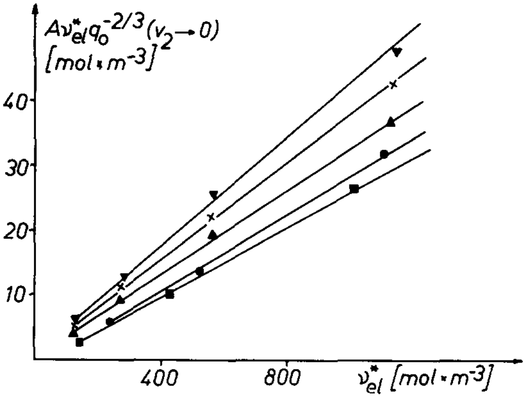

Fig. 4. Determination of the topological factor $Aq_o^{-2/3}$
Samples: I ■ ,II ● ,III ▲ ,IV × ,V ▼

It can be seen the deviation between the experimental and theoretical data is considerable.

In addition, data given in Table 3 show, that the $Aq_o^{-2/3}$ values of the gels obtained by cross-linking the polydisperse polymers are between that of the cross-linked monodisperse systems.

Thus we can conclude that the elastic modulus is particularly determined by the quantity of the elastically active chains and the amount of the terminal chains has no significant role in the change of Helmholtz-energy accompanied by the deformation of the networks.

TABLE 3

Molecular parameters of PVA gels

Sample	$Aq_o^{-2/3}$	$A\ (q_o = q_c)$	$q_o\ (A=1)$	$q_o\ (A=0.5)$
I	0.028	0.161	213.4	75.5
II	0.030	0.173	192.5	68.0
III	0.033	0.190	166.8	58.9
IV	0.038	0.219	135.0	47.7
V	0.043	0.248	112.1	39.7
PD I	0.031	0.179	183.2	64.8
PD II	0.034	0.196	159.5	56.4
PD III	0.036	0.207	146.4	51.8

q_c: the volume degree of swelling at the stage of cross-linking

The effect of the topo-analogous transformation on the molecular parameters

Let us examine the change of the $A\nu^*_{el}\, q_o^{-2/3}$ values with the topo-analogous transformation of the gels. In Fig. 5 the experimental relationship for PVA-water and PVAc-acetone systems is presented. All the points are on a straight line with a slope of 1.3.

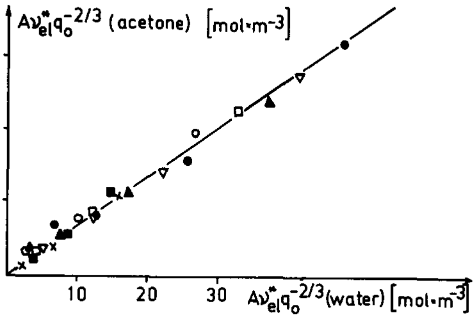

Fig. 5. The effect of the topo-analogous transformation on $A\nu^*_{el}\, q_o^{-2/3}$

The ratio of the $A\nu^*_{el}\, q_o^{-2/3}$ values can be calculated theoretically. As A does not vary with the topo-analogous transformation, we may write:

$$\frac{A\nu^*_{el} q_o^{-2/3}\,(\mathrm{PVAc})}{A\nu^*_{el} q_o^{-2/3}\,(\mathrm{PVA})} = \frac{d_2^{\mathrm{PVAc}}}{d_2^{\mathrm{PVA}}}\ \frac{\bar{M}_{c(\mathrm{PVA})}}{\bar{M}_{c(\mathrm{PVAc})}}\ \frac{\langle r^2\rangle_d^{\mathrm{PVAc}}}{\langle r^2\rangle_d^{\mathrm{PVA}}}\ \frac{\langle r^2\rangle_{os}^{\mathrm{PVA}}}{\langle r^2\rangle_{os}^{\mathrm{PVAc}}} \qquad (4)$$

where d_2^{PVAc} and d_2^{PVA} are the densities of the pure polymers, $\bar{M}_{c(\mathrm{PVA})}$ and $\bar{M}_{c(\mathrm{PVAc})}$ are the relative average molecular mass of the network chains.

On the basis of the Flory-Fox and the Kuhn-Mark-Houwink equations introducing the numerical values we obtain:

$$\frac{A\nu_{el}^{*}\, q_o^{-2/3}\ (\mathrm{PVAc})}{A\nu_{el}^{*}\, q_o^{-2/3}\ (\mathrm{PVA})} = 2.27 \left[\frac{\bar{M}^{0.64}_{c\,(\mathrm{PVA})}}{\bar{M}^{0.72}_{c\,(\mathrm{PVAc})}}\right]^{2/3} \qquad (5)$$

The constants of the Kuhn-Mark-Houwink equation:
PVA-water: $K=4.28\mathrm{x}10^{-4}$, $a=0.64$ (MATSUMOTO and OHYANAGI 1960);
PVAc-acetone: $K=0.86\mathrm{x}10^{-4}$, $a=0.72$ (CHINAI et al. 1955).

For the systems studied $0.4 < \left[\bar{M}^{0.64}_{c\,(\mathrm{PVA})} / \bar{M}^{0.72}_{c\,(\mathrm{PVAc})}\right]^{2/3} < 0.6$ which means that the agreement between the experimental and theoretical values is satisfactory.

Thus it can be concluded that the described analysis - the estimation of the chain dimensions in the reference state on the basis of the hydrodynamical properties of the uncrosslinked polymer chains - is applicable to give information concerning the molecular parameters of the gels.

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