Importance of Dye Partition Coefficient in Thermal Dye Transfer Printing Efficiency

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Abstract

The importance of dye partition coefficients in thermal dye transfer printing efficiency is demonstrated by computational modeling, direct experimental measurements of dye partition coefficients, and printing efficiency measurements. Previous calculations of the effects of printing power, print head efficiency, line time, and media materials properties using the one-dimensional LaFleche-Ozimek model have predicted that a higher dye partition coefficient P should lead to higher thermal dye transfer printing efficiency. However, little or no experimental data on receiver/donor dye partition coefficients have been reported. In this work we report direct experimental measurements of dye partition coefficients for various dye/binder combinations. Values for P ranging from 0.24 to greater than 10 were obtained. Thermal printing efficiency is observed to increase with increasing partition coefficient, in agreement with the LaFleche-Ozimek model.

Introduction

Image density of a thermal print is related to the amount of dye transferred between a dye-donor layer of a dye-donor element and a dye-receiving layer of a receiving element. The amount of dye transferred between the dye-donor layer and the receiving layer can be described by the receiver/donor dye partition coefficient P, also known as the solubility coefficient, which is a measure of the amount of dye transferred from the dye-donor layer to the receiving layer at a given print speed and temperature. As the receiver/donor dye partition coefficient increases, the amount of dye transferred increases, resulting in higher image densities. Higher partition coefficients can enable reducing print energies while maintaining a given image density, increasing an image density at the same print energy, or maintaining a given image density while increasing print speed.

In this work, the receiver/donor dye partition coefficient, P, between the dye in the dye-donor layer of the donor element and the dye in the dye-receiving layer of the receiver element, is defined as the ratio of the concentration (in wt. %) of the dye in the dye-receiver layer, c_R, to the concentration (in wt. %) of the dye in the dye-donor layer, c_D, after the two layers are held in intimate contact at a temperature above the higher glass transition temperature of the dye-receiving layer or dye-donor layer for a time sufficient to achieve equilibrium in the distribution of dye between the dye-donor layer and the dye-receiving layer, for example, at 140ºC for 10 min.

$$P = c_R/c_D \qquad (1)$$

The receiver/donor dye partition coefficient P describes the equilibrium thermodynamic partitioning of a dye between two polymer films. It is a fundamental quantity of the dye/donor-polymer and dye/receiver-polymer film combination that can be independently specified. It does not depend upon the film thickness, the method of producing the partitioning between the films, or the rate of diffusion of the dye, so long as the two films are in thermodynamic equilibrium.

Modeling of the thermal dye printing system has shown that one of the most important materials characteristics that affects dye printing efficiency is the partition coefficient between the donor and receiver binder polymers [1-3]. Values of P greater than 1 are desirable, and higher values of P indicate greater dye transfer efficiency during thermal printing. As mentioned earlier, this higher efficiency can be utilized to print at higher speed and/or to print at the same speed using less dye or using lower voltages, the latter of which could extend printer head lifetime [1-3].

There have been little or no prior published data available on dye partition coefficients for thermal systems. Thus, the impact of increasing P has been modeled, but it has not been experimentally verified.

Materials Investigated

Binders representing several polymer classes were investigated in this work: polyacetals such as polyvinyl butyral, or Butvar, and polyvinylhexal [4]; cellulose esters and ethers, such as cellulose acetate proprionate, or CAP, and ethyl cellulose, or EC; acrylic polymers such as poly(methyl methacrylate), or PMMA; phenoxy resin; polyesters such as those derived from 1,4-cyclohexanedicarboxylic acid, 1, 4-cyclohexanedimethanol, and 4,4'-bis(2-hydroxyethyl)bisphenol-A [5], and polycarbonates such as those derived from bisphenol-A and diethylene glycol, or PC-1 [6]. A number of representative classes of cyan, magenta, and yellow dyes were investigated as well. These dyes and binders were coated in various combinations to investigate the relationships between dye and binder structure on the partition coefficient.

Measurement of the Partition Coefficient P

In order to measure the partition coefficient, a new technique was developed. The technique consists of coating a dye-containing donor layer on top of a receiver polymer layer of equal thickness, about 5 μm, and then heating at 140ºC for 10 min to allow the dye to partition to equilibrium between the two layers. The layers are then peeled apart and dissolved separately, and their dye concentrations measured by UV-Visible spectrophotometry. As shown in equation (1), the ratio of the concentration in the receiver polymer layer to the concentration of the dye in the donor polymer layer, normalized for mass by using weight percentages, is defined as the partition coefficient P.

The dissolution method is the most precise and accurate method for determining the dye concentration in the donor and receiver layers. The method avoids the complications of receiver dye solvatochromism, dye aggregation, nonadherence to Beer's Law, and substrate reflectivity effects that may be present in the donor and receiver at high dye concentrations. Microtoming of the original donor/receiver film sample followed by microscopy of the film cross-sections allows an independent qualitative or semiquantitative check of the solution results.

Results and Discussion

Dye partition coefficient results for CAP donor and a variety of polymer receivers are shown for four dyes in Table 1.

Table 1. Dye partition coefficient P results for CAP donor and various polymeric receivers for four dyes.

ID	Receiver	Dye	P
1	PC-1	Magenta #1	1.6
2	PC-1	Magenta #2	1.8
3	Blend-1	Magenta #1	2.1
4	Blend-1	Magenta #2	2.2
5	Butvar B76	Magenta #1	1.3
6	Butvar B76	Magenta #2	1.4
7	Polyvinylhexal	Magenta #1	1.1
8	Polyvinylhexal	Magenta #2	1.1
9	PC-1	Yellow #1	1.4
10	Blend-1	Yellow #1	1.7
11	Butvar B76	Yellow #1	1.6
12	Polyvinylhexal	Yellow #1	1.8
13	PC-1	Cyan #1	2.2
14	Blend-1	Cyan #1	2.0
15	Butvar B79	Cyan #1	1.6
16	Polyvinylacetal	Cyan #1	2.1
17	Phenoxy Resin	Cyan #1	1.8
18	PMMA	Cyan #1	1.0
19	CAP 482-20	Cyan #1	1.0

The receiver binder polymers listed in Table 1 are described in the Materials section. Blend-1 is an 80/20 blend of the polyester described in the Materials section and bisphenol-A polycarbonate. The data of Table 1 show that the dye partition coefficient P varies from 1.0 to 2.2 for the various dyes and polymers investigated when CAP is used as the donor binder. Other donor-receiver combinations of these same binders gave similar results. Because there is no a priori prediction of the dye partition coefficient for these materials, the values for P observed are not readily interpreted in terms of the polymer and dye structures. Nevertheless, it is surprising that the range of partition coefficients observed is so small, given that they represent a wide variety of polymer binders.

In Table 2, the dye partition coefficients are reported for the same dyes in the same polymers as receivers, but using EC as the donor. Surprisingly, the dye partition coefficients are up to 4.5 times larger for EC donor vs. CAP donor for this series of dyes and receivers. Again, as there is no a priori relationship or understanding of polymer/dye partition coefficients, an explanation for these data is not readily apparent. As a practical matter, however, the higher partition coefficients should result in higher dye transfer efficiency in a thermal printer. This point will be examined later.

Table 2. Dye partition coefficient P results for EC donor and various polymeric receivers for four dyes.

ID	Receiver	Dye	P
20	PC-1	Magenta #1	4.8
21	PC-1	Magenta #2	8.1
22	Blend-1	Magenta #1	5.6
23	Blend-1	Magenta #2	7.7
24	CAP 482-20	Magenta #1	1.6
25	CAP 482-20	Magenta #2	2.4
26	Blend-1	Yellow #1	5.4
27	PC-1	Yellow #1	4.8
28	CAP 482-20	Yellow #1	2.1
30	PC-1	Cyan #1	4.9
31	Blend-1	Cyan #1	5.6
32	Butvar B76	Cyan #1	4.6
33	Polyvinylhexal	Cyan #1	2.8
34	CAP 482-20	Cyan #1	1.5

The fact that there is a significant difference in P for EC vs. CAP donor suggests that there may be other combinations of dyes and polymeric donors and receivers that show high partition coefficients. An example verifying this is shown in Table 3.

Table 3. Dye partition coefficient P results for three donor-receiver polymeric binder combinations for cyan dye #2.

ID	Receiver	Donor	P
35	Polyvinylhexal	CAP 482-20	0.24
36	PC-1	CAP 482-20	1.5
37	PC-1	Polyvinylhexa l	11.0
38	Butvar B76	CAP 482-20	0.44
39	PC-1	Butvar B76	4.7

As shown in Table 3, cyan dye #2 exhibits a low partition coefficient, 0.24, when CAP is the donor and polyvinylhexal is the receiver. When CAP is the donor and PC-1 is the receiver, the partition coefficient is 1.5. These results suggest that combining polyvinylhexal as the donor with PC-1 as the receiver should give a high partition coefficient, and, as shown in Table 3, P = 11.0 for this combination. This is one of the highest thermal dye partition coefficients that we have observed.

A similar result is seen for the donor-receiver combinations involving Butvar B76, CAP, and PC-1. Cyan dye #2 exhibits a low partition coefficient, 0.44, when CAP is the donor and Butvar B76 is the receiver. When CAP is the donor and PC-1 is the receiver, the partition coefficient is 1.5. Combining Butvar B76 as the donor with PC-1 as the receiver results in a partition coefficient of 4.7.

It was of interest to examine the thermal dye transfer printing efficiency of some of the dye-polymer combinations whose partition coefficients are reported in Tables 1–3. As mentioned earlier, the LaFleche-Ozimek model predicts that a higher dye partition coefficient should produce a significantly higher dye transfer efficiency during printing, all other variables such as the dye diffusion coefficient being equal. When we examined the thermal dye transfer printing efficiency, a general correlation was observed between the dye partition coefficient and the thermal dye transfer efficiency. Examples of this correlation are shown in Table 4.

Table 4. Thermal dye printing efficiency results for dye-donor-receiver combinations having various dye partition coefficients. Printing was done using line times of 0.52 msec and printing energies of 0.653 J/cm^2.

ID	P	Dye	Density at 0.653 J/cm^2
P-1	6.4	Magenta #1, #2	1.00
P-2	1.7	Magenta #1, #2	0.77
P-3	4.8	Yellow #1	1.20
P-4	5.4	Yellow #1	0.96
P-5	1.4	Yellow #1	0.95
P-6	1.7	Yellow #1	0.71
P-7	4.7	Cyan #2	1.30
P-8	1.5	Cyan #2	1.09
P-9	0.44	Cyan #2	0.45

As can be seen in Table 4, there is not an exact quantitative correlation between print reflection density and the dye partition coefficient. Thermal dye transfer printing efficiency is affected not only by the receiver/donor dye partition coefficient P, which is an equilibrium thermodynamic quantity, but also by the diffusion coefficient of the dye, which is a kinetic quantity. We report here no quantitative data on diffusion coefficients. Nevertheless, it is clear from Table 4 that high print reflection densities are obtained only for those donor-receiver combinations having high dye partition coefficients, especially for donor-receiver combinations having P values greater than 2.5. Conversely, the lowest reflection densities are from those combinations having the lowest partition coefficients.

Summary and Conclusions

In this work we report direct experimental measurements of dye partition coefficients for various dye/binder combinations. Values for P ranging from 0.24 to greater than 10 were observed. Thermal printing efficiency is observed to increase at higher P values, especially for those greater than 2.5, and to decrease at lower P values, in agreement with the LaFleche-Ozimek model.

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Author Biography

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