

Introduction

A crosslinked polymer, when placed in a good solvent, rather than dissolving completely, will absorb a portion of the solvent and subsequently swell. The swollen gel can be characterized as a solution, although it is an elastic one rather than a viscous solution. The extent of swelling represents a competition between two forces. The free energy of mixing will cause the solvent to penetrate and try to dilute the polymer solution. This entropic increase may be enhanced by increasing the temperature. As the polymer chains in the crosslinked polymer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The volumetric swelling reaches steady state when the two forces balance each other.

Given that the steady state swelling ratio is a direct function of extent of crosslinking in the sample, swelling experiments are a simple and low-cost technique to characterize polymer networks. At the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of crosslinking. At a higher level of analysis, the crosslink density, molecular weight between crosslinks, and number of crosslinks/chain can be computed if one knows the Flory interaction parameter for the polymer-solvent system.

Theory

The free energy change of mixing when an isotropic polymer sample is placed in a pure solvent can be written in terms of the ordinary free energy of mixing ΔF_m and the free energy associated with expansion of the polymer network ΔF_{el} as

$$\Delta F = \Delta F_m + \Delta F_{el} \quad (1)$$

The free energy of mixing is described in terms of the number of solvent molecules n_1 , the volume fractions of solvent and polymer, \mathbf{u}_1 and \mathbf{u}_2 , and the Flory interaction parameter \mathbf{c}_1 as

$$\Delta F_m = kT [n_1 \ln \mathbf{u}_1 + \mathbf{c}_1 n_1 \mathbf{u}_2] \quad (2)$$

The elastic component of the free energy ΔF_{el} is associated with the change in the entropy as the network is deformed, and can therefore be written in terms of the linear deformation factor \mathbf{a}_s as

$$\Delta F_{el} = [kT \mathbf{n}_e / 2] [3\mathbf{a}_s^2 - 3 - \ln \mathbf{a}_s^3] \quad (3)$$

where \mathbf{n}_e is the effective number of chains in the network. The chemical potential of the solvent in the gel is defined as

$$\mathbf{m}_1 - \mathbf{m}_1^0 = N(\partial \Delta F_m / \partial n_1)_{T,P} + N(\partial \Delta F_{el} / \partial \mathbf{a}_s)_{T,P} (\partial \mathbf{a}_s / \partial n_1) \quad (4)$$

where N is Avagadro's number. It is noted that $\mathbf{a}_s^3 = V/V_0$ where V_0 is the volume of the unswollen network and V the volume of the swollen network. Accordingly, $V_0/V = \mathbf{u}_2$. Incorporating the molar volume of the solvent \mathbf{j}_1 to compute the solvent contribution to the volume yields the expression:

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$$a_s^3 = 1/u_2 = (V_0 + n_e j_1 / N) / V_0 \quad (5)$$

Therefore, one can evaluate equation 4 with equations 3, 2, and 5 to yield:

$$m_1 - m_1^0 = RT \left[\ln(1 - u_2) + u_2 + c_1 u_2^2 + j_1 (n_e / V_0) (u_2^{1/3} - u_2 / 2) \right] \quad (6)$$

At equilibrium, the chemical potential of the solvent in the polymer will equal the pure solvent, so that the left side of equation 6 will be equal to zero. Rearranging equation 6 yields

$$-\left[\ln(1 - u_2) + u_2 + c_1 u_2^2 \right] = j_1 (n_e / V_0) (u_2^{1/3} - u_2 / 2) \quad (7)$$

Rewriting the number of chains/unit volume in terms of the specific volume of the polymer \bar{v} and the molecular weight between crosslinks M_c such that $n_e / V_0 = 1 / \bar{v} M_c$, and further rearrangement gives the final expression for the crosslink density n_x .

$$\frac{1}{\bar{v} M_c} = n_x = - \frac{\ln(1 - u_2) + u_2 + c_1 u_2^2}{j_1 (u_2^{1/3} - u_2 / 2)} \quad (8)$$

Experimentally, one measures the swell ratio $q = V/V_0 = 1/u_2$ and, knowing the Flory interaction parameter (see Appendix A), computes the crosslink density and molecular weight between crosslinks $M_c = 1/\bar{v} n_x$.

Experimental Technique

Researchers use two principal techniques for measuring the swell ratio of crosslinked polymer networks. The first technique, a gravimetric approach, is discussed in ASTM D2765-95 (Method C). In this method, a sample is carefully weighed (W_d), then immersed in a solvent at the required temperature for 24 hours. At the end of this period, the sample is again carefully weighed (W_g), and the swell ratio is computed from this data and the ratio of the densities of the solvent to the polymer, K , as

$$q = \frac{W_d + \rho_g - W_d K}{W_d} \quad (9)$$

While this technique is a simple, low-cost approach to measuring the swell ratio, it is difficult to obtain accurate measurements when volatile solvents are used, since the solvent evaporates as the sample is being weighed. Additionally, it is difficult to determine when steady state is achieved.

Consequently, more researchers are turning to techniques that use a probe to measure the change in height of a sample as it swells. Assuming that the sample swells isotropically, the swell ratio is computed from the change in the height $H(t)$ as $q = H/H_0$. This technique allows one to measure both the transient and the steady state swell ratio and does not require the removal of the specimen from the solvent to make a measurement.

Cambridge Polymer Group has developed the *SRT-I*TM, which uses a laser micrometer to measure the change in height of the sample. The *SRT-I*TM has been successfully used to measure swell ratios in crosslinked polyethylene, vulcanized rubber, and hygroscopic biopolymers.

In Figure 1, the swell response of radiation crosslinked ultra high molecular weight polyethylene in xylene at 130°C is shown. Steady state is reached after 150 minutes.

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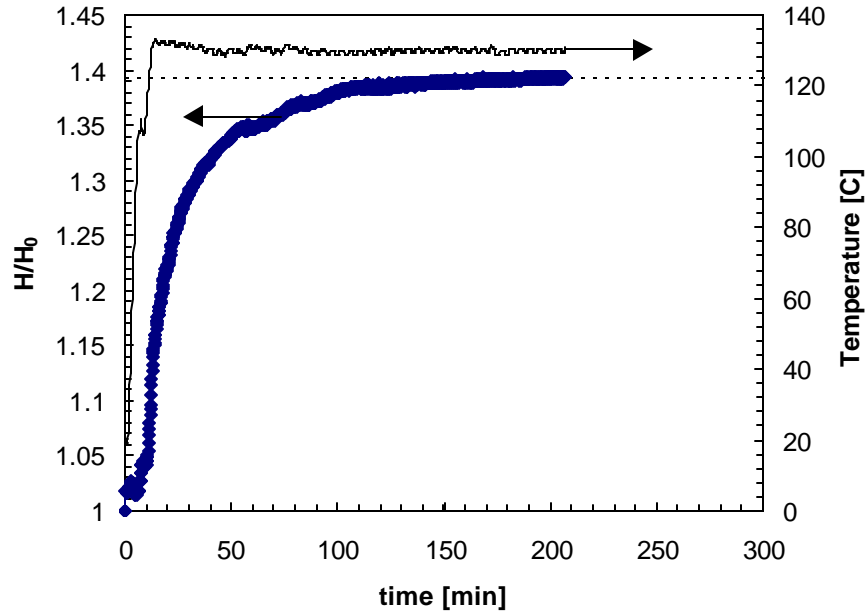


Figure 1: Transient change in height of radiation-crosslinked ultra high molecular weight polyethylene swelled in xylene at 130°C.

A series of samples with different molecular weight distributions were examined to determine the effects of polydispersity index ($PDI = M_w/M_n$) on crosslink density for identical levels of chemical crosslinking. The results of this study are shown in Figure 2.

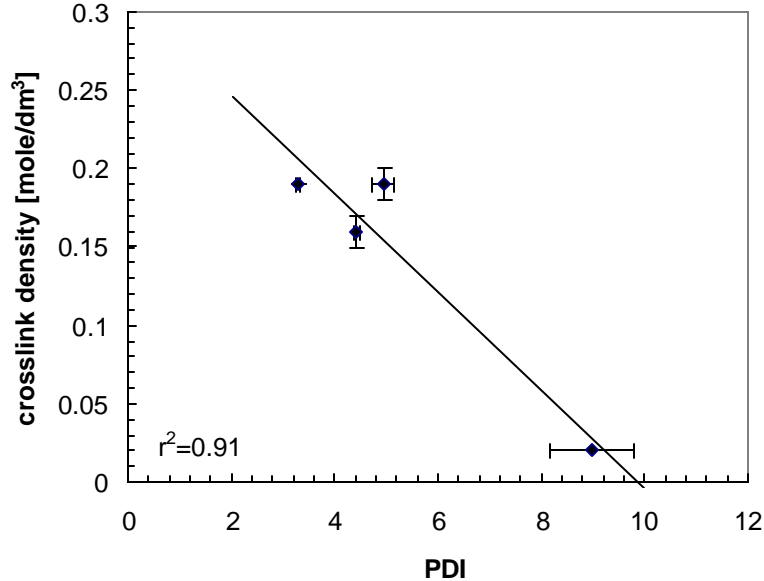


Figure 2: Dependence of crosslink density on polydispersity index of ultrahigh molecular weight polyethylene crosslinked with peroxide chemistry.

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Appendix A: Determination of the Flory Interaction Parameter

Flory interaction parameters have been measured for a large number of polymer-solvent pairs. The determination of c_1 is a time-consuming task, requiring careful measurements with a vapor-phase osmometer. In this technique, one places a dry, crosslinked sample against a sensitive thermister in the osmometer. Solvent is added, and the degree of swelling u_2 is determined from volume uptake in the vapor compartment of the osmometer. At the same time, the temperature difference between the swelling sample and the reference solvent is measured, from which one calculates the chemical potential:

$$m_1 - m_1^0 = -\frac{LM_1}{RT_0^2} \Delta T \quad (10)$$

where L is the specific heat of evaporation of the solvent, M_1 is the molecular weight of the solvent, and T_0 is the reference temperature.

The only remaining unknown in equation 6 is the interaction parameter c_1 . Rearranging equation 6 yields

$$\frac{\frac{\Delta m_1}{RT} - \ln(1 - u_2) - u_2 - u_2 j_1 (n_e/V_0)(u_2^{1/3} - u_2/2)}{u_2} = c_1 u_2 \quad (11)$$

A series of measurements of Δm_1 vs. u_2 , and plotting the data with the left side of equation 11 vs. u_2 should yield a straight line with a slope equation to c_1 , as shown in Figure 3.

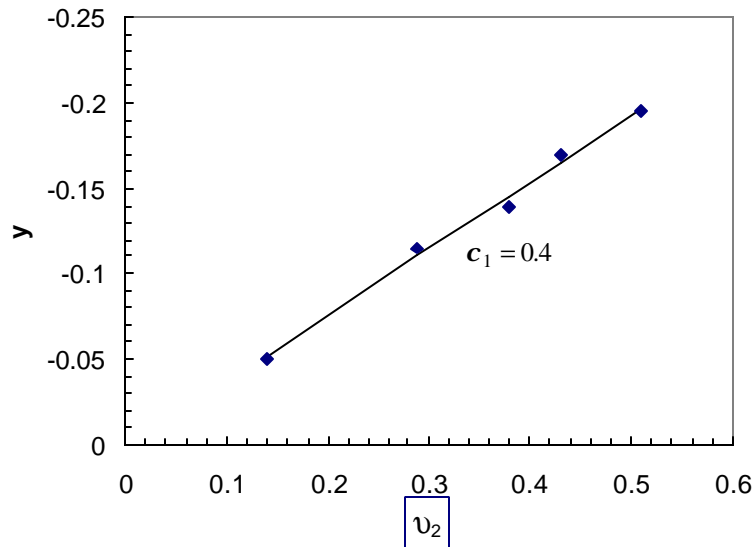


Figure 3: Plot of y (left side of equation 11) vs u_2 for determination of the Flory interaction parameter.