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Model for the permeability of functionalised solutes in polymers above the glass transition involving specific interactions

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Dye diffusion thermal transfer printing involves the transport of dyes from a dye-donor film to a dye-acceptor film at high temperature, well above the glass transition of most amorphous polymers. A model has been developed for the transport of a fixed dye solute from a common dye-donor. Using the solution–diffusion model of permeability as a starting point, equations have been developed to correlate solute permeability with dye and dye-acceptor polymer structural characteristics. In this analysis, diffusivity is controlled by polymer T_g, whereas solubility is controlled by the balance of endothermic physical forces and exothermic specific interactions between dye and dye-acceptor polymer. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The control of dye transport is an important phenomenon in the dyeing of polymer fibres for coloured fabrics and the dyeing of polymer films for imaging applications. There are several publications in the literature where the importance of the polymer glass transition temperature to dye transport is highlighted in the conventional dyeing of fibres[1,2] and films[3-5]. A variety of publications have illustrated that the variation of dye diffusion coefficient above T_g is well represented by the Williams–Landel–Ferry (WLF) equation[6]. Generally, this has been proved at low dye concentrations[7,8], but is also applicable at high concentration provided that plasticisation is taken into account[9].

The control of dye delivery is also important in dye diffusion thermal transfer printing, which is a method for producing high quality continuous-tone colour images from an electronic source[10]. The printing process involves the transfer of dye from a donor ribbon to an acceptor sheet which are brought in intimate contact at high temperature and pressure. The temperature of dye transfer and the print time can vary but maximum values are typically 300°C and 12 ms, respectively. In addition to being technologically important, a thermal transfer printer represents a well-controlled and defined experimental test-bed for studying the diffusion of solutes in polymers. Typically, both the donor ribbon and acceptor sheet for thermal transfer printing are multilayer structures with each layer performing a particular function[10]. The dye transfers from a polymer coating in the donor sheet (dye-donor) to an acceptor polymer coating in the receiver sheet (dye-acceptor). It has been shown that the mechanism for dye transfer is diffusion between polymers rather than sublimation[11]. Therefore, the dye transfer process can be viewed as permeability from a dye-donor polymer to a dye-acceptor polymer where the temperature of transport is above the glass transition temperatures of both the donor and acceptor matrices. The dye transfer process has been modelled previously. Hann and Beck[10] illustrated that the use of a model involving diffusion coefficients and partition coefficients was reasonable in predicting dye transfer. More recently, Shinozaki and Hirano[12] have proposed a mechanism involving adsorption followed by diffusion.

Recently, we reported the permeability of a functionalised dye solute in various amorphous polymers above the glass transition temperature using dye diffusion thermal transfer printing[13]. For a constant temperature profile, dye permeability was a function of both diffusivity and solubility. An excellent correlation was made for solute permeability as a function of dye-acceptor polymer T_g and the solubility parameter difference between dye and dye-acceptor polymer. The limit of applicability of this previous work was defined as the transport of large solutes in amorphous polymers above T_g and in the absence of strong specific interactions. In this paper, a model is introduced to extend this study by including the effects of strong specific acid–base interactions on the transport properties of dye solutes in polymer matrices above the glass transition. Future publications will compare experimental data against this model.

METHOD

Dye diffusion thermal transfer printing

The dye transfer process occurs at temperatures of 150–300°C at the interface of dye-donor and dye-acceptor layers, well above the glass transition temperatures of these matrices. It should be noted that the temperature is not discrete during dye diffusion thermal transfer printing. During a particular print time, there is a temperature distribution since the temperature rises, peaks at a maximum and then falls[10]. Therefore, the printing process provides a very well-defined, constant temperature profile or cycle rather than a fixed, single temperature. Previous mathematical modelling[10] indicates that the maximum temperature at

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the interface between the dye-donor and dye-acceptor polymer matrices is 300°C for a print time of 13 ms. The following model has been developed to focus on the factors which affect dye transport in the dye-acceptor layer when both the dye solute and the dye-donor are constant.

Development of the solution–diffusion model of permeability

From the solution–diffusion model of permeability[14], the permeability coefficient (P) of a solute in a polymer,

$$P = D \cdot S \tag{1}$$

where D is the diffusion coefficient of the solute in the polymer and S is the solubility coefficient. For application to our system, where there is a specific temperature profile rather than a constant single temperature, P, D and S are *effective* coefficients averaged over a constant temperature range.

Fujita *et al.*[15] stated that the diffusion coefficient of a solute in a polymer can be related to free volume by the equation,

$$D = RTA_{\mathrm{d}} \cdot \exp\left(\frac{-B_{\mathrm{d}}}{f}\right) \tag{2}$$

where R is the gas constant, T is the temperature, f is the fractional free volume and both A_{d} and B_{d} are constants.

The solubility coefficient of a solute in a polymer, S, can be described by the equation[14],

$$S = S_0 \cdot \exp\left(\frac{-\Delta H}{RT}\right) \tag{3}$$

where S_0 is pre-exponential factor and ΔH is the molar heat of solution of the solute in the polymer. Expansion of equation (1) in logarithmic form followed by substitution for D and S by equations (2) and (3), leads to the expression

$$\ln P = \left\{\ln(RTA_{\mathrm{d}}) - \left(\frac{B_{\mathrm{d}}}{f}\right)\right\} + \left\{\ln S_0 - \left(\frac{\Delta H}{RT}\right)\right\} \tag{4}$$

R is constant and T has a constant profile at a constant print time. If it is further assumed that A_{d}, B_{d} and S_0 are invariant for solute–polymer combinations when the solute is constant then equation (4) becomes

$$\ln P = a_1 - b_1\left(\frac{1}{f}\right) - c_1(\Delta H) \tag{5}$$

where a_1, b_1, c_1 are constants for a particular solute in a series of polymers. It is known that the free volume is constant up to T_{g} and increases linearly with temperature above T_{g}, the fractional free volume $f\,(= \nu_f/\nu$, where ν_f is the free volume between molecules, whereas ν is the total volume) being given by

$$f = f_g + \alpha(T - T_g) \tag{6}$$

where f_{g} is the fractional free volume at the glass transition, and α is the difference between the expansion coefficients of the liquid (α_{l}) and the expansion coefficient of the glass (α_{g}), i.e. $\alpha = (\alpha_{\mathrm{l}} - \alpha_{\mathrm{g}})$. In the WLF interpretation of free-volume[6], both f_{g} and α are found to have universal values of 0.025 and 4.8×10^{-4}, respectively. Also, since the temperature profile T during thermal transfer printing is fixed at constant print time, then f is proportional to $(-T_{\mathrm{g}})$ and equation (5) can be rewritten as

$$\ln P = a_2 + b_2\left(\frac{1}{T_{\mathrm{g}}}\right) - c_2(\Delta H) \tag{7}$$

where a_2, b_2, c_2 are constants for a particular solute in a series of polymers.

The effect of non-specific interactions

In our previous paper, it has been assumed that ΔH is the heat of mixing between the two components and is defined by the equation[16,17],

$$\Delta H = \phi_{\mathrm{d}}\phi_{\mathrm{p}}(\delta_{\mathrm{d}} - \delta_{\mathrm{p}})^2 \tag{8}$$

where ϕ_{d} and ϕ_{p} are the volume fractions of dye and polymer, respectively, and δ_{d} and δ_{p} are the solubility parameters of solute and polymer, respectively. Since ϕ_{d} and ϕ_{p} are constant in the dye-donor, substitution of equation (8) into equation (7) leads to

$$\ln P = a_3 + b_3\left(\frac{1}{T_{\mathrm{g}}}\right) - c_3(\delta_{\mathrm{d}} - \delta_{\mathrm{p}})^2 \tag{9}$$

where a_3, b_3, c_3 are constants for a particular solute in a series of polymers. Equation (8) only relates to endothermic enthalpy changes and dictates that ΔH is usually positive with a minimum of zero when $\delta_{\mathrm{d}} = \delta_{\mathrm{p}}$. This results in a maximum contribution to permeability in equation (9). Therefore, equation (8) (and equation (9) which is partially derived from it) do not take account of strong, specific interactions which are known to give rise to negative enthalpy changes. Equation (9) was previously shown to be successful for the permeability of dye solutes in the absence of specific interactions[13].

Accounting for specific interactions

In order to account for specific interactions, it is further assumed that

$$\Delta H = \Delta H_{\mathrm{physical}} + \Delta H_{\mathrm{specific}} \tag{10}$$

where $\Delta H_{\mathrm{physical}}$ is now the unfavourable endothermic contribution to mixing related to dye–polymer solubility parameter differences and previously given in equation (8). If the dye contains a hydroxyl group, $\Delta H_{\mathrm{specific}}$ is the favourable specific hydrogen bonding interaction between the hydroxyl group on the dye solute and an electron-donating functional group on the dye-acceptor polymer. For a dye solute with hydroxyl groups, the strength of the specific interaction can be estimated by the infra-red absorption resulting from the vibration of O–H groups involved in intermolecular interaction. Typically, a free O–H vibration causes absorption in the infra-red spectrum at $3630\ \mathrm{cm}^{-1}$[18]. Hydroxyl groups which are subject to intermolecular specific interactions cause absorption at lower frequencies with the lowest frequencies being indicative of the strongest interactions. Therefore, it is assumed that

$$\Delta H_{\mathrm{specific}} = \mathrm{function}(\nu_{\mathrm{inter}} - \nu_{\mathrm{free}}) \tag{11}$$

where ν_{free} is the infra-red absorption frequency of free hydroxyl, whereas ν_{inter} is the infra-red absorption frequency of O–H resulting from the specific intermolecular interaction between the dye solute hydroxyl group and a polymer electron-donating functional group. Substitution of equation (10) and equation (11) into equation (7) leads to

$$\ln P = a_4 + b_4\left(\frac{1}{T_g}\right) - c_4(\delta_d - \delta_p)^2 - d_4(\nu_{\mathrm{inter}} - \nu_{\mathrm{free}}) \quad (12)$$

where a_4, b_4, c_4, d_4 are constants for a particular solute in a series of polymers.

The non-linear relationship between infra-red frequency shift and enthalpy change

A schematic representation of the specific interaction between a dye hydroxyl group and a polymer electron-donating functional group is illustrated below:

polymer — X H — O — **dye**

Hydrogen bonding between these groups affects the bond energies of the polymer–X bond, the H–X bond and the O–H bond. In the previous analysis, the frequency of O–H absorption has been used as a measure of the total energy of interaction. It should be recognised that $(\nu_{\mathrm{inter}} - \nu_{\mathrm{free}})$ actually indicates the energy changes to the O–H bond only. By using the hydroxyl frequency as a measure of the total energy of interaction it has been implicitly assumed that the strengths of polymer–X and H–X are independent of the polymer type and the nature of X. When X is constant, this is a valid assumption and the hydroxyl frequency can be used as an accurate prediction of the overall energy of hydrogen bond formation. When X varies substantially then this assumption breaks down. There have been a number of studies on hydrogen bonding between small molecules which show this to be the case. Various experiments have attempted to correlate interaction energies from calorimetric measurements with frequency shifts via infra-red spectroscopy. These are detailed in the excellent reviews by Murthy and Rao[19] and Pimentel and McClellan[20]. Successful linear correlations have been achieved for particular electron acceptors when the electron donors are similar, resulting in similar hydrogen bond energies or hydrogen bond lengths. However, studies on phenols and alcohols with a variety of electron donors show that the relationship between the total energy of hydrogen bond formation and hydroxyl frequency shift to be nonlinear, especially for electron donors giving rise to exceptionally weak or strong hydrogen bonds (i.e. exceptionally long or short hydrogen bond distances, respectively). This literature suggests that the relationship is better represented by a quadratic function of frequency rather than a linear relationship. Using a quadratic function of the hydroxyl frequency shift, equation (12) can be developed so that the permeability can be expressed as

$$\ln P = a_5 + b_5\left(\frac{1}{T_g}\right) - c_5(\delta_d - \delta_p)^2 - d_5(\nu_{\mathrm{inter}} - \nu_{\mathrm{free}}) - e_5(\nu_{\mathrm{inter}} - \nu_{\mathrm{free}})^2 \quad (13)$$

where a_5, b_5, c_5, d_5, e_5 are constants for a particular solute in a series of polymers. Equation (13) suggests that high permeability and strong, vivid colours will be obtained when the dye-acceptor T_g is low, when the solubility parameters of dye and dye-acceptor polymer are equal and when the specific interaction between dye and dye-acceptor polymer is strong. Conversely, equation (13) predicts that low permeability or barrier type properties will be obtained when the dye-acceptor T_g is high, when the difference in solubility parameters between dye and dye-acceptor polymer is large and when there are no specific interactions between dye and dye-acceptor polymer.

Comments on assumptions made during the derivation

Part of the model assumes that diffusivity is controlled solely by the T_g of the acceptor polymer, independent of the type of polymer used with the interval $(T - T_g)$ likely to have significance. It is assumed that the large-scale co-operative movement characteristic of T_g represents a large step-change in the diffusion coefficient of the solute molecule as a function of temperature, since the molecular weight of the dyes are usually 4–5 times that of a typical repeating polymer unit. This implies that the diffusion coefficient of a particular constant dye solute at the high temperatures of printing does not depend on the differences in interactions between the dye and the various dye-acceptor matrices. It is assumed that the high temperatures experienced by the dye and polymer matrices (150–300°C) increase free volume and reduce the effectiveness of intermolecular forces on diffusion coefficients. Recent work by Byers[21] on the diffusion of dyes in polycarbonate above T_g at 180°C suggests that this is a reasonable assumption. Numerous dye structures were investigated, partly to explore the effects of intermolecular hydrogen bonding. He found that dye diffusion in this constant matrix at this temperature was controlled by the shape of the dye molecule with no discernible effect of intermolecular forces on diffusion coefficients.

The development of the solute–polymer solubility terms in equations (10)–(13) has been partly based on analogous work in the field of polymer–polymer blends. In the last decade, Coleman *et al.*[22] have pioneered an approach to predict the miscibility of polymer–polymer blends. This approach has been successful in predicting the phase behaviour of a number of polymer–polymer blends involving strong, specific acid–base interactions. Practically, the miscibility of a polymer–polymer blend is governed by balancing the contribution of endothermic and exothermic interactions. Physical interactions resulting from solubility parameter differences produce unfavourable endothermic contributions to mixing. This is counteracted by the favourable specific interactions which produce negative contributions to mixing, and can be determined via equilibrium constants from infra-red spectroscopy. These considerations have been developed to include the balance of physical forces and specific interactions in our model of solute transport (see equations (12) and (13)).

CONCLUSIONS

The solution–diffusion model of permeability has been developed to describe the transport of a given dye solute from a constant dye-donor polymer to a variety of dye-acceptor polymers. It has been assumed that the diffusivity at high temperature depends on free volume and T_g, whereas solubility is governed by the relative contributions of endothermic physical forces and exothermic specific interactions. The model predicts that high permeability will be obtained when the dye-acceptor T_g is low, when the solubility parameters of dye and dye-acceptor polymer are equal and when the specific interaction between dye and dye-acceptor polymer is strong.

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