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Elastic behaviour of solution cross-linked poly(isobutylene) gels under large compression

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Abstract

Modulus of elasticity of loosely cross-linked poly(isobutylene) gels are measured under large compressive deformations. Gels of perfect spherical shape are prepared by the suspension cross-linking technique of dilute toluene solutions of butyl rubber using sulfur monochloride as a cross-linking agent. Compressive deformation is applied by a calibrated stainless steel cantilever to spherical poly(isobutylene) beads of sizes ca. 1.0–4.0 mm in diameter swollen in toluene. The relationship between force and deformation is obtained by using the constitutive relations from molecular theory of elasticity. Moduli are measured immediately after applying compression, and after full relaxation which obtains after solvent exudes the gels under compression. The instantaneous moduli are an order of magnitude larger than equilibrium moduli. Results of mechanical measurements, which are presently of a preliminary type, are compared with those from independent thermodynamic estimates of shear moduli. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(isobutylene) gels; Suspension cross-linking; Elastic modulus

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1. Introduction

Soft polymer gels have an important role in many emerging technological areas such as drug delivery, sensors and superabsorbent materials [1]. In many of the applications, precise information on the molecular constitution of the gels as well as their elastic properties is required. Polymer gels formed in the presence of a diluent are soft and fragile when handled in the swollen state. Most gels of scientific and technological interest fall into this category. Several interesting molecular features control the elastic properties of the gels. Among the most important factors is the state of disentanglement of the chains that form the network. Forming the gel in the highly swollen state causes the chains to disentangle prior to cross-linking. Due to the absence of entanglements, and low degrees of cross-linking, the network can swell highly when exposed to a good solvent. Typically, swollen gels of this type have moduli in the order of kiloPascals, whereas typical unfilled engineering rubbers have moduli in the order of milliPascals when used in the dry state. Fragility of the swollen networks results because the chains are in a highly stretched state when swollen [2].

Mechanical measurements on gels provide significant information on their molecular constitution, such as the degree of cross-linking, osmotic compressibility, lengths of chains between cross-links, etc. [2]. Since simple tension tests cannot be applied to highly swollen gels due to fragility at the clamps, compression tests, in general, are preferable. Experimental errors in small compressive deformations of highly swollen gels are in general large. Therefore such measurements have to be made under large deformations. Compressive deformations that exceed a few percent result in changes in the geometry of the test sample, such as barrelling, and often results in mechanical instabilities, such as buckling. The experiment cannot continue after the onset of instabilities. Also, if the instantaneous modulus of elasticity is investigated, the experiment has to be performed rather quickly to prevent the escape of the solvent from the gel due to increasing osmotic pressure. A convenient shape for a sample in a compression test for which mechanical instability is not of consequence is a sphere.

Recently, Knaebel et al. reported results of carefully executed compression experiments to determine the moduli of super-absorbent gel beads under small degrees of compression and interpreted the results of measurements by employing the Hertz contact problem which yields the modulus of a sphere in linear, i.e. small deformation ranges

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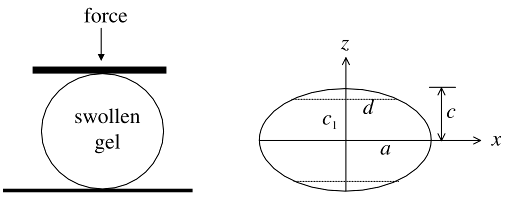

(a) (b)

Fig. 1. (a) Undeformed and (b) deformed geometry of the swollen poly (isobutylene) gel.

[3]. In the present work, we report elastic behaviour of gels under large degrees of compression, by employing a calibrated cantilever beam that applies a compressive force on an initially spherical bead of cross-linked poly(isobutylene) immersed in excess toluene. Here, we solve the finite compression problem of a sphere by an approximate elasticity formulation and compare the moduli obtained by this formulation with results obtained independently from swelling measurements.

2. Elasticity of swollen networks

The elastic behaviour of swollen networks is well described by molecular theories [2]. In this section, we define the important variables of the gel elasticity problem, and give the equation of state for gels cross-linked in the presence of solvent. This derivation is important for the proper interpretation of elasticity measurements on gels, whose elastic parameters, unlike dry elastomer, depend strongly on the state of formation and the highly swollen state at which measurements are made.

The correct reference state for a gel is the state at which it is formed. Let V_0 define the volume at which the network is formed. Also, let V and V_d denote the volume at which the elasticity measurements are made and the dry volume, respectively. V is not necessarily equal to V_0 which may result from difference in the temperature or the solvent quality in the two cases. The following volume fractions are defined: $v_2 = V_\mathrm{d}/V$, $v_{2\mathrm{c}} = V_\mathrm{d}/V_0$, where v_2 and $v_{2\mathrm{c}}$ are the volume fractions of polymer in gels subjected to elasticity measurements and after preparation, respectively. The state of deformation of a network may be defined in terms of three principal extension ratios, $\lambda_t = L_t/L_{0t}$, where L_t is the deformed length along the tth direction ($t = 1, 2$, and 3), and L_{0t} the corresponding length during the state of formation. The two simplest molecular models of a network are the phantom and the affine network models [2]. The elastic free energy for these models is

$$\Delta A_\mathrm{el} = F\xi \mathrm{k}T(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{1}$$

where, $F = 1/2$ and 1 for a tetrafunctional phantom and an affine network, respectively, and ξ is the cycle rank of the network, representing the number of chain cuts required to reduce the connected gel structure to a tree. k is the Boltzmann constant and T is the absolute temperature. Highly swollen gels are shown to obey the phantom network model, because constraints from the neighbouring chains that diminish the fluctuations of a given cross-link become weaker with swelling [2]. Removal of entanglements by solution cross-linking makes the networks even closer to a phantom one. In the other extreme case where the cross-link density is extremely low, resulting in extremely long network chains, the network behaviour approaches the affine limit, i.e. $F = 1$ [4]. A conclusive study of the onset of affine behaviour with increasing chain length is not available yet, however.

Eq. (1) represents the total elastic free energy change in passing from the unstrained, after-preparation state to the strained swollen state, i.e. from length L_{0t} to the length L_t. However, in deformation experiments, measurements are made relative to the swollen unstrained length L_{it}. We define

$$\alpha_t = \frac{L_t}{L_{it}} = \frac{L_t}{L_{0t}}\frac{L_{0t}}{L_\mathrm{d}}\frac{L_\mathrm{d}}{L_{it}} = \lambda\left(\frac{v_2}{v_{2\mathrm{c}}}\right)^{1/3} \tag{2}$$

The elastic free energy change associated with the initial isotropic swelling from length L_{0t} to L_{it} is

$$\Delta A_\mathrm{el} = F\xi \mathrm{k}T\left[3\left(\frac{v_{2\mathrm{c}}}{v_2}\right)^{2/3} - 3\right] \tag{3}$$

The elastic free energy change during deformation of the swollen network is the difference between Eqs. (1) and (3), i.e.

$$\Delta A_\mathrm{el} = F\xi \mathrm{k}T\left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\left(\frac{v_{2\mathrm{c}}}{v_2}\right)^{2/3}\right] \tag{4}$$

Substitution of Eq. (2) into Eq. (4) and for the case of uniaxial deformation of phantom networks ($F = 1/2$, $\alpha_1 = \alpha$, and $\alpha_2^2 = \alpha_3^2 = 1/\alpha$) one obtains

$$\Delta A_\mathrm{el} = \frac{1}{2}\xi \mathrm{k}T\left(\frac{v_{2\mathrm{c}}}{v_2}\right)^{2/3}\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \tag{5}$$

The force f and the true stress t are obtained respectively as $f = \partial\Delta A_\mathrm{el}/\partial L$ and $t = f/A$, where L is the deformed length and A is the deformed cross-sectional area. Performing the differentiation leads to the expression for the uniaxial stress as

$$t = G\left(\alpha^2 - \frac{1}{\alpha}\right) \tag{6}$$

where the shear modulus G of the swollen gel is defined as

$$G = \left(\frac{\xi \mathrm{k}T}{V_\mathrm{d}}\right)v_2^{1/3}v_{2\mathrm{c}}^{2/3}. \tag{7}$$

3. Deformation of the spherical gel

The deformed shape of an originally spherical gel of

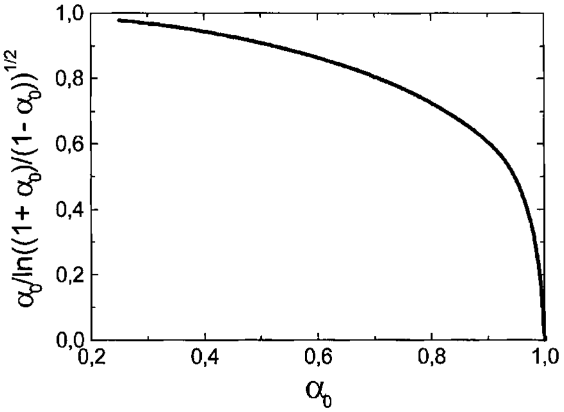

Fig. 2. Dependence of the front factor upon compression ratio.

radius a_0 is shown in Fig. 1. Our observations show that (1) the initial contact of the gel with the wall does not form a point contact but forms a contact area of radius d_0, and (2) the deformed boundary of the sample under the two compressing plates can be approximated by an ellipsoid with two truncated caps. The major radius is a, the minor radius is c, the half height between the walls is c_1, the intermediate distance from the centre to a plane parallel to the walls is z, and the contact radius in the compressed state is d, all indicated in Fig. 1. The formation of a nonzero area of contact when no external compressive force is applied on the sample results from the balance of the attractive energy between the wall and the gel and the local strain energy of deformation of the gel upon forming the contact area. The surface energy and the contact energy of elastic solids have been widely studied following the pioneering work of Johnson et al. [5]. In the present study, the free energy arising from large compressive forces are dominant, and effects arising from the deformation of the gel due to contact forces are neglected. However, for small deformations, deformations due to contact forces compete with deformations due to external compressive forces, and therefore should be taken into consideration.

The deformation α is a function of position along the height z of the sphere due to dependence of the cross-sectional area on z. In a more refined treatment, α should be taken also to depend on position in the cross-section. This dependence is taken into consideration in the linear theories of elasticity [6]. In the present nonlinear treatment, we ignore this dependence and consider $\alpha(z)$ to be the same at any point in the cross-section. The force f similarly depends on position in the cross-section independent of z, as treated in the linear theory of elasticity. The total force at a given cross-section, however, is independent of z, as follows from statics. The mean value of the term $((\alpha^2(z)) - (1/\alpha(z)))$ in Eq. (6) may be approximated in terms of the externally applied deformation $\alpha_0(= c_1/c)$ by the expression

$$\alpha_0^2 - \frac{1}{\alpha_0} = \frac{1}{c_1}\int_0^{c_1}\left(\alpha^2(z) - \frac{1}{\alpha(z)}\right)\mathrm{d}z \tag{8}$$

On the left-hand side of Eq. (4), the stress is a function of the distance z from the centre due to dependence of the cross-sectional area on z. The cross-sectional area may be approximated by the expression $A = \pi a^2(1 - (z^2)/(c^2))$ for an ellipsoidal shape. Substituting the expression for the area into Eq. (6), integrating both sides from 0 to c_1, and using the expression given by Eq. (8) leads to the expression for the shear modulus

$$G = \frac{\ln\left(\dfrac{1+\alpha_0}{1-\alpha_0}\right)^{1/2}}{(\alpha_0^3 - 1)}\frac{f}{\pi a^2} \tag{9}$$

Eq. (9) may be rearranged as

$$t = \frac{f}{A} = G\left[\frac{\alpha_0}{\ln\left(\dfrac{1+\alpha_0}{1-\alpha_0}\right)^{1/2}}\right]\left(\alpha_0^2 - \frac{1}{\alpha_0}\right) \tag{10}$$

Written in this manner, and compared with Eq. (6), the term in the square brackets denotes the correction from the effects of the geometry of the test sample, i.e. the deviation of the shape from a cylindrical one. The term in the square brackets shows the effects of the sample shape only. Effects from nonuniform stress distribution over a cross-section are ignored. The latter effects are important in the case of hard elastic solids as shown by theories of linear elasticity [6]. The dependence of the front factor on α_0 is shown in Fig. 2. It is interesting to see that the front factor approaches unity rather sharply with increasing compression. For α_0 less that 0.6, for example, the front factor is already larger than 0.9, and within 90% of the simple cylindrical case.

4. Experimental

The poly(isobutylene) spherical gels used in our experiments were prepared using suspension cross-linking technique [7]. The main component in the gel synthesis is butyl rubber, which was purchased from Exxon Chem. Co. The butyl rubber sample Butyl 268 used in this work contained 1.5–1.8 mol% isoprene units with the rest being isobutylene units. This polymer sample was purified by reprecipitation from toluene solution in acetone. Its weight-average molecular weight $\bar{M}_w$ was determined to be 3.9×10^5 g/mol on a gel permeation chromatograph with polystyrene standards (Waters, Model M-6000A). The polydispersity index $\bar{M}_w/\bar{M}_n$ was 2.5. The cross-linking agent sulfur monochloride, S_2Cl_2, was purchased from Aldrich Co. Toluene (Merck) was used as the solvent for the solution cross-linking process.

For the synthesis of PIB gels in the form of beads, suspension cross-linking technique was employed with water as the continuous phase. The principal problem in suspension cross-linking of butyl rubber was to distribute the toluene solution of butyl rubber in the form of small droplets inside

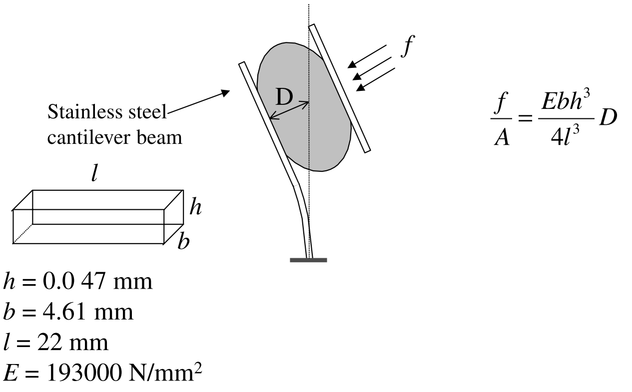

Fig. 3. Experimental set-up for compressing a swollen gel between a stainless-steel cantilever beam and a flat metal plate.

the continuous water phase and to prevent the coalescence of these droplets during the cross-linking process. Our preliminary experiments showed that the stabiliser system consisting of gelatine, bentonite and sodium chloride, used before in the suspension cross-linking copolymerisation of styrene and divinylbenzene, is also effective for the present system [8]. The degree of agitation was also important for the present system and it was fixed at 450 rpm.

First, butyl rubber dissolved in toluene (50 ml) was mixed with the cross-linker sulfur monochloride in an Erlenmeyer flask and nitrogen was bubbled through the organic solution for 10 min. Separately, 200 ml of water containing bentonite (0.5 g), gelatine (0.2 g), and sodium chloride (0.8 g) were introduced into a 500 ml round bottom reactor and stirred at 450 rpm under nitrogen atmosphere for 10 min. The toluene solution was then transferred into the reactor and the reaction was allowed to proceed for 8 h at room temperature (20 ± 1°C) under nitrogen atmosphere. After polymerisation, the beads were separated from the water phase and they were sieved using ASTM sieves, washed several times first with water, then with acetone and finally with toluene. The beads were left in toluene for two weeks during which toluene was refreshed every other day. Spherical poly(isobutylene) gels of sizes 1.0–2.0 mm in the dry state were prepared by using the technique described above at 10%w/v butyl rubber concentration in toluene and using 4 and 20%v/w S_2Cl_2 (with respect to butyl rubber) as the cross-linker.

Experimental procedure for determination of gel deformation and the corresponding force, that is, α_0 and f, is depicted in Fig. 3. A swollen gel with radius of about 2 mm was compressed between a stainless steel cantilever beam and another metal plate. The system was immersed in toluene and the sphere's deformation and the corresponding beam deflection were monitored using an image analysing system consisting of a stereo microscope (Olympus Stereomicroscope SZ), a video camera (TK 1381 EG) and Pentium-II PC with a data analysing software (BS-200 BAB).). Physical properties of the stainless steel cantilever beam, namely the Young's modulus (E), thickness (h), width (b) and length (L) were chosen to be 193×10^3 N/mm, 0.047, 4.61 and 22 mm, respectively. One can determine force f through the cantilever's deflection D as the sphere is compressed [9]

$$f = \frac{Ebh^3}{4L^3} D \tag{11}$$

since $Ebh^3/4L^3 = 2.17 \times 10^{-3}$ N/mm, Eq. (11) can be expressed as

$$f = 2.17 \times 10^{-3} D \text{ N/mm.} \tag{12}$$

5. Results and discussion

The swollen poly(isobutylene) spheres were compressed as described in Fig. 3. The deformation in the spheres was quite large, approximately around fifty percent of the gels' original diameter. Measurements were made immediately following the application of the force. The time elapsed between the application of the force and the measurements was in the order of seconds. We refer to these measurements as 'instantaneous'. Measurements were also made 24 h after the application of the force. This time was sufficiently long for the equilibration of the solvent between the sample and its environment. We refer to these measurements as 'equilibrium'.

Fig. 4 shows the shear modulus G versus inverse of the deformation $1/\alpha$. Filled and open circles represent results for gels containing 4 and 20% cross-linker, respectively; upper and lower sets of data represent shear moduli calculated from instantaneous and equilibrium measurements, respectively. As can be seen in the vertical axis of the plot, the shear modulus is in the Pascal range. This is due to the fact that our gels were slightly cross-linked and highly swollen. The equilibrium volume fraction of polymer in the 4 and 20% cross-link containing gels was 0.010 and 0.0204, respectively. The volume fraction of polymer at cross-linking was 0.0474. Therefore, the shear modulus is very low, as expected. Although 4 and 20% cross-linking agent sulfur monochloride (S_2Cl_2) was used, together with the main component butyl rubber (containing 1.5–1.8 mol% isoprene), to prepare such gels, we believe that some significant portion of the cross-linker remained inactive, or was hydrolysed during the synthesis of the spheres. Therefore, it may not be appropriate to call such gels as 4 or 20% cross-linked poly(isobutylene) spheres since we are not too sure about the exact amount of the cross-linker in the material after the gel synthesis. One can observe that the shear moduli for 4 and 20% type spheres increase significantly against $1/\alpha$ at instantaneous loadings; and, especially for 4% type sphere, it approached a steady value of around 43 Pa. The two dashed lines show the shear modulus for 4% (lower dashed line) and 20% (upper) type swollen gels, which were obtained independently from swelling experiments and are in good agreement with the equilibrium

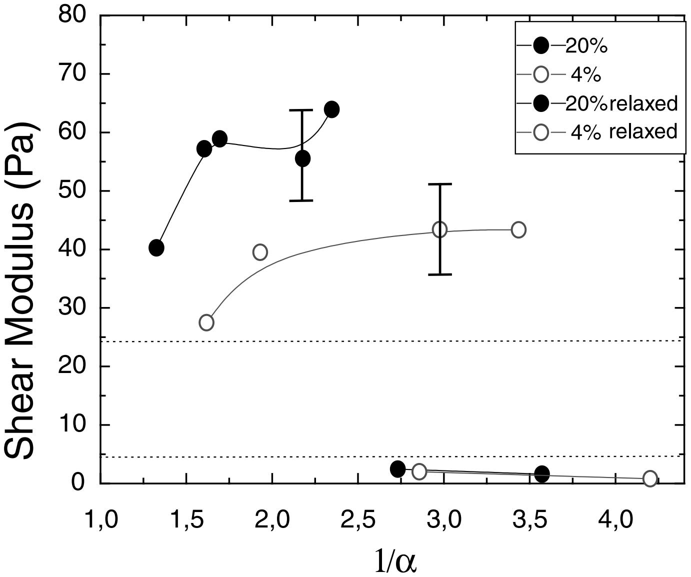

Fig. 4. Shear modulus of poly(isobutylene) gels versus inverse of compression ratio. Filled circles are for gels with 20% cross-linker, open circles are for gels with 4% cross-linker. Upper set of data is for results of instantaneous measurements. Lower set shows data from equilibrium measurements. Upper and lower dashed lines indicate moduli expected from equilibrium calculations for the 20 and 4% samples. Error bars are obtained from measurements on different samples of the corresponding network structure.

elasticity of 4% type gel that we measured using the above experimental procedure.

It is interesting that the equilibrium elasticity of the 20% type gel fall into the same scale as that of the 4% one. One possibility might be because of a phase separation (or phase segregation) which was indeed observed in the 20% samples. According to these observations, the gels with higher cross-link densities (more than 10%) exhibited two phases in the swollen undeformed state at equilibrium. The core was less swollen and semi-transparent, and the outer shell was highly swollen and transparent. The thickness of the outer shell was around 10% of the gel's diameter. An example to a phase segregated sample is pictured in Fig. 5. The boundary of the outer shell is dotted to guide eye and avoid ambiguity. The formation of core–shell structure of the gel beads can be explained with the possible hydrolysis of the cross-linker S_2Cl_2 during the gel formation process by the suspension polymerisation technique. S_2Cl_2 is known to easily hydrolyse in water at room temperature. One may expect that most of the S_2Cl_2 molecules locating at the surface layer of the beads hydrolyse in contact with the water phase during the gelation process leading to the formation of regions of lower cross-link density than the interior of the beads.

A gel deformed in a solvent is a semi-open system where the solvent enters the gel under a tensile force and leaves under compression. For example, in the present experiments the equilibration of small spheres (ca. 1 mm diameter) under compressive stresses is in the order of hours. Therefore the problem may be studied as a quasi-static process. The excess chemical potential $a_1(t)$ of the solvent in the gel at time t after the application of the compressive force may be written for the phantom network model as [10]

$$\ln a_1(t) = \mathrm{R}T[\ln(1 - v_2'(t)) + v_2'(t) + \chi v_2'(t)^2] + \left(\frac{\xi \mathrm{k}T}{V_0}\right)\bar{V}_1 \lambda_\perp^2(t) v_2'(t) \tag{13}$$

Here, R is the gas constant, χ the interaction parameter between polymer and solvent, $\bar{V}_1$ the molar volume of solvent, $\lambda(t)$ the extension ratio perpendicular to the direction of compression and $v'_2(t)$ the volume fraction of polymer in the gel at time t. For the interest of generality, both the extension ratio and the volume fraction of polymer are shown here as a function of time. In the general experimental procedure, a constant compressive deformation is applied to the sample, and the relaxation of the system as the solvent exudes is followed. In this case only v'_2 is an increasing function of time. When the system reaches equilibrium, the excess chemical potential of solvent in the gel becomes zero, and v'_2 equates to the equilibrium value $v_{2,\mathrm{eq}}$ under the given compressive stress. Eq. (13) may be used in this case to predict the equilibrium volume fraction of polymer in the compressed gel.

In Fig. 6, the results of a typical compression–relaxation experiment is shown. The figure on the left shows the experimental setup at the start. A compressive force is applied to the sample for 48 h. During this time, the solvent exudes from the sample. In the figure on the right, the force is instantly removed, and the snapshot is shown before solvent starts entering into the sample again. Volume measurements of the initial and the final shapes show that the sample has lost approximately 37% of its solvent during compression.

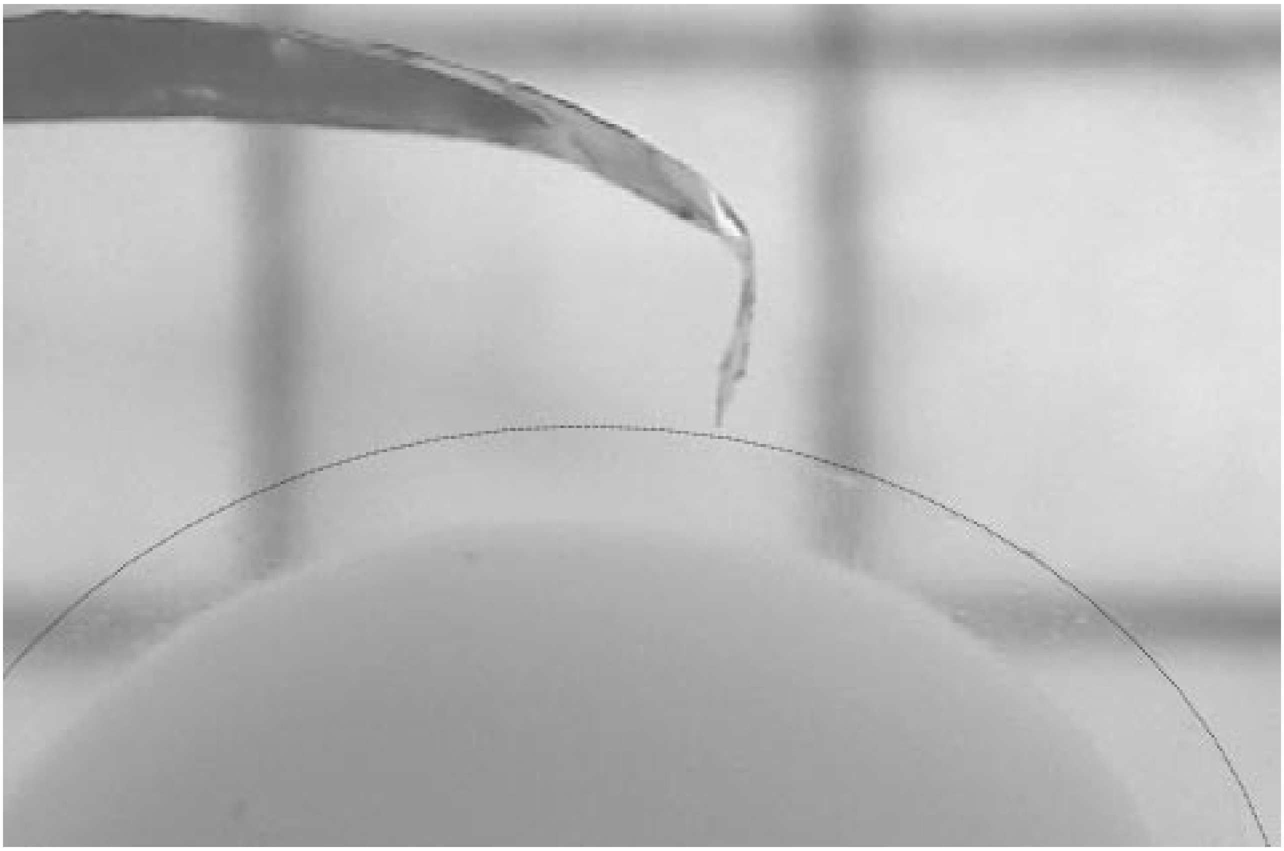

Fig. 5. Phase separation in a poly(isobutylene) gel of 10% cross-link density. The boundary of the outer shell was dotted to guide the eye. The very lightly cross-linked region forms the outer shell. The opaque inner higher cross-linked part is in the interior. The tip of the cantilever is located where the force starts being registered.

At equilibrium under a fixed deformation, equating Eq. (13) to zero leads to the determination of $v_{2,\mathrm{eq}}$ as a function of deformation. In general, the resulting $v_{2,\mathrm{eq}}$ is a single valued function of deformation. However, depending on the nature of the interaction parameter between the polymer and solvent, and the gel structure, critical conditions and a collapse under the load may be obtained [4]. Our preliminary results indeed show that this is possible for the slightly cross-linked poly(isobutylene) gels under large compressive deformation. In Fig. 7, results of experiments on the 4% sample under a compression for 4 h are shown. In Fig. 7a the sample before the application of the force is seen. The sample is shaded for clearer visibility. Fig. 7b shows the sample just after compression. Fig. 7c shows the gel 4 h after the application of the compressive force. The collapse of the sphere is clearly seen in Fig. 7c by observing the decrease in the lateral dimensions. Compression in one direction results in expansion in the lateral direction, as seen in Fig. 7a and b. This is because the Poisson ratio of materials is between 0 and 0.5, and a positive value means increasing in lateral dimensions under compression. In Fig. 7c, however, a shrinkage in the lateral dimensions is observed after 4 h, indicating a sudden collapse with shrinkage in all dimensions. The results shown in this work on collapse are only preliminary and qualitative. More detailed work on collapse under compression is in progress, however.

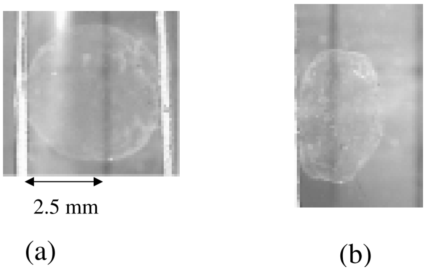

Fig. 6. The 4% type gel (a) before and (b) after equilibrium measurements performed for 48 h.

6. Conclusions

Elastic behaviour of loosely cross-linked spherical poly (isobutylene) gels under large degrees of compression was reported. At large degrees of compression, the stress–strain expression obtained for the compression of spherical samples approaches the expression for the compression of cylindrical samples. Shear moduli predicted by molecular theory and our mathematical formulation are in agreement for uniformly swollen gels. Shear moduli values for

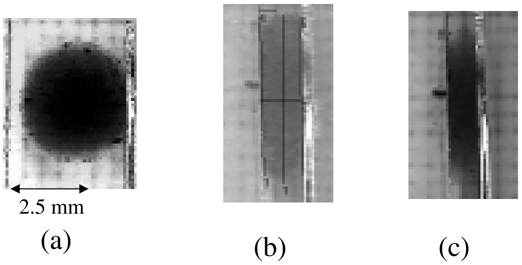

Fig. 7. Three snapshots of a sphere that exhibits collapse under compression: (a) undeformed; (b) just after compression; (c) after 4 h.

nonhomogeneously swollen gels are much lower than the predictions of the molecular theory. We also showed, qualitatively, that significant amount of solvent leaves the gel under compression, even leading to a collapse of the gel under high levels of compression. Our results in this respect are preliminary, and quantitative characterisation of the phenomena and more detailed work is in progress.

The mechanical tests reported in this work can be applied to spheres with micrometer diameters. Micron size samples are finding increasing use in advanced technological applications of gels, and sound methods for their thermomechanical characterisation are important. The present study is an attempt in this direction.

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