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Swelling behavior of emulsion polymer particles: comparison between fully cross-linked and partially cross-linked poly(acrylate) latexes

Ferenc Horkay, Daniel H. Craig

GE Corporate Research and Development, Schenectady, NY 12301, USA

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Summary

Measurement of swelling is used to estimate the extent of cross-linking of latex particles prepared by emulsion polymerization. In this paper we report swelling data as a function of solvent activity for two latexes: (1) a poly(butylacrylate) (PBA) latex, and (2) a poly(isodecylacrylate) latex. In the latter case comparison is made between the swelling behavior of fully cross-linked, i.e., networks without free polymer chains, and partially cross-linked latexes. It is demonstrated that the equilibrium swelling properties are only slightly affected by the presence of uncross-linked chains. Swelling gives reliable results for the cross-link density only if the latex does not contain free chains.

Introduction

The knowledge of the network structure, such as cross-link density, within latex particles is particularly important because the structure of these microspheres can affect the end use properties of materials containing them[1-3]. For instance, in the design of impact modified engineering thermoplastics, the microstructure of the rubber particles contained therein is frequently a critical factor in determining the performance of the material.[4-6] Nevertheless it has been difficult to characterize the relationship between microstructure and physical properties because of the lack of reliable experimental methods.

The scope of this paper is to describe a simple technique that allows assessment of the cross-link density of elastomeric materials via swelling measurements. In addition limitations of the swelling method relative to characterization of cross-linked polymers containing entrapped mobile chains are also discussed.

There are two different techniques used to measure the swelling of latex particles:

- gravimetric determination of the solvent uptake of films cast from latex particles,
- light scattering measurement of the diameter of latex particles in an appropriate solvent.

In the case of the gravimetric method inaccuracies may arise from several sources, e.g. adsorption of the diluent and dissolved components (surfactant, etc.) on the surface of the particles, diluent retained in the pores of the polymer, air bubbles (voids) within the polymer film, and liquid bridge formation between neighboring particles.

Particle size measurement in dilute dispersion provides a straightforward way to avoid uncertainties inherent in the gravimetric method. In this case the aforementioned affects are not significant.

In this paper assessment of swelling by light scattering measurement of the diameter of particles are reported for poly(butylacrylate) and poly(isodecylacrylate) latexes made by emulsion polymerization. The elastic modulus of the cross-linked polymer estimated from swelling measurements is compared with that obtained from direct rheological observations. The effect of free polymer chains (sol fraction) on the equilibrium properties is also investigated.

Theoretical Considerations

Swelling of fully cross-linked latex particles

At equilibrium with a pure solvent the osmotic (swelling) pressure of a polymer, which tends to expand the network, and the elastic response of the cross-linked polymer, which causes the network to shrink, are equal, i.e.,

$$\Pi - G = 0 \qquad (1)$$

where Π is the osmotic pressure of the network polymer and G is the elastic modulus. The latter is expected to vary with the concentration c of the polymer within the swollen latex particle, as[7,8]

$$G = G_0 c^m \qquad (2)$$

where G_o is the modulus of the unswollen network and the exponent m=1/3. II follows a power law dependence on the polymer concentration[9]

$$\Pi = A c^n \qquad (3)$$

where A and n depend on the particular polymer/solvent system but independent of the cross-link density of the network. It can be seen that the swelling equilibrium concentration depends on both the cross-link density, through G, and the solvent quality, through Π.

At equilibrium with the pure solvent we have

$$Ac_0^n = G_0 c_0^m \qquad (4)$$

where c_o is the polymer concentration of the fully swollen particles.

Replacing the pure solvent with a polymer solution of solvent activity a_1, we have

$$\Pi - G = RT \ln a_1 \qquad (5)$$

and re-expressing eq.4 as $A= G_o c_o^{m-n}$, from eqs. 1-5 follows that

$$RT \ln a_1 = G_0[c^m - c_0^{m-n} c^n] \qquad (6)$$

where R is the gas constant and T is the absolute temperature.

The diameter, d, of the individual latex particles is directly related to the concentration c through the relationship, $d=(6m/c\rho\pi)^{1/3}$, where m is the mass of the polymer, and ρ is the density of the polymer. Thus, measurement of the particle diameter as a function of the solvent activity a_1 yields G_o which is proportional to the cross-link density ν, ie., the average number of chemical junctions within the unit volume of an unswollen particle[8]

$$G_0=CRT\nu \qquad (7)$$

where C is a constant (front factor).

Swelling of partially cross-linked latex particles

To consider the effect of free (mobile) polymer chains on the swelling equilibrium concentration of polymer latex particles eq. (6) derived for a perfectly cross-linked polymer needs to be modified to account for the effect of free polymer on the activity of the diluent.

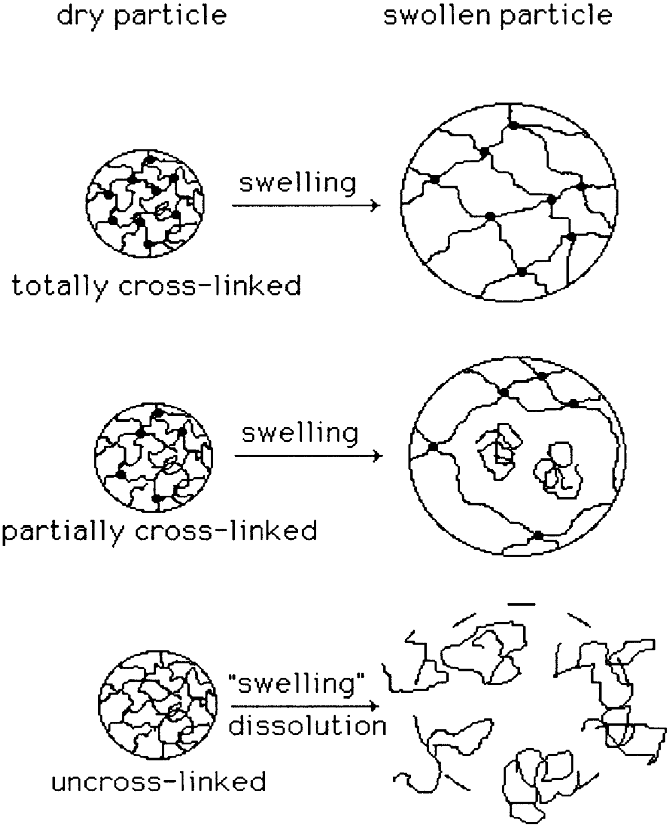

Figure 1. Swelling of latex particles. Filled circles (•) represent chemical cross-links.

Since the network polymer and the uncross-linked chains are chemically identical it is reasonable to assume that the constants (A, n and m) remain unchanged. The osmotic term can now be written as

$$\Pi = A c_{tot}^{n} \qquad (8)$$

where c_{tot} is the total polymer concentration ($c_{tot}=c_{net}+c_{free}$, c_{net} is the concentration of the network polymer and c_{free} is the concentration of the free (uncross-linked) polymer in the latex). Supposing that the presence of free chains does not alter the elastic properties of the cross-linked polymer eq.(2), combining with eq.(6), yields

$$RT\ln a_1 = G_0[c_{net}^{m} - c_0^{n-m} c_{tot}^{n}] \qquad (9)$$

The effect of cross-linking on the swelling of the resulting latex particles is illustrated in Figure 1. Perfectly cross-linked latex particles (first line) swell uniformly in a good solvent. In this case there is no soluble portion of the polymer. If the polymer in the dispersion is not cross-linked (last line) it is completely dissolved. The partially cross-linked latex sample (second line) exhibits an intermediate behavior. An increase of the cross-link density causes a decrease in the portion of soluble polymer.

Experimental

Latex preparation

A poly(butylacrylate) latex was made by emulsion polymerization via the semi-continuous addition of a monomer pre-emulsion according to a method described by Craig[10]. The reactor pre-charge consisted of 1661g distilled water and 0.5g sodium persulfate, adjusted to pH=6.5 with aqueous acetate buffer solution. A pre-emulsified mixture of 324g distilled water, 22g sodium lauryl sulfate, 1134g of butylacrylate, and 2.2g butyleneglycoldiacrylate was added to the reactor concurrently with an aqueous solution of 2.0g sodium persulfate in 200g water over two hours to complete the synthesis. Reaction temperature was maintained at 85°C throughout the entire reaction sequence. For the poly(isodecylacrylate) example butylacrylate was replaced by isodecylacrylate monomer and butyleneglycoldiacrylate was replaced by dicyclopentenyloxyethylacrylate. This latex contained 20% soluble material. The amount of soluble polymer was determined, after extraction in methylethylketone, by separation of the insoluble material from the liquid phase. The concentration of the liquid phase was determined gravimetrically by evaporation of the solvent. The accuracy of this method is better than 5%.

Measurement of particle size

Particle size measurements were carried out utilizing a Nicomp 370 Submicron Particle Sizer instrument applying a gaussian analysis protocol. For equilibrium swelling, the liquid phase of the aqueous emulsion was replaced by acetone (or methylethylketone) then stirred for 48 hours at 25 C. Previous experiments indicated that the time required to reach equilibrium was 2 days.

Latex particles were also equilibrated with poly(vinyl acetate) solutions of known osmotic pressure reported in the literature.[11,12] At equilibrium the solvent activity in the swollen particles is the same as in the liquid phase. The solvent activity was calculated from the osmotic pressure data using the equation $-\Pi V = RT \ln a_1$ where V is the molar volume of the solvent. Particle size was determined as a function of the activity of the diluent.

Rheological measurements

A Rheometrics RDS-7700 dynamic mechanical spectrometer equipped with a 2000 gcm force transducer was used for the rheological. measurements. Cylindrical polymer specimens were produced in a special mold. Parallel plate (25 mm diameter) geometry was used. The frequency sweeps were studied at 10% strain.

Results and discussion

In Figure 2 is shown the variation of the diameter of poly(butylacrylate) latex particles in acetone and methylethylketone solutions as a function of the poly(vinyl acetate) concentration. The extent of swelling is greater in methylethylketone indicating that methylethylketone is a better solvent for poly(butylacrylate) than acetone.

The swelling results were analyzed by least-squares fitting to eq.6. The exponents n and m were iteratively adjusted to minimize the variance of $\ln a_1$ for each set of experimental data points. The parameters obtained from the fits are displayed in Table 1 and were used for calculating the continuous curves in Figure 2. It can be seen that the agreement between the elastic moduli (last column) determined in acetone (G_o=3.9 kPa) and methylethylketone (G_o=4.2 kPa) is reasonably in agreement with the expectation that the cross-link density is independent of the solvent quality.

In order to independently determine the elastic modulus dynamic mechanical measurements were performed on polymer films cast from the latex. In Figure 3 are shown the rheological data for the poly(butylacrylate) sample. The horizontal straight line represents the elastic modulus calculated from the parameters reported in Table 1. In view of the fact that the two techniques (swelling and rheological measurements) are completely independent the agreement between the results is satisfactory.

Table 1

Fitting parameters of equation 6 to poly(butylacrylate) latex

Solvent	A/kPa	m	n	G_o/kPa
acetone	3260	0.34	2.32	3.9
methylethylketone	4180	0.33	2.29	4.2

In order to determine the effect of free polymer chains present inside the cross-linked particle (see middle picture in Figure 1) on latex swelling behavior we compared the dependence of the solvent activity as a function of total polymer concentration for a cross-linked poly(isodecylacrylate) (PIDA) latex before and after extraction of the mobile chains. The results are shown in Figure 4.

It can be seen that the two sets of experimental data almost coincide. This finding indicates that the swelling properties are primarily determined by the osmotic (second) term in eq. 9, and the soluble polymer fraction of the latex primarily acts as a diluent. Thus for partially cross-linked latices swelling measurements do not yield direct information on the cross-link density.

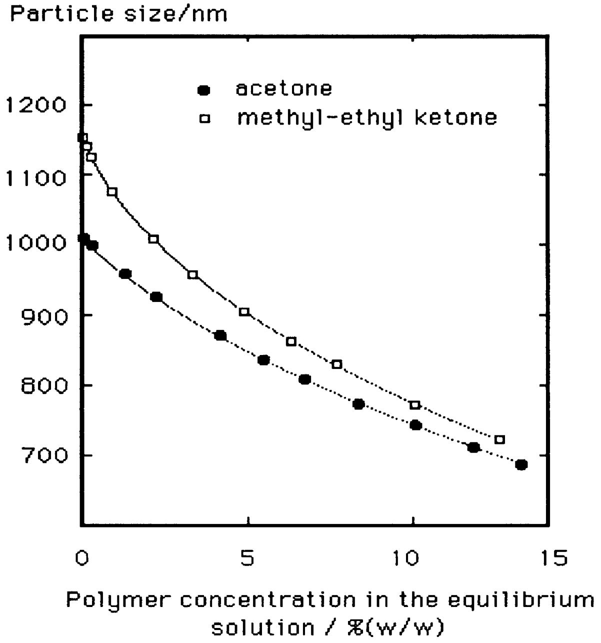

Figure 2. Variation of the diameter of poly(butylacrylate) latex particles as a function of the poly(vinyl acetate) concentration in acetone and methylethylketone solutions.

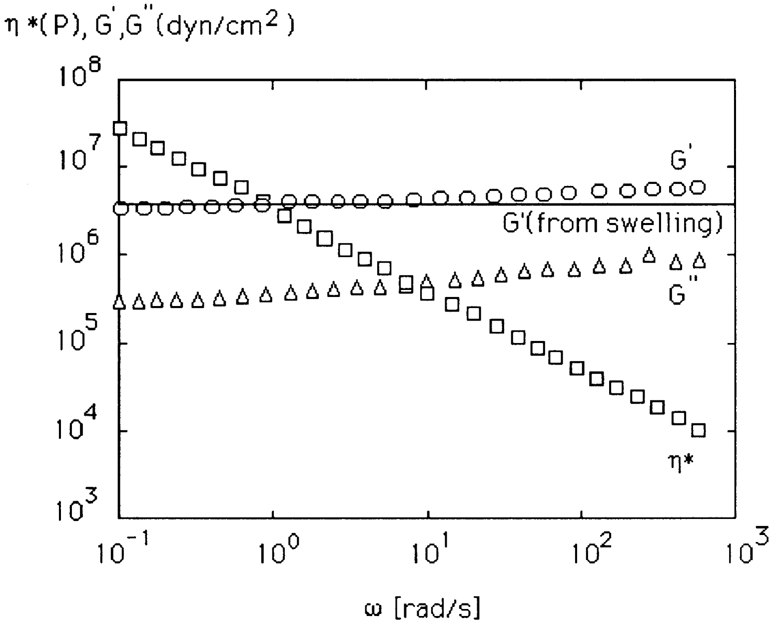

Figure 3: Frequency sweep at 25 °C displaying the storage (G') and loss (G") moduli of poly(butylacrylate) sample. η* is the complex viscosity of the material.

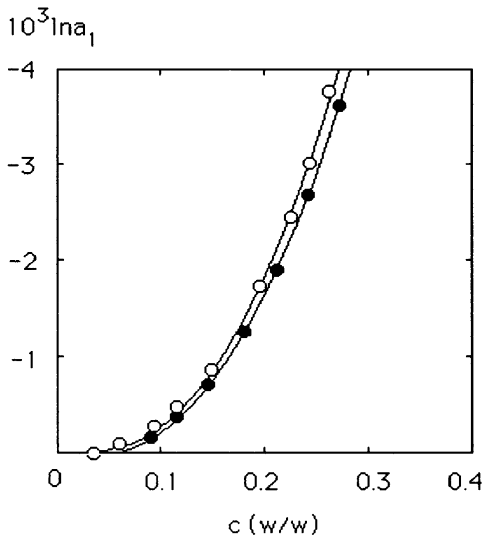

Figure 4.: Solvent activity a_1 as a function of polymer concentration in polyisodecylacrylate/methylethylketone system. (•) latex with free polymer chains; (o) the same latex after extraction of the soluble polymer fraction.

Conclusions

Measurement of particle size as a function of the activity of the diluent provides a simple way to estimate the cross-link density of latex particles. It was demonstrated that the cross-link density is independent of the solvent quality. However, the actual measured swelling degree strongly depends on the diluent. Good agreement has been found between the results obtained for the elastic modulus from independent swelling and rheological measurements. Consequently this method enables the comparison of cross-link densities of chemically different latices swollen by different diluents.

The results presented here clearly demonstrate that the equilibrium concentration of the network is rather insensitive to the presence of soluble polymer fraction, i.e., in partially cross-linked polymer latices, swelling measurements do not provide straightforward information on the cross-link density.

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