

Two-Component Hydrogels

4. Elasticity Theory and Compression Measurements

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Summary

The elastic equations of state for 2-component networks are derived from a joint Gaussian distribution function composed of Gaussians for each component. The free energy of elasticity is then applied to the case of uni-directional deformations for compatible systems. The stress-strain equations are shown to be equivalent to those for a single component network except in the case where the macroscopic strain is sufficient to cause the ratio of average chain lengths of the components to change with the strain. The stress-strain equations are developed for both dry and swollen networks.

Introduction

Multicomponent polymer systems have been an intense area of work for many years. Most such systems studied in the crosslinked form have been interpenetrating networks (IPN) and, although the crosslinks are not covalently permanent, multiblock polymers are generally incompatible. Another type of multicomponent system can exist, in which the different types of polymer chains are joined as graft copolymers. If the termini of one component are all joined with the chains of the other component in a random fashion, one obtains what might be referred to as a terminally crosslinked graft copolymer (TCGP). Polymers of this type were first introduced by Bamford et. al.¹ and experimental work dealt with differences in physical properties as a consequence of variation of the relative glass transition temperature of the two components. Other heterogeneous systems studied include polyether-polypeptide combinations.² Bamford's networks proved to be incompatible and exhibited phase separation³ while the polyether-polypeptide combinations proved to be compatible. All of these papers are concerned with experimental determination of physical properties and none attempt a derivation of equations of state from which their behavior may be explained. To be sure, true single phase behavior as opposed to heterophase behavior is a central issue here, and as long as nearly complete phase separation occurs, the theories of Helfand⁴ and Meier⁵ concerning block copolymers can be applied. However, an application of classical

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theories of solvent mixing and elasticity to TCGP's has not appeared. Therefore, for the situation of single phase behavior, we will apply some well-known concepts to the elastic properties of two-component TCGP's. Our assumptions are:

1. The two polymer components are inherently compatible, or can be made compatible by swelling in a mutually good solvent.
2. Both sets of chains belong to a Gaussian distribution, not necessarily the same one.
3. Deformations of the mixed network are taken to be affine in the macroscopic strain with respect to each set of chains.

Theory

Henceforth, component two refers to the end-linked component (grafted segment) and component three refers to the "host" polymer. If both sets of chains have Gaussian probability density functions, it can be shown that the joint Gaussian must be a product of the individuals,

$$Q(r_2 r_3) = Q(r_2)Q(r_3) \quad (1)$$

where $Q(r_j)$ is the partition function for component j having end to end distance r_j . If the combined network undergoes a homogeneous deformation in which the average end to end vector undergoes an affine deformation for each component, the properties of the Gaussian function allow us to write,

$$\lambda_{ij} = x_{ij}/x_{oij} \quad (2)$$

where component j is strained in the i direction to a deformation ratio of λ_{ij} , where $i = 1, 2, 3$ corresponding to the principle strain axes. If one writes the Boltzman entropy change as a result of the deformation, we have,

$$\Delta S = k \ln \{Q(r_2, r_3)/Q(r_{o2}, r_{o3})\} \quad (3)$$

which transforms to cartesian coordinates as,

$$\Delta S = k \sum_{j=2}^3 \beta_j^2 \sum_{i=1}^3 x_{oij} (1 - \lambda_{ij}^2) \quad (4)$$

where β_j is the constant appearing in the Gaussian for each component j and is related to the contour length of each set of chains. If we define the root mean square end to end distance for each set of chains in the usual way,

$$\langle r_j^2 \rangle_o = v_j^{-1} \sum_{\nu_j} r_{\nu_j}^2 = 3/2\beta_j^2 \quad (5)$$

where v_j represents the number of chains of type j and recall that chain vectors are randomly placed so that,

$$\sum_j v_j x_{oij} = (1/3) \sum_j v_j r_{oj} \quad ; \quad i = 1, 2, 3 \quad (6)$$

we can combine equations (4), (5) and (6) to obtain,

$$\Delta S = (-k/2) \sum_{j=2}^3 v_j \sum_{i=1}^3 (\lambda_{ij}^2 - 1) \quad (7)$$

which is just the entropy change associated with affine deformation of each component as though the other served only as an independent partner in the process. As long as a suitable reference state can be found which can be characterized as following Gaussian statistics and the deformation of one set of chains does not perturb the statistical nature of the other set, equation (7) should hold. We have followed a line of reasoning above which does not include the controversial logarithmic term which appears in the Flory-Wall^{6,7} version of the theory but does not appear in the James and Guth^{8,9} version. This term should be included, and if one assumes the additivity of the volumes of each component, the free energy change upon deformation for the two-component system is,

$$\Delta F_{\text{net}} = (AkT/2) \sum_{j=2}^3 v_j \sum_{i=1}^3 (\lambda_{ij}^2 - 1) + BkT \sum_{j=2}^3 v_j \ln \prod_i \lambda_{ij} \quad (8)$$

where A and B are utilized to reflect the unsettled question as to their proper values.¹⁰ We are not presently concerned with this issue, but rather, with the form of the equations as it applies to TCGP's. We proceed with the stress-strain relations for two-component networks. The macroscopic strain for component j in the i direction is,

$$\alpha_{ij}^2 = \lambda_{ij}^2 \langle r_{j0}^2 \rangle / \langle r_{jk}^2 \rangle \quad (9)$$

where $\langle r_{j0}^2 \rangle$ are the ideal reference dimensions defined by an equivalent uncrosslinked system and $\langle r_{jk}^2 \rangle$ are the reference dimensions in the isotropic undeformed real^j network. The volume of component j in the strained state relative to the k th reference state is,

$$\alpha_{1j} \alpha_{2j} \alpha_{3j} = V_j / V_{kj} \quad (10)$$

while for the specimen itself, the analogous relation for the whole system is,

$$\alpha_1 \alpha_2 \alpha_3 = V / V_k \quad (11)$$

Since we wish to relate the relative volumes of the two components in terms of their chain dimensions, in the strained and unstrained states we must take cognizance of the possibility that the relative chain dimensions may change upon deformation. This is done by writing,

$$\alpha_{1j} \alpha_{2j} \alpha_{3j} = f_j V / f_{kj} V_j \quad (12)$$

where f_j and f_{kj} are volume fractions of component j in the strained and unstrained states, respectively. We define a parameter, P as follows,

$$P = (f_j / f_{kj})^{2/3} = \rho (1 + \rho_k^{3/2})^{2/3} \rho_k^{-1} (1 + \rho^{3/2})^{-2/3} \quad (13)$$

where,

$$\rho_k = \langle r_{jk}^2 \rangle / \langle r_{1k}^2 \rangle \quad ; \quad \rho = \langle r_{1j}^2 \rangle / \langle r_{11}^2 \rangle \quad (14)$$

and reflects the relative dimensions of the two components in each state. If $\rho_k = \rho$, then $P=1$. However, if the deformation of one component perturbs the Gaussian behavior of the other component, the relative dimensions will be different in the two states and $P \neq 1$, but rather will be a function of the strain. What this means is that finite extensibility of one set of chains will produce an additional strain dependence on the macroscopic stress. Having defined this possibility, we make the final affine transformation as,

$$\lambda_{ij}^2 = P \alpha_i^2 \langle r_{jk}^2 \rangle / \langle r_{j0}^2 \rangle \quad (15)$$

We consider the case of a uni-directional deformation in the one direction in which,

$$\lambda_{1j}^2 = P \alpha_1^2 \langle r_{jk}^2 \rangle / \langle r_{j0}^2 \rangle$$

$$\lambda_{2j}^2 = \lambda_{3j}^2 = PV \langle r_{jk}^2 \rangle / \alpha_{1k} V_k \langle r_{j0}^2 \rangle \quad (16)$$

where V/V_k is the macroscopic volume change on deformation. Substitution into equation (8) with subsequent differentiation according to,

$$f = (\partial \Delta F_{\text{net}} / \partial X)_{V,T} \quad (17)$$

where the one direction is now the X direction produces,

$$f = (V_k \text{ARTP} / X_o) (\alpha - V / \alpha^2 V_k) \sum_{j=2}^3 v_j^* \langle r_j^2 \rangle_k / \langle r_j^2 \rangle_o \quad (18)$$

where f is the force, X_o is the undeformed dimension and v_j^* is the number of network chains of type j per unit dry volume of the total network. Equation (18) expresses the idea that the two-component network should behave in the strain exactly as a one-component network until the parameter P becomes strain dependant. It is expected, however, that for any reasonable Gaussian distribution, the deviation of P from unity would occur only at large strains.

Experimental

The two-component systems described in this paper are hydrogels and consist of poly-vinyl-pyrrolidone (PVP) crosslinked with polyethylene glycol (PEG) oligomers. The method of functional oligomer preparation will be reported elsewhere, although the allylic termini of the PEG components were prepared in a fashion similar to that described in our earlier publications^{11,12} concerning one-component networks. The PEG component varied in molecular weight from 600 to 4,000 and four crosslink densities were prepared from each oligomer by copolymerization with N-vinyl pyrrolidone. The networks were subsequently washed for several weeks and swollen to equilibrium in water. Cylindrical samples were carefully cut from the swollen sheets and uni-directional compression measurements were performed using a modified depth gauge as described by Cluff, et.al.¹³ The specimens were surrounded by water at all times in order to prevent water loss due to evaporation.

Results and Discussion

Compressive strains applied to swollen networks result in small solvent losses which are normally approximated as being proportional to the square root of the strain.¹⁴ Taking this (and the fact that the networks are swollen) into account, equation (18) reads,

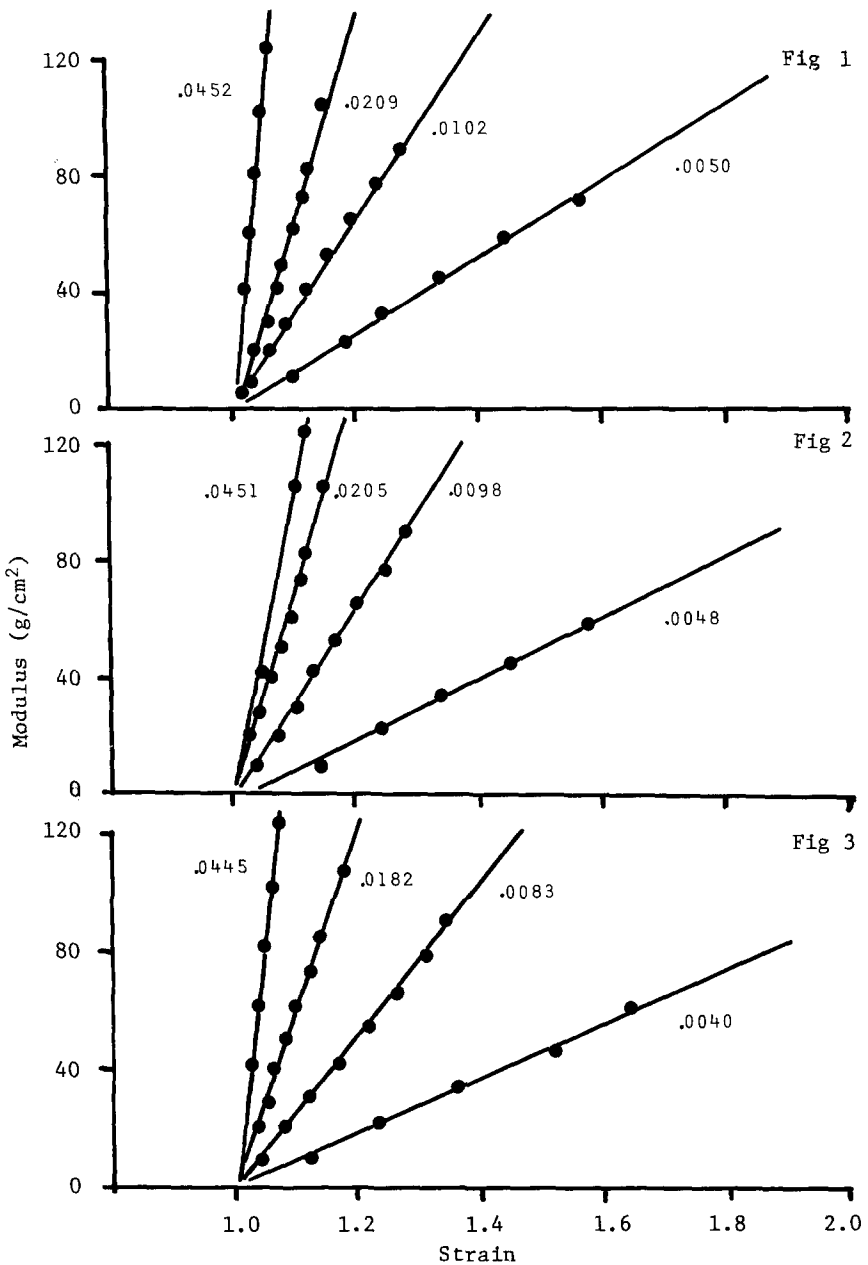
$$f = (V_k \text{ARTP} \phi_g^{-2/3} / X_o) (\alpha - \alpha^{-3/2}) \sum_{j=2}^3 v_j^* \langle r_j^2 \rangle_k / \langle r_j^2 \rangle_o \quad (19)$$

TABLE I

Results of Compression Measurements on Water-Swollen Two-Component Networks

| Network | PEG M _n | Crosslink Density* | Degree of Swelling (ϕ_g^{-1}) | Slope (g/cm ²) | -Intercept (g/cm ²) |
|---------|--------------------|--------------------|--------------------------------------|----------------------------|---------------------------------|
| 2D-1 | 615 | .0452 | 4.79 | 2314.3 | 2313.3 |
| 2D-2 | | .0209 | 7.22 | 883.5 | 875.9 |
| 2D-3 | | .0102 | 10.99 | 363.9 | 364.5 |
| 2D-4 | | .0050 | 18.62 | 183.2 | 179.6 |
| 2E-1 | 974 | .0451 | 5.01 | 1932.3 | 1896.3 |
| 2E-2 | | .0205 | 7.49 | 777.9 | 777.5 |
| 2E-3 | | .0098 | 12.00 | 383.4 | 380.8 |
| 2E-4 | | .0048 | 19.96 | 168.9 | 163.1 |
| 2F-1 | 3119 | .0445 | 6.07 | 1878.6 | 1875.6 |
| 2F-2 | | .0182 | 8.76 | 690.7 | 687.9 |
| 2F-3 | | .0083 | 14.56 | 312.7 | 310.9 |
| 2F-4 | | .0040 | 29.41 | 132.1 | 129.7 |

* Approximated from initial monomer feed composition and total conversion.



Figures (1-3): Compression modulus as a function of strain for 2-component hydrogels. Numbers on curves are crosslink densities. PEG crosslinking agents have $M_n = 615, 974, \text{ and } 3119$, respectively.

where ϕ_g represents the volume fraction of network in the swollen undeformed specimen. Since the specimens utilized were cylinders the unswollen, undeformed volume can be expressed as,

$$V_k = \phi_g S X_o \quad (20)$$

where S is the crosssectional area of the already swollen undeformed specimen. Substitution of (20) into (19) with subsequent division of both sides by the strain, provides an expression which relates the modulus of the swollen network, G, to the strain,

$$G = ARTP\phi_g^{1/3}(1 - \alpha^{-5/2}) \sum_{j=2}^3 v_j^* \langle r_{j,k}^2 \rangle / \langle r_{j,o}^2 \rangle \quad (21)$$

Hence, if P is independent of strain, a plot of the modulus, G, versus $\alpha^{-5/2}$ will give a straight line with slope related to the total number of elastic chains. Moreover, if P is strain independent, the slope and intercept of the plot should be equivalent in magnitude but opposite in sign. In Figures 1-3 we exhibit the plots suggested by equation (21) for the networks prepared with PEG crosslinking agents of molecular weight 600, 1000 and 3000, respectively. In all cases, the plots are linear and extrapolated intercepts agree quite well with the slopes. Table I tabulates the results of these calculations along with the crosslink densities and degrees of water swelling for the networks studied. It is apparent from these results that the relative chain lengths of the 2-components remain constant over this range in strain. Due to the uncertainty in the value of A in the theory and the unknown values of the individual memory terms (coefficients of v_j^*) it is impossible to quantitatively calculate the number of elastic network chains from these data. However, it is obvious that the calculated crosslink densities are very nearly directly proportional to the slopes of the stress-strain curves.

Although these measurements cannot provide the number of elastic chains, they do provide valuable information which will be applied to swelling measurements on the same networks to be reported upon in a future publication.

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