JOURNAL OF MATERIALS SCIENCE 23 (1988) 4141–4143

Origins of phase separation in gels

I. M. LOW*, R. McPHERSON
Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Melbourne, Australia.

The phenomenon of phase separation in gels is established both theoretically and experimentally. The origin is attributed to the unfavourable free energy of mixing and/or the inherent polymerization and condensation of polymer species in gels.

1. Introduction

Phase separation is a common phenomenon in glass systems and polymer solutions. It can bring about important influences on the material properties of glasses and polymers. Phase separation can occur both stably and metastably. The former prevails in the melt and is a common feature in aqueous and organic solutions [1–3], where separation of a liquid into two immiscible liquid phases occurs. On the other hand, the metastable or glass-in-glass phase separation is confined at temperatures below the liquidus temperature of crystallization [4].

Recent developments in the gel technology have indicated that the phenomenon of phase separation is also prevalent in desiccated gels [5–8]. However, the origin of this fascinating phenomenon in gels remains enigmatic although Tanaka [5] and Brinker and Scherer [7] have, respectively, attempted to explain it in terms of thermodynamics and polymer chemistry.

In this paper, results are reported from experimental evidence of phase separation in gels by electron microscopy, and two theoretical concepts are advanced to verify the existence of this phenomenon in desiccated gels.

2. Experimental procedure

Commercial purity silicon tetraethoxide and laboratory-prepared zirconium tetraethoxide and aluminium isopropoxide were used as starting raw materials for the preparation of gels. The mixed alkoxide solution was initially dissolved in carbon tetrachloride and diluted in ethanol. The mixture solution was then hydrolysed dropwise with water while stirring vigorously. The molar ratio of water/alkoxide was about 50 : 1. Upon completion of hydrolysis, a plastic film with several holes was used to seal the container and the solution was allowed to gel over a period of several days in a constant humidity oven in which the temperature was increased in steps from 40 to 80° C. Heat treatment of these gels at higher temperatures was carried out in a differential thermal analysis (DTA) furnace with a heating rate of $10^\circ\mathrm{C\,min^{-1}}$. Three samples of gels with different compositions were prepared: (a) SiO_2 + 20 wt % ZrO_2, (b) SiO_2 + 20 wt % ZrO_2 + 3 wt % Al_2O_3, (c) SiO_2 + 30 wt % ZrO_2 + 32 wt % Al_2O_3. The electron microscopy of the gels was performed on the sample directly, whereby a few grains of finely ground powders were placed on a 400 mesh copper grid and observed under a transmission electron microscope (Joel 100c) at 100 kV.

3. Results

Electron micrographs of three gel samples in the silica–aluminia–zirconia system apparently exhibit the phenomenon of microscopic phase separation at ambient temperatures (Fig. 1). The phase-separated structures also appear to persist in the gels at higher temperatures (Fig. 2). Evidently, the phenomenon of phase separation in gels is indicated.

4. Discussion

The origin of this intriguing phenomenon in gels may be conceptualized from two schools of thought.

1. Both experimental and theoretical evidence suggest that phase separation will occur during polymerization and condensation as the polymers formed are mutually insoluble with solvent-rich phases and they tend to adopt structures with the lowest degree of polymerization, giving rise to microscopic phase separation with the formation of spheroidal polymers uniformly dispersed in the solvent. As a result, a microphase-separated, interconnected structure is formed.

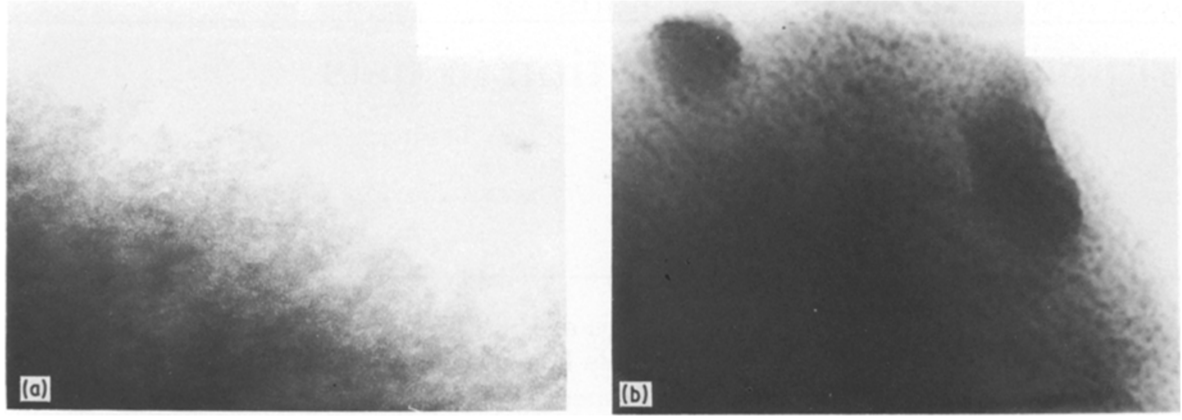
2. As the process of gelling involves polymerization, the partially hydrolysed alkoxides may be viewed as polymer species. The Gibb's free energy of mixing, G^m, is applicable in gels and it dictates the compatibility of these different polymer species during mixing. According to Gibb's expression $\Delta G^m = \Delta H^m - T\Delta S^m$, the blending of two different polymer species into a homogeneous solution is dependent on the heat (H^m), T, and entropy of mixing, S^m. To achieve homogeneity at the molecular level, the condition $G^m < 0$ must be fulfilled. The gain in the free energy of mixing due to the entropy S^m, is negligible when long chain polymers are involved.

Flory's formula [9] for free energy of mixing of gels may also be used to demonstrate the compatibility of multi-component polymer species in gels as a function of temperature and composition. According to Flory,

---

**Present address:* Department of Chemical and Materials Engineering, University of Auckland, Auckland, New Zealand.

0022-2461/88 $03.00 + .12



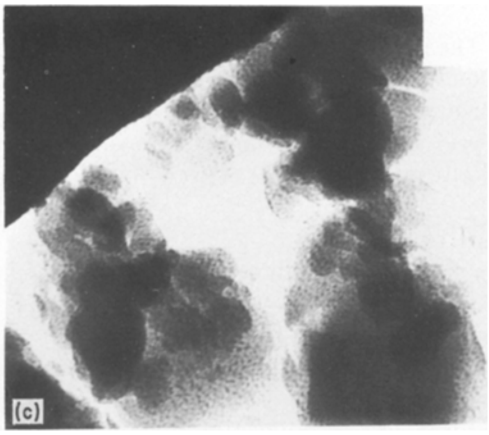


Figure 1 Transmission electron micrographs of gel sampler at ambient temperature. (a) Sample a,(b) Sample b, (c) Sample c. × 225 000.

the osmotic pressure, π, in a gel may be represented by

$$\pi = -RT\left\{\ln(1-\phi) + \phi + \frac{\theta}{2T}\phi^2 + \nu_0\left[\left(\frac{\phi}{\phi_0}\right)^{1/3} - \frac{\phi}{2\phi_0}\right]\right\} \qquad (1)$$

where R is the gas constant, T the absolute temperature, θ the theta temperature, ϕ the volume fraction occupied by the network in the gel, ϕ_0 the volume fraction of an uncross-linked single polymer chain in the absence of interaction between segments in the chain, and $\nu_0 = n_0/u_0$ where n_0 is the number of cross-links per unit volume of gel with the volume fraction $\phi = \phi_0$, and u_0 is the effective volume of each cross-link.

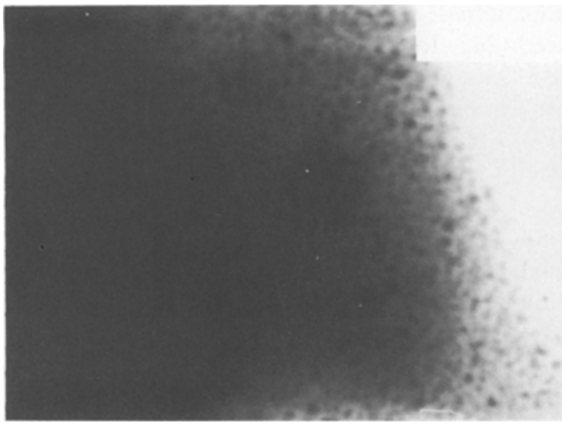


Figure 2 Transmission electron micrographs of gel sample b treated at around 500° C. × 225 000.

The first two terms in Equation 1 represent the entropy and the third term the enthalpy of mixing of the polymer network and the fluid. The last term represents the excess rubber elasticity of the network due to the volume changes of the gel. The theory predicts that if π is negative, the gel separates into two phases for which $\pi = 0$.

Equation 1 may be used in conjunction with the Gibb's expression to show that gels are thermodynamically unstable at all temperatures and compositions, favouring the phenomenon of microphase separation to take place. From Equation 1

$$\Delta H^{\mathrm{m}} = \frac{\theta}{2T}\phi^2$$

$$\Delta S^{\mathrm{m}} = \phi + \ln(1-\phi)$$

Substitution of ΔH^{m} and ΔS^{m} into the Gibb's expression, gives

$$\begin{aligned}
\Delta G^{\mathrm{m}} &= \frac{\theta}{2T}\phi^2 - T[\phi + \ln(1-\phi)] \\
&= \frac{\theta}{2T}\phi^2 - T\left[1 - \left(\phi + \frac{\phi^2}{2} + \frac{\phi^3}{3} + \frac{\phi^4}{4} + \cdots + \frac{\phi^n}{n}\right)\right], \quad n \neq 0 \\
&= \frac{\theta}{2T}\phi^2 + T\left(\frac{\phi^2}{2} + \frac{\phi^3}{3} + \frac{\phi^4}{4} + \cdots + \frac{\phi^n}{n}\right) \\
&= \phi^2\left[\frac{\theta}{2T} + T\left(\frac{1}{2} + \frac{\phi}{3} + \frac{\phi^2}{4} + \cdots + \frac{\phi^{n-2}}{n}\right)\right], \quad n \neq 0 \\
&\geqslant 0, \quad n \geqslant 2
\end{aligned}$$

Clearly, for all compositions and temperatures, the Gibb's free energy of mixing in gels is always positive and greater than zero, a condition which is conducive for gels to separate into polymer-rich and solvent-rich phases. However, homogeneity of multi-component gels is still maintained in the polymer-rich phases and persists during drying and calcination where the solvent-rich phases are eliminated, giving rise to a microporous but homogenous gel matrix.

The above model provides a powerful insight into the inherent phenomenon of microphase separation in gels which may have profound influence on the crystallization behaviour of gel-derived glasses. Using a similar approach, Tanaka [5] has extended Flory's formula to predict and observe the collapse of polyacrylamide gels upon changing the temperature or fluid composition. Phase separation in gels was also observed by Schaefer and Keefer [8]. Brinker and Scherer [7] pointed out that conditions during the process of gelation favour the occurrence of phase separation in gels. As the gelling point is reached, fluctuations in polymer density grow larger in amplitude and scale as the gel separates into regions of high and low polymer density. These density fluctuations are believed to promote additional cross-linking as unreacted terminal groups (OH and OR) come into contact in regions of higher polymer density. This increased cross-linking will tend to accelerate the phase-separation process. However, they believed that the process of phase separation could be completely suppressed in acid catalysed gels as observed by Brinker *et al* [10] and Nogami and Moriya [11]. A perusal of gel microstructures obtained by the latter workers (their Figs 4 [10] and 7 [11], respectively) does not indicate that homogeneous or single-phase gels were achieved as claimed, but that phase separation persisted although at a finer scale. Hence, it is very unlikely that phase separation in gels can be completely suppressed although its scale may be monitored to approach, but not reach, single phase. These results serve to indicate a close similarity between various gels (in relation to their microstructure) irrespective of mixing history or polymer species and a striking resemblance to the phenomenon of phase separation during blending of polymers in the plastic industries.

5. Conclusions

The phenomenon of phase separation in gels has been both theoretically and experimentally indicated. The origin of this intriguing phenomenon was attributed to the unfavourable free energy of mixing and/or to the inherent polymerization and condensation of polymer species in a gel, giving rise to the formation of polymer-rich and solvent-rich phases, which when dried yield a microporous gel structure.

Acknowledgements

The author thanks R. McPherson and M. Gani for their useful discussions, and Monash University for providing the financial assistance in the form of a research scholarship.

References

1. J. GRIEG, *Amer. J. Sci.* **13** (1972) 1.
2. F. P. GLASSER, J. WARSHAW and R. ROY, *Phys. Chem. Glasses* **1** (1960) 39.
3. E. M. LEVIN, in "Phase Diagram", Vol. 3, edited by A. M. Alper (Academic, New York, 1970) p. 143.
4. M. WANATABE, H. NOAKE and T. AIBA, *J. Amer. Ceram. Soc.* **42** (1959) 593.
5. T. TANAKA, *Phys. Rev. Lett.* **40** (1978) 820.
6. *Idem, Sci. Amer.* **244** (1981) 110.
7. C. J. BRINKER and G. W. SCHERER, *J. Non-Cryst. Solids* **70** (1985) 301.
8. D. W. SCHAEFER and K. D. KEEFER, in "Better Ceramics Through Chemistry", edited by C. J. Brinker, D. E. Clark and D. A. Ulrich (North Holland, New York, 1984) p. 1.
9. P. J. FLORY, "Principles of Polymer Chemistry" (Cornell University Press, Ithaca, 1953) p. 495.
10. C. J. BRINKER, K. D. KEEFER, D. W. SCHAEFER and C. S. ASHLEY, *J. Non-Cryst. Solids* **48** (1982) 47.
11. M. NOGAMI and Y. MORIYA, *ibid.* **37** (1980) 191.

Received 10 July
and accepted 9 October 1987