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Vapor pressure over stressed coating films

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Summary

During formation of films from solutions of reactive polymers, crosslinking and solvent evaporation occur simultaneously but with different rates. If the film adheres to the substrate, the formed network shrinks only in the direction normal to the film surface and lateral strains develop. It was demonstrated theoretically that the lateral strain reduces the activity of the solvent in the film and thus lowers the evaporation rate.

Introduction

During formation of organic coating films from solvent-based formulations, including high-solid compositions, several processes take place simultaneously (1,2):

- solvent or a mixture of solvents evaporate
- chemical reaction proceeds by which molecular weight of the polymer binder increases and a three-dimensional network is formed
- the glass transition temperature of the system increases as a result of both the proceeding crosslinking reaction and decreasing solvent concentration

The progress of chemical reaction and the rate of solvent evaporation determine the increase in T_g. When T_g approaches or exceeds the reaction temperature, the curing reaction becomes diffusion-controlled and greatly retarded; the solvent evaporation slows down as well. The so-called *solvent retention* (retention of residual solvent in the coating film even after long drying times especially in the case of ambient temperature drying) is a very serious problem affecting the quality and durability of coating films. In a number of papers (cf., e.g., Ref.(3)), the coating film formation with simultaneous crosslinking reaction and solvent evaporation was modeled resulting in drying regime maps as a function of film thickness. In these studies, ideal solution behavior and validity of Raoult law were assumed. However, thermodynamic interactions and gradients of chemical potential play an important role among factors affecting the film formation and solvent retention. In this communication, the effect of developing strain in adhering films on solvent vapor pressure is analyzed.

The rate of solvent evaporation is proportional to or a function of the vapor pressure, p_1, at the film surface, which is considered to be in dynamic equilibrium with the

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upper layer of the film. In equilibrium, the vapor pressure is a function of the solvent activity, a_1, in the film

$$p_1 = p_1^0 a_1 \tag{1}$$

The solvent activity, first in the uncrosslinked and later in the crosslinked film, is a function of concentration, polymer-solvent interaction parameter, and molecular weight or crosslinking density. Three limiting situations can arise:

1. The coating film *does not adhere* to the substrate: when the network is formed and the solvent evaporates, the film shrinks isotropically in all directions. If a network is formed before evaporation of a major part of the solvent, a change in the memory term, ϕ_2^0 (see below), must be considered.

2. The film *adheres* to the substrate and *solvent evaporation is much faster* than the crosslinking reaction; the network is formed in an almost dry system. The network structure is normal.

3. The film *adheres* to the substrate and the *chemical reaction is much faster* than solvent evaporation. Then, on solvent evaporation, the film becomes anisotropic because it can shrink only in the direction normal to the surface

The aim of this contribution is to demonstrate the effect of the film adherence to the substrate and of the resulting anisotropy of the swollen film on the vapor pressure of the solvent over the film. The Flory/ Flory-Erman (4-6) theories will be used.

Thermodynamics of Swelling

The change in Gibbs energy associated with swelling, ΔG_{sw}, of a non-ionized gel can be considered to be composed of the mixing and network contributions, ΔG_{mix} and ΔG_{net}, respectively. It is further assumed that these contributions are additive (4)

$$\Delta G_{\mathrm{sw}} = \Delta G_{\mathrm{mix}} + \Delta G_{\mathrm{net}} \tag{2}$$

The term ΔG_{net} is associated with deformation of the elastically active network chains (EANC) and other deformation dependent entropic changes originating in fluctuation of junctions (crosslinks) (4-6). In further considerations, a constant external pressure is assumed.

For Gaussian chains

$$\frac{\Delta G_{\mathrm{net}}}{\mathrm{k}T} = A_{\mathrm{f}} n_{\mathrm{e}} \left(\frac{L_x^2}{L_{0x}^2} + \frac{L_y^2}{L_{0y}^2} + \frac{L_z^2}{L_{0z}^2} - 3 \right) - B n_{\mathrm{e}} \ln(L_x L_y L_z / L_{0x} L_{0x} L_{0x}) \tag{3}$$

where L_k is the length of the deformed sample in the direction of the *k* axis; L_{0k} is the corresponding value at a reference state at which the chains have their unperturbed dimensions; n_{e} is the number of elastically active network chains. A_{f} is the front factor which, within the framework of the Flory-Erman junction-fluctuation rubber-elasticity theory, varies between $(f_{\mathrm{e}} - 2) / f_{\mathrm{e}}$ and 1 for phantom and affine models, respectively; f_{e} is the average functionality of an elastically active crosslink; *B* varies between 0 (phantom network) and 1 (affine network).

For the mixing contribution, ΔG_{mix}, of N_2 base units of the polymer (the volume of a base unit is equal to the volume of a solvent molecule) with N_1 solvent molecules, $N_1 + N_2 = N$, the Flory-Huggins theory was used

$$\Delta G_{\text{mix}} = kTN(\phi_1 \ln \phi_1 + (\phi_2/r)ln\phi_2 + \chi\phi_2\phi_1) \tag{4}$$

where ϕ_2 and ϕ_1 are volume fractions of the polymer and solvent in the swollen network, respectively; χ is the polymer-solvent interaction parameter (possibly concentration-dependent) r is the number of polymer segments equivalent to a solvent molecule (proportional to the degree of polymerization or molecular weight of the polymer); $r \to \infty$ for a network.

The deformation ratios with respect to the reference state are defined by

$$\Lambda_x = \frac{L_x}{L_{0x}}, \quad \Lambda_y = \frac{L_y}{L_{0y}}, \quad \Lambda_z = \frac{L_z}{L_{0z}}$$

Vapor Pressure over Isotropically Swollen Network

For isotropic swelling, $\Lambda_x = \Lambda_y = \Lambda_z = \Lambda$, so that

$$\Delta G_{\text{sw}} = kTN_2(\phi_1 \ln \phi_1 + (\phi_2/r)ln\phi_2 + \chi\phi_2\phi_1) + 3kTn_{\text{e}}\left(A_{\text{f}}\Lambda^2 - B\ln\Lambda\right) \tag{5}$$

The deformation ratio Λ is related to ϕ_2 as follows

$$\Lambda = \phi_2^{-1/3}(\phi_2^0)^{1/3} \tag{6}$$

where ϕ_2^0 refers to the reference state at network formation; ϕ_2^0 is assumed to be equal to the volume fraction of polymer during network formation (7).

The equilibrium degree of swelling is determined by the equality of chemical potentials, μ_i, of any components i in both phases. The chemical potentials are obtained by differentiation of ΔG_{sw} with respect to the number of moles of the solvent.

$$\frac{\Delta\mu_1}{\text{R}T} = \ln a_1 = \ln(1-\phi_2) + \phi_2(1-\frac{1}{r}) + \chi\phi_2^2 + \nu_{\text{e}}\bar{V}_1(A_{\text{f}}(\phi_2^0)^{2/3}\phi_2^{1/3} - B\phi_2/2) \tag{7}$$

In this equation, a_1 is the solvent activity, $\bar{V}_1$ is the molar volume of the solvent, and ν_e is the concentration of elastically active network chains (EANC) in unit volume of dry network; as before, for a network (infinite molecule) $1/r = 0$.

For equilibrium with pure solvent, $a_1 = 1$, so that the right-hand side of Eq. (7) is equal to 0. For volume fractions of the polymer higher than those corresponding to maximum swelling, $\Delta\mu_1$ is related to vapor pressure of the solvent, p_1,

$$p_1 = p_1^0 a_1 = \exp\{\ln(1-\phi_2) + \phi_2(1-1/r) + \chi\phi_2^2 + \nu_{\text{e}}\bar{V}_1(A_{\text{f}}(\phi_2^0)^{2/3}\phi_2^{1/3} - B\phi_2/2)\} \tag{8}$$

Vapor Pressure over a Strained Network

For strained crosslinked films, the isotropy condition ($\Lambda_x = \Lambda_y = \Lambda_z = \Lambda$) does not hold any longer. During solvent evaporation, only the thickness changes (the coordinate x by definition), whereas the y and z dimensions do not change.

The extension ratios for one-dimensional deformation of the film as a result of evaporation are expressed by the following relations

$$\Lambda_x = L_x/L_{0x}, \quad \Lambda_y = \Lambda_z = 1$$

Futhermore,

$$\Lambda_x = \frac{L_x}{(L_x)_{\mathrm{dry}}} \frac{(L_x)_{\mathrm{dry}}}{L_{0x}} = \phi_2^{-1}\phi_2^0 \tag{9}$$

and

$$\Delta G_{\mathrm{net}} = (A_{\mathrm{f}} kTn_{\mathrm{e}}/2)(\Lambda_x^2 - 1) - BkTn_{\mathrm{e}}/2\Lambda_x \tag{10}$$

After differentiation with respect to N_1 and rearrangements, one gets for the respective contribution to the chemical potential

$$\Delta\mu_1 = RT\nu_{\mathrm{e}}\bar{V}_1[A_{\mathrm{f}}(\phi_2^0)^2\phi_2^{-1} - (B/2)\phi_2] \tag{11}$$

and the equation relating the chemical potential, activity, and vapor pressure to the solvent concentration reads

$$p_1 = p_1^0 a_1 = \{\exp \ln(1-\phi_2) + \phi_2(1-1/r) + \chi\phi_2^2 + \nu_{\mathrm{e}}\bar{V}_1[A_{\mathrm{f}}(\phi_2^0)^2\phi_2^{-1} - (B/2)\phi_2]\} \tag{12}$$

The only difference exists in the elastic terms $(\Delta\mu_1)_{\mathrm{e1}}$:

$$\begin{array}{ll} \text{isotropic} & \nu_{\mathrm{e}} A_{\mathrm{f}} \bar{V}_1 \phi_2^{1/3}(\phi_2^0)^{2/3} \\ \text{strained} & \nu_{\mathrm{e}} A_{\mathrm{f}} \bar{V}_1 \phi_2^{-1}(\phi_2^0)^2 \end{array}$$

A quick inspection shows that for $\phi_2^0 = \phi_2$ which corresponds to the incipient evaporation, both terms are identical because

$$\phi_2^{1/3}(\phi_2^0)^{2/3} = \phi_2^{-1}(\phi_2^0)^2 = \phi_2$$

In the region of interest ($\phi_2 > \phi_2^0$), the contribution of the network term to $\Delta\mu_1$ is smaller if the film is strained compared with the isotropic case. This means that the solvent activity in the strained film is lower than in a free film. This retards the solvent evaporation. Figure I shows fictive examples of dependences of the relative vapor pressure of a solvent on solvent concentration for different values of the polymer-solvent interaction parameter χ. Constant values of $\chi = 0.40$ and concentration-dependent $\chi = 0.40 + 0.30\phi_2$ (in Eqs. 7, 8, 12) were chosen.

The glass transition temperature is always considered lower than the film-drying temperature, which means that the network is in the rubbery state. One can see that the effect of strain can be quite considerable. The vapor pressure of solvent over the strained film in the affine limit ($A = 1$, $B = 1$ is lower by a factor of 2 (Fig. 1a). In the phantom network limit ($A = 1/2$, $B = 0$), the differences are smaller. However, for low concentration of solvent the affine limit behavior seems to be more realistic. In this fictive example, some of the parameters (ν_{e}, V_1, ϕ_2^0) are close to experimental values. One can see, however, that in several cases the relative vapor pressure reaches the value 1 when $\phi_2 > \phi_2^0$. This can happen in two cases: (1) if crosslinking is much faster than evaporation, phase separation must occur and, consequently, ϕ_2^0 changes, or (2) evaporation occurs and ϕ_2^0 also changes. This case is discussed below.

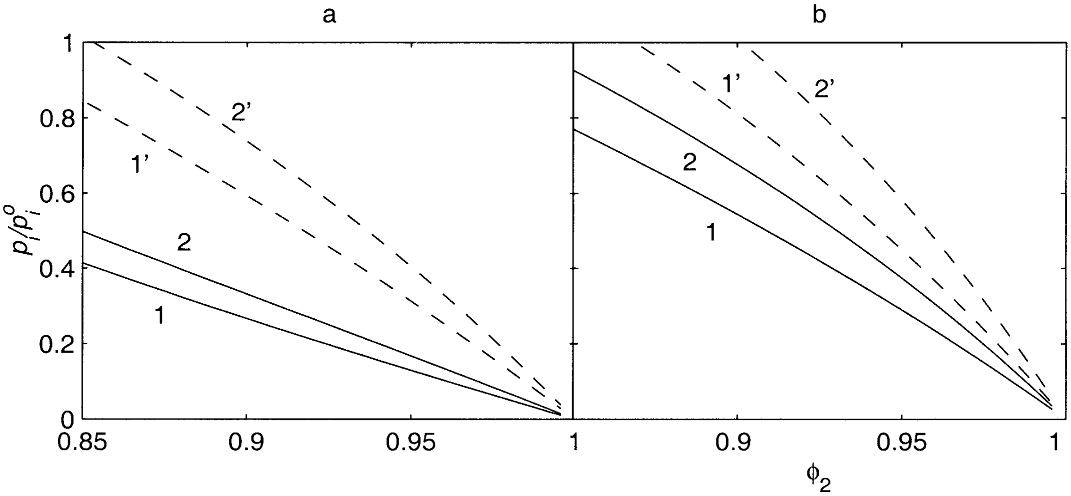

Figure 1
Dependence of the relative vapor pressure, p_1/p_1^0, for different values of the interaction parameter χ ($\nu_e = 0.0228$ mol/ml, $V_1 = 131$ ml/mol, $\phi_2^0 = 0.567$); values of χ: *1,1'* 0.40, *2,2'* $0.40 + 0.30\phi_2$; *1,2* strained state (adhering film); *1',2'* isotropic state (non-adhering film). Fig.1a, affine limit: $A = 1$, $B = 1$; Fig. 1b, phantom limit: $A = 1/2$, $B = 0$.

Simultaneous Evaporation and Crosslinking

If the network is built-up simultaneously with solvent evaporation, both the solvent content and the concentration of elastically active network chains change. The memory term ϕ_2^0 changes simultaneously. To express this change, one can extend the two-network hypothesis proposed by Andrews et al. (8,9) which was employed later in the theoretical description of phase separation during network formation (10). For a system composed of two networks prepared in stages 1 and 2, respectively, Eq. (13) holds

$$\overline{\phi_2^0} = \frac{1}{\Delta(\nu_e)_1 + \Delta(\nu_e)_2}\left[(\phi_2^0)_1\Delta(\nu_e)_1 + (\phi_2^0)_2\Delta(\nu_e)_2\right] \tag{13}$$

where the total crosslinking density ν_e is a sum of contributions by crosslinks introduced in stages 1 and 2

$$\nu_e = \Delta(\nu_e)_1 + \Delta(\nu_e)_2 \tag{14}$$

For a continuous change of the solvent content and crosslinking density,

$$\overline{\phi_2^0} = \frac{1}{\nu_e}\int_{\nu=0}^{\nu_e}(\phi_2^0)\mathrm{d}\nu \tag{15}$$

The integration starts at the gel point where $\nu_e = 0$ and the value of $\phi_2^0 = (\phi_2^0)_g$ corresponds to the dilution at the gel point. The quantity $\overline{\phi_2^0}$ then replaces ϕ_2^0 in the equations given above.

Before the gel point, the change in vapor pressure is controlled mainly by the increasing molecular weight expressed by the variable r and possibly by a change in the interaction parameter χ. Beyond the gel point, p_1 is determined mainly by the increase in concentration of EANC's, ν_e. Closer to the gel point, the combined effect of sol (composed of molecules of finite molecular weights) and gel (infinite molecular weight) is to be considered. Contributions by sol and gel are considered to be additive.

To predict the dependences of vapor pressure on solvent content given by ϕ_2, a branching theory offering network parameters like r, ν_e, and sol and gel fractions as functions of conversion of functional groups and thermodynamics of the system should be combined.

Conclusions

It has been demonstrated theoretically that anisotropic deformation of the network as a result of solvent evaporation from films adhering to the substrate causes a decrease in the solvent vapor pressure over the film and assists solvent retention. The faster is the crosslinking reaction relative to solvent evaporation, the lower is the vapor pressure over the film due to earlier gelation and onset of the strain effect. The solvent retention is expected to be higher.

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References

1. Dušek K, Havlíček I (1993) *Prog. Org. Coat*. 22: 145
2. Dušek K (1996) *Polym. Networks Gels* 4: 383
3. Cairncross RA, Francis LF, Scriven LE (1996) *AIChE J*. 42: 55
4. Flory PJ (1953) *Principles of Polymer Chemistry*, Oxford Univ.Press, Ithaca
5. Flory PJ (1976) *Proc. R. Soc., Ser. A*, 351: 351
6. Erman B, Flory PJ (1982) *Macromolecules* 15: 806
7. Dušek K, Prins W (1969) *Adv. Polym. Sci*. 6: 1
8. Flory PJ (1960) *Trans. Faraday Soc*. 56: 722
9. Andrews RD, Tobolsky AV, Hanson EE (1946) *J. Appl. Phys*. 17: 352
10. Dušek K (1967) *J. Polym. Sci., Pt. C* 16: 1289