Effective medium approximations for penetrant sorption in glassy polymers accounting for excess free volume

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ABSTRACT

An accurate determination of a penetrant volume fraction in a swollen polymer is of crucial importance in a range of different technologies. Using optical methods, such as in-situ spectroscopic ellipsometry, it is possible to extract the thickness and refractive index of dry and swollen polymer films. The volume fraction of the penetrant can then be calculated from the change in thickness, or from the refractive index using effective medium approximations. For thermodynamically equilibrated and ideal swollen rubbery polymers, these calculations yield accurate results. However, for glassy polymers the influence of the excess free volume trapped within the polymer network during vitrification is rarely taken into account. In this work we investigate the effect of excess free volume in the calculations of penetrant volume fraction in a model glassy polymer − penetrant system. The influence of the excess free volume is included by extrapolating the properties of an equilibrium polymer matrix from above its glass transition temperature. The error between the approaches that do, and do not, take account for the non-equilibrium of the glassy polymer is quantified and the implications for other systems are discussed. The errors are shown to be very significant, especially when the dry polymer has a large excess free volume. Such materials are particularly relevant in membrane applications.

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1. Introduction

Penetrant-swollen thin films are encountered in a range of technologies, including drying processes, coatings, and membrane applications [1–3]. The properties of such thin films are strongly affected by the presence of the penetrant. This calls for methods that allow accurate study of the extent of penetrant uptake in the thin film.

Properties of thin swollen films have been studied with different optical methods, such as in-situ spectroscopic ellipsometry [4–26], white light or laser interferometry [27–31] and optical reflectivity [32]. These optical methods usually provide the extent of thickness dilation, as well the change in the refractive index of the films upon penetrant (de)sorption. It is possible to estimate the solvent volume fraction from this information. The changes in dilation can be directly related to changes in volume, and hence in a volume fraction. From the refractive index of the swollen films, a volume fraction of solvent can be estimated using effective medium approximation (EMA) methods [33]. An EMA method describes the macroscopic properties of a mixture by averaging the properties of the components it consists of on a molecular level. EMA's have been successfully used for accurate quantification of sorption of, chemically similar, penetrants in rubbers [4,14–16,19,23,34,35]. For these binary systems, it is reasonable to assume that the individual properties of the penetrant and polymer matrix remain unchanged upon mixing. In contrast to rubbers, dry glassy polymers are inherently non-equilibrium systems. In glassy polymers excess free volume exists. This excess free volume is trapped kinetically within the polymer matrix due to a dramatic increase of polymer chain relaxation times upon vitrification. In effect, the excess free volume renders the dry polymer to be a two-component mixture; an equilibrium polymer matrix containing an additional void fraction. In EMA calculations on polymer swollen from an initial non-equilibrium state, the excess free volume is often not accounted for [6,10,11,15,18,20,21,24,36–42]. This may lead to inaccurate, usually underestimated, results. Optical investigations of sorption in glassy polymers that do consider the influence of the unrelaxed excess free volume are very rare [26,31].

In this work, the effect is investigated of excess free volume on the quantitative determination of solvent uptake by an initially

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glassy polymer film. Two well-known EMA methods are compared and confronted with a simple volume balance based on dilation. An approach is proposed to appropriately take the excess free volume fraction into account by considering the extrapolated properties of a hypothetical equilibrium liquid polymer, below the glass transition. Sorption of n-octane by polystyrene (PS) is used here as an illustrative model glassy polymer−liquid penetrant system. The method can be readily extended to other systems, and estimates are given for the error introduced in typical polymer−penetrant systems.

2. Theory

2.1. Contributions to volume in glassy polymers

According to the Free Volume Theory of glass transition [43], glassy polymers contain a certain excess free volume fraction that is trapped within the material structure below the glass transition temperature. In Fig. 1 the specific volume of a glassy polymer in the temperature range covering the glass transition is schematically presented.

The molar volume of a polymer is often divided into several components. The occupied volume is the hard sphere volume of atoms and molecules building the polymer chains. It is sometimes referred to as van der Waals volume and can be approximated by the group contribution calculations [45]. It is usually hard to access it experimentally. The Interstitial volume represents the effective volume of a polymer chain. It is considered non-permeable neither for macromolecular segments or diffusing small molecules. The difference between the interstitial free volume and the macroscopic volume of a polymer specimen, represented by the topmost line in Fig. 1, is referred to as fractional or Hole free volume. The macroscopic volume of a dry liquid polymer, v_{DL}, can be considered a sum of the interstitial and Hole free volumes.

For ideal systems above their glass transition temperature, rubbers or liquids, it is expected that macroscopic partial liquid volumes of the polymer and a liquid penetrant mix additively. The partial molar volumes of the components in the mixture do not differ from their pure partial molar volumes. In a dry glassy polymer, however, a certain excess free volume exists, v_{EFV}, which is a result of inability of the material volume to relax to its equilibrium liquid volume upon vitrification. This excess free volume contributes to the macroscopic volume of a dry glassy system, v_{DG}. When a penetrant mixes with a glassy polymer and the sorption induces glass transition in the mixture, the excess free volume is fully relaxed, and its fraction becomes zero. The mixture can then be
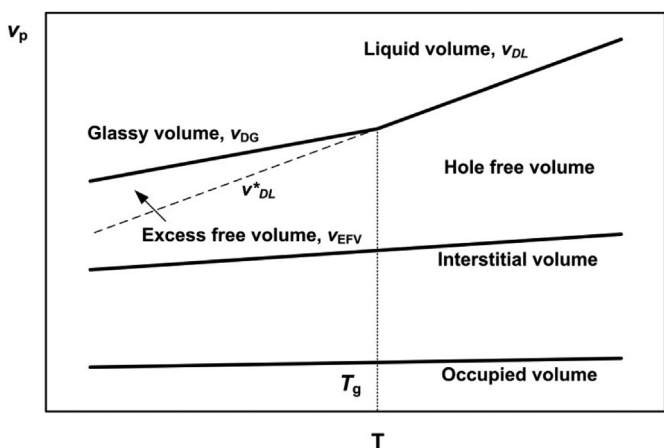

Fig. 1. Schematic representation of contributions to the molar volume in a glassy polymer in the glass transition temperature range, adapted from Ref. [44].

again considered an ideal equilibrium mixture of a penetrant and a liquid polymer. This time, however, the molar volume of the liquid polymer is different to its macroscopic (glassy) molar volume. It can be obtained by extrapolation of the equilibrium liquid volume down to the temperature where the sorption occurs, v_{DL}^{*}.

In optical reflection methods, instead of volumes the refractive indices of thin film samples are often measured. Independently, also thicknesses of thin film samples are determined. This gives the possibility to measure changes both in the (optical) density and volume of the polymer films upon sorption of various penetrants.

2.2. Methods to determine volume fractions of components in polymer − penetrant mixtures

2.2.1. From polymer film dilation

The simplest approach uses the change in the dimensions of the sample upon sorption of the penetrant. This approach inherently implies additivity of volumes of the components. For thin films the samples are assumed to swell only in the direction perpendicular to the substrate, thus the volume dilation is equal to thickness dilation (swelling). The solvent volume fraction from dilation, $\phi_S^{dil.}$, can be calculated as:

$$\phi_S^{dil.} = \frac{v_{SP} - v_{DP}}{v_{SP}} = \frac{h_{SP} - h_{DP}}{h_{SP}} \tag{1}$$

In eq. (1) v_{SP}, h_{SP} stand for the volume and thickness of the swollen polymer, v_{DP}, h_{DP} stand for the volume and thickness of the dry polymer. Eq. (1) does not distinguish whether the dry polymer was an equilibrium liquid (rubber) or a non-equilibrium glass before contact with the penetrant.

2.2.2. Bruggeman effective medium approximation (BEMA)

The optical properties of a mixture of two or more materials can be calculated using an EMA. Such an EMA theory provides a mix of the optical dispersions of the components, using their dielectric constants, ε, or refractive indices, n. For transparent materials $\varepsilon = n^2$ holds. The most commonly used EMA formulation by Bruggeman (BEMA) [33], is expressed for two materials as:

$$\phi_1 \frac{n_1^2 - n_{mix}^2}{n_1^2 + 2n_{mix}^2} + \phi_2 \frac{n_2^2 - n_{mix}^2}{n_2^2 + 2n_{mix}^2} = 0 \tag{2}$$

where ϕ_1 and ϕ_2 are the volume fractions of material 1 and 2; n_1, n_2, n_{mix} are refractive indices of material 1, 2, and their mixture, respectively. The volume fraction of material 2 can be also expressed as $(1-\phi_1)$. For porous materials, for instance, material 2 is void ($n_2 = 1$) and eq. (2) can be used to determine the porosity. Eq. (2) uses the n_{mix} as a reference, which makes it self-consistent. The BEMA assumes that the mixing of both materials occurs on a length-scale that is much smaller than the wavelength of the probing light. This is usually valid for the sorption of small molecules in polymers when light around visible region is used. The mixture is assumed isotropic.

2.2.3. Clausius − Mossotti relationship

For the estimation of mass concentrations in binary mixtures (for example polymer − penetrant) the effective medium approximation approach based on Clausius − Mossotti relationship is frequently used. It takes advantage of the dependence of the refractive index of a pure substance on its mass density ρ,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{M_w} \rho \tag{3}$$