Crosslinked Poly(ethylene oxide) Hydrogels

Shahriar Hojjati Emami, R. Salovey

Department of Chemical Engineering, University of Southern California, Los Angeles, California 90089-1211

ABSTRACT: Poly(ethylene oxide) with a molecular weight of 2,000,000 was crosslinked by a difunctional peroxide in the molten state. We determined the molecular weight between crosslinks by swelling the samples with deionized water and by indentation and dynamic mechanical analysis. Results were compared with the calculated optimum molecular weight between crosslinks. Fair agreement was obtained between the experimental methods. However, the efficiency of peroxide-induced crosslinking was very low. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1451–1455, 2003

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INTRODUCTION

Poly(ethylene oxide) (PEO) is composed of flexible polymer chains that on crosslinking and swelling with water produce a soft hydrogel. This hydrogel is inert and, therefore, suitable for various applications, such as baby diapers, female hygiene products, wound dressings, controlled release drug systems, and solid electrolytes for batteries. PEO was first crosslinked in 1966 by gamma irradiation of aqueous solutions at the laboratories of Union Carbide.[1] Later, methods based on chemical crosslinking through end groups were suggested.[2] Chemical crosslinking was reported for low molecular weight (MW) polymers by the reaction between the end groups in PEO and multifunctional crosslinking agents.[2] Recently, it has been shown that PEO containing a photoinitiator could be successfully crosslinked by irradiation with ultraviolet (UV) light.[3,4] However, crosslinking by UV radiation is limited to a thin layer up to about 200 μm from the surface.[4] Crosslinking with gamma irradiation was efficient for dilute aqueous solutions, whereas crosslinking in the bulk or solid state required more than 100 Mrad of irradiation.[5]

One of the main properties of interest in characterizing hydrogels is the ability of network chains to expand to accommodate solvent molecules. This is simply related to the molecular weight between crosslinks (M_c). In 1943, Flory and Rehner suggested an equation to calculate M_c:[6–8]

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{(\nu/V_1)[\ln(1-\nu_{2,s}) + \nu_{2,s} + \chi\nu_{2,s}{}^2]}{\left(\nu_{2,s}{}^{1/3} - \left(\frac{\nu_{2,s}}{2}\right)\right)} \quad (1)$$

where M_n is the number-average molecular weight of the polymer before crosslinking, ν is the specific volume of the polymer, V_1 is the molar volume of the swelling agent, $\nu_{2,s}$ is the polymer volume fraction in the equilibrium swollen polymer, and χ is the Flory–Huggins constant. χ, is a dimensionless parameter and is determined by the energies of interaction between pairs of polymer segments, between pairs of solvent molecules, and between a polymer segment and a solvent molecule. In terms of the heat of mixing of the polymer and solvent (ΔH_m), χ is given by

$$\chi = \Delta H_m / RTN_1\phi_2 \quad (2)$$

where R is the gas constant, T is the absolute temperature, N_1 is the number of solvent molecules, and ϕ_2 represents the volume fraction of the polymer. For athermal solutions, χ is zero, and for mixtures of components that are chemically similar, χ is small compared to unity.[9,10] However, χ may be calculated experimentally from the Flory–Rehner equation, which includes rubber elasticity theory.[11,12] A network placed in contact with solvent expands until the chemical potential of mixing counterbalances the elastic reaction of the network. Thermodynamically, we write $\mu_{\mathrm{mix}} = \mu_{\mathrm{el}}$, where μ_{mix} is the chemical potential because of mixing and μ_{el} is the chemical potential of the elastic force. If the network is charged, an additional contribution due to the ionic interaction must be taken into consideration. The elastic term is expressed by the Flory rubber elasticity theory for Gaussian chains. The Flory–Rehner equation is setup for a gel crosslinked in the bulk state and composed of Gauss-

ian chains that are swollen to equilibrium in the absence of ionic charges.[13]

In addition to equilibrium swelling behavior, M_c can also be calculated from the depth of indentation of a sphere into the surface of the gel. Sperling[14] described stress/strain studies of interpenetrating polymer networks. Baker et al.[15] used indentation to investigate the deformation properties of hydrogels. The indentation modulus is closely related to Young's modulus (E). E may be determined from indentation with the Hertz equation:[16]

$$E = \frac{3(1 - \nu^2)F}{4h^{\frac{3}{2}}r^{\frac{1}{2}}} \qquad (3)$$

where F represents the force of a sphere against the surface, h is the depth of indentation of a sphere, r is the radius of the sphere, and ν is Poisson's ratio. E is related to crosslink density through rubber elasticity theory:

$$E = 3nRT \qquad (4)$$

Assuming a tetrafunctional crosslinking mode

$$E = 6\rho_x RT \qquad (5)$$

where n represents the number of active chain segments in the network and ρ_x is the crosslink density (moles of crosslinks per unit volume; $\rho_x = 1/\nu M_c$, where ν is the specific volume of the polymer).

Dynamic mechanical analysis (DMA) may be used to separate the ability of a material to store energy and its ability to dissipate energy. Articles[17–20] have reported on applications of this method to characterize gel and elastomers. McEvoy et al.[21] used this method to measure the gel modulus. When an oscillating stress is imposed on a viscoelastic material, if the material is purely elastic there is no phase difference between stress and strain waves. If the material is purely viscous, the phase difference is 90 degrees. Most materials are viscoelastic and, therefore, have phase differences between these values. Rheometers are used to control three parameters in any given test: frequency of oscillation, amplitude of oscillation, and test temperature. In a frequency sweep (a sweep is a continuous variation of parameter), the test frequency is varied to determine the frequency dependence of a material. It can be used to establish the response of a material to the length of time a force is applied to it. This is fundamental to understanding its internal structure. Applying a deformation very slowly enables the material to flow as a viscous liquid. Applying the deformation more quickly causes the elastic behavior to predominate, as there is insufficient time

to flow. From these measurements, the modulus and M_c are derived.

The purpose of this study was to characterize the M_c of PEO hydrogels by equilibrium swelling and mechanical experiments in compression and shear modes. M_c values, calculated as if all of the crosslinking agent were incorporated into the polymer network during the crosslinking reaction, were compared to experimental values.

EXPERIMENTAL

Materials

2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane Luperox 101 (AtoFina Chemicals; purity > 90%) was used without further purification. The half-life of Luperox 101 at 140°C is 1 h. Commercial PEO (Aldrich Chemicals) with a MW of 2,000,000 was used as received. Acetone (VWR; purity > 99%) was used for diluting peroxide. Deionized water was used for sol extraction and swelling.

Sample preparation

PEO (0.5 g) was weighed and mixed with peroxide–acetone solutions at concentrations of 3, 10, and 30% or 9.07×10^{-4}, 3.02×10^{-3}, and 9.07×10^{-3} mol/0.5 g of polymer, respectively. The mixture was stirred with a glass rod and allowed to remain in a hood to evaporate excess acetone. The samples were crosslinked at 160°C for 15 min. Deionized water was added to each sample, and samples were allowed to swell.

Sample characterization

The crosslinked PEO networks were extracted with water for 72 h. Fresh water was replaced every day. After extraction of sol, fresh water was added to the gels, which were allowed to equilibrate for 2 more days. The swelling weight was measured with a Teflon sieve with a hook. Excess water was removed by wiping. After weighing, samples were allowed to dry slowly under the hood.

Indentation

An indentation method was used to calculate M_c. We measured the deflection by placing steel (30.1 g, radius = 0.95 cm) and ceramic (18.7 g, radius = 1.21 cm) balls on the gels and measuring the indentation depth. The height of the ball from the surface of the gel was determined with a compass with two needle arms and a caliper with a 0.1-mm graduation. To obtain repeatable data, after each measurement, the ball was removed to allow the sample to recover to its original

TABLE I
M_c **as Determined by Different Methods**

Method	3%	10%	30%
H$_{(optimum)}$	551	165	55.5
Swelling	338,000	114,000	53,000
Indentation	—	121,500	61,600
DMA	—	166,000	65,000

MW = 2,000,000.

height. Gels with nonsmooth surfaces are potential sources of error, so the ball was used in many positions and compared. Reproducible test measurements showed the best place for locating the ball. Because cracks or trapped bubbles had a crucial effect on modulus values, the ball was gently on the surface because dropping the ball could damage the hydrogel.

DMA

Crosslinked PEO gel in the swollen state was placed on the Peltier plate of a CSL^{2}100 rheometer (TA Instruments). A 2-cm crosshatched parallel plate was used to minimize slippage between the gel and the plate surface. A frequency sweep was performed, and a graph of the storage modulus (G' Pa) versus frequency was obtained in a range of 1–10 Hz, at a constant temperature of 20°C.

RESULTS AND DISCUSSION

M_c was tabulated from three experimental methods including swelling, indentation, and DMA, and we also calculated an optimum value (Table I).

The number of crosslinks per polymer molecule was calculated from the molar ratio of polymer to biperoxide. We considered that each peroxide molecule led to two crosslinks because a peroxide molecule containing two functional groups was used. We assumed that each peroxide group led to two free radicals, each of which abstracted a hydrogen atom from the polymer, each peroxide group producing two polymeric radicals. The combination of two polymeric radicals yields one crosslink. Therefore, each molecule of Luperox 101 yielded two crosslinks. However, because approximately one half of the peroxide was consumed by crosslinking at 160°C for 15 min, half of the moles of peroxide were involved in crosslinking. Thus, we could estimate the number of crosslinks per polymer molecule by dividing the number of moles of diperoxide by the number of moles of polymer. Then, we obtained the optimum molecular weight between crosslinks [M_c $_{(optimum)}$] by dividing the molar mass of the polymer by the number of crosslinks per polymer molecule.

Apparently (Table I), the efficiency of crosslinking was very low. Moreover, as the concentration of per-

oxide increased, the efficiency of chemical crosslinking decreased. The efficiency of crosslinking was probably reduced by the recombination of radical fragments from the peroxide, the occurrence of many radical side reactions, the reduced mobility of polymeric radicals in the molten state, the limited solubility of the peroxide in acetone, and intramolecular crosslinking or cyclization.

The preference for hydrogen abstraction by peroxy radicals from the polymer over peroxy radical recombination during crosslinking determines the reaction efficiency. Some idea of the preference for specific radical reactions may be obtained by a consideration of the energy level of alternative radical products. For example, an alkoxy radical from peroxide decomposition with an energy of 105 Kcal/mol can abstract a hydrogen atom attached to a secondary carbon in polyethylene (PE), producing a polymeric radical with a reduced energy of 97 Kcal/mol.[22] Abstraction of a hydrogen atom from a secondary carbon in PEO would be even more favorable, yielding a radical of increased stability. However, the crosslinking process was less efficient in PEO than in PE. We suggest that an increased presence of tertiary hydrogens in PE led to a much higher efficiency of crosslinking. Alkoxy radical abstraction of tertiary hydrogen atoms produces a radical with energy of 91 Kcal/mol.[22] Tertiary hydrogen atoms result from branching in PE. Apparently, hydrogen abstraction is thermodynamically more favorable in PE than in PEO because of the presence of tertiary structures.

Another reason that peroxide crosslinking may be more efficient in PE than in PEO relates to the exposure and mobility of the polymeric radicals necessary for crosslinking. Enhanced chain flexibility leads to a lower end-to-end distance in PEO as compared to PE, with increased shielding of polymeric radicals and suppression of the diffusion necessary for radical combination.

For our studies on PEO gels, we selected dialkyl peroxides to initiate crosslinking. Among peroxides, dialkyl peroxides have the highest activation temperature and are among the most efficient and widely used commercial peroxides. Peroxides that generate weaker (peroxyketal) or stronger (acyl peroxide) primary radicals are either less efficient in abstracting hydrogens from PEO or are more susceptible to the peroxy radical recombination.

Although the decomposition temperature for Luperox 101 was not particularly appropriate for crosslinking PEO, with a melting point of only 65°C, we selected the dialkyl peroxide because of its high efficiency in crosslinking as indicated by a high percentage active oxygen content of 10.03–10.25% (manufacturer's data).

M_c was estimated from the swelling experiment with the Flory–Rehner equation [eq. (1)]. M_n of the
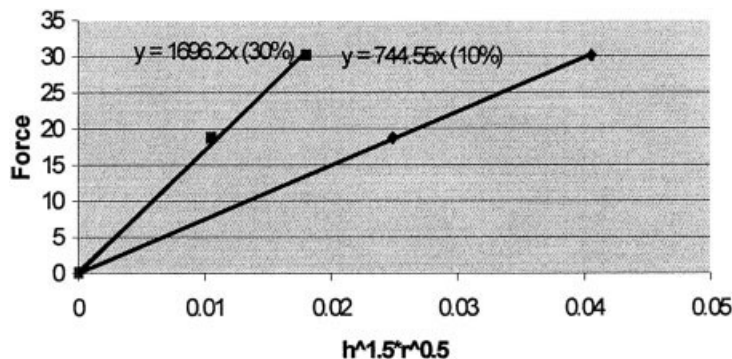
Figure 1 Indentation results at 10 and 30% peroxide concentrations, as calculated from the Hertz equation (MW = 2,000,000).

original polymer was approximated by the viscosity-average molecular weight. The specific volume of polymer was $1/1.13$ cm^3/g, the molecular volume of the swelling agent (water) was 18 cm^3/mol, and $\nu_{2,S}$ was calculated by the relation of the weights of the swollen and dry polymers by the following equation:

$$\nu_{2,s} = \frac{V_d}{V_s} = \frac{\dfrac{W_d}{\rho_p}}{\dfrac{W_d}{\rho_p} + \left[\dfrac{W_s - W_d}{\rho_0}\right]} \qquad (6)$$

where V_d and V_s are the dry and swollen polymer volumes, respectively; W_d and W_s are the dry and swollen polymer weights, respectively; and ρ_p and ρ_0 are the polymer and solvent densities, respectively. The Flory interaction parameter, χ, in eq. (1), was considered to be constant for PEO gels and water at 0.45. For gels involving long PEO chains, that is, MW > 4000, swollen in water, values of χ equal to 0.45 have been shown to provide reasonable results with crosslinked PEO samples.[3,11,12]

E at a constant force was investigated with spherical steel and ceramic balls weighing 30.1 and 18.7 g, respectively. The modulus was obtained from the slope of a force/indentation curve [eq. (3)]. Figure 1 shows indentation graphs for hydrogels at 10 and 30% peroxide concentrations. Average deflections (h's) after three measurements were 0.12 and 0.07 cm for the steel ball and 0.075 and 0.045 cm for the ceramic ball at 10 and 30% peroxide concentrations, respectively. The remaining factors in the Hertz equation were constant and equal to 551.812 cm/s^{2d}. The slope of the line including the origin was used to find modulus values of 41,000 and 93,600 Pa for 10 and 30% peroxide concentrations, respectively. Indentation measurements were not successful for PEO crosslinked with 3% peroxide. Because this gel was ruptured by the placement of the sphere, we believe that the gel was weak because of a low crosslinking density.

To derive M_c from DMA, G' was measured in a parallel plate rheometer with a frequency sweep of swollen gels from 1–10 Hz. It was assumed that by the extrapolation of the oscillation graph to zero fre-
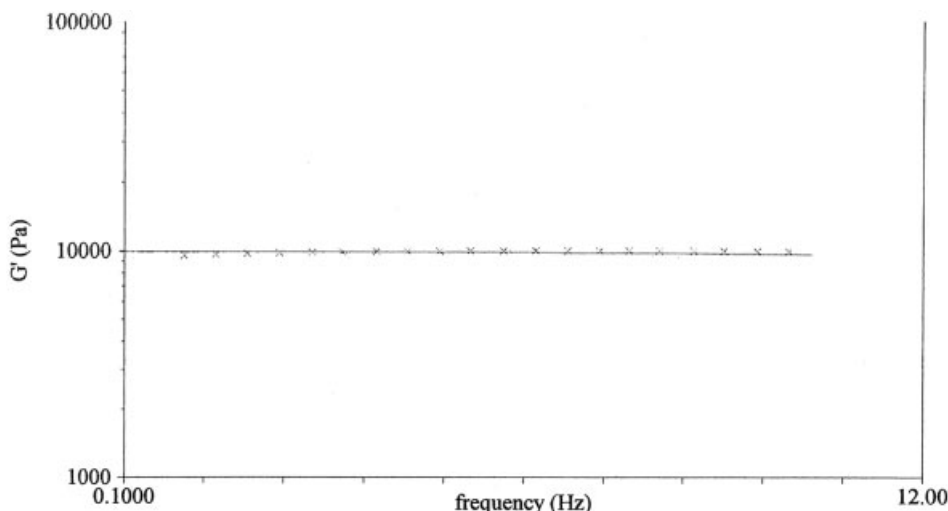

Figure 2 Extrapolation of the G' to 0.1 Hz at 10% peroxide concentration (semilog plot; PEO MW = 2,000,000, 10% oscillation).

quency, a static shear modulus (G) might be obtained. The time scale for the indentation experiment was about 10 s for each measurement. Actually, we extrapolated oscillation graphs to 0.1 Hz. Moreover, we linearized these data by plotting G' against log frequency. Extrapolated values of G' were estimated to be 10,000 and 29,500 Pa for 10 and 30% peroxide concentrations, respectively (Fig. 2). These values were converted to E (E $= 3G$), and M_c was calculated from rubber elasticity theory.

The data presented previously demonstrate good agreement between M_c from modulus determinations, that is, from indentation and DMA. However, M_c as figured by swelling was somewhat less than that figured by the mechanical methods, and the reason may be attributed to entanglements. Generally, such physical crosslinks are more effective in mechanical measurements than in equilibrium swelling data.[9]

CONCLUSIONS

PEO with a MW of 2,000,000 was crosslinked in the molten state by 2,5-dimethyl-2,5-di(*t*-butylperoxy)-hexane, at several concentrations. We achieved crosslinking by heating at 160°C for 15 min. The swelling behavior of the resultant hydrogels was examined by the measurement of equilibrium swelling in deionized water. M_c was determined from swelling with the Flory–Rehner equation and compared with ball indentation DMA and the calculated $M_{c\ (optimum)}$. Results indicate reasonable agreement between all the experimental methods, especially at low M_c or at high crosslinking density.

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