Accessibility of Acrylic Fiber to Basic Dye

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Received 11 July 2006; accepted 3 April 2007
DOI 10.1002/app.26744

ABSTRACT: The accessibility of the fiber to dye is considered to be related to the fraction of the polymer segment which is mobile. This is studied by dyeing the acrylic fiber at temperatures within a 40°C range while treating the samples with different carriers. The relation of the equilibrium dye uptake (dyeability) of the acrylic fiber to the structural parameter, $\int_{20}^{T} (\tan\delta)_c \, dT$, with the presence or absence of carrier in solution is linear, confirming the validity of the hypotheses, where $(\tan \delta)_c$ is the loss tangent correlated at a temperature of 20°C. Moreover, The effect of carrier to swell the amorphous region of the acrylic fiber was less effective as temperature beyond T_g (mechanical). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 189–193, 2009

Key words: dye; fiber; modeling; structure-property relations

INTRODUCTION

The dyeability of a fiber is a measure of the ability to fix the dye molecules within the fiber. It involves a process of adsorption–exhaustion and fixation of dye molecules.[1–3] The dyeing process of an acrylic fiber is governed essentially by an ion-exchange equilibrium between the dye sites accessible and the dye cations.[4,5] Therefore, the dyeability (equilibrium dye-uptake) of an acrylic fiber is affected by the dyeing conditions and the fiber structure itself, e.g., dye concentration, dyeing temperature, pH in dye solution, the use of carrier and the degree of copolymer composition in the fiber (the amount of vinyl chloride or methyl acrylate segment in acrylic fiber).[6–12] The effect of each parameter to the dyeability is also complicated by the mutual interaction during the dyeing. In this report, we would like to classify the possible parameter into two main contributing factors, that is, the thermodynamic factor and the structural factor.[13,14]

Theoretical basis

We assume that the total dye-uptake of a fiber is mainly governed by the thermodynamic and the structural factor, i.e.,

$$C_\infty = K_T \cdot K_S \tag{1}$$

where C_∞, K_T, and K_S are the equilibrium dye-uptake of a fiber, the parameter for thermodynamic factor, and the parameter for the structural factor (the factor which is related to the dyeing available sites in the amorphous region of acrylic fiber), respectively. The thermodynamic factor K_T in eq. (1) could be expressed in terms of dye concentration C_b, temperature T, and chemical composition of a fiber f.

$$K_T = K_T(C_b, T, f) \tag{2}$$

In case of the same fiber, the chemical composition f is a constant, therefore eq. (2) can be rewritten as

$$K_T = K_T(C_b, T) \tag{3}$$

Since the effect of temperature is considered to be Arrhenius,[4] eq. (3) is

$$K_T = K_{To}(C_b)e^{-E/RT} \tag{4}$$

Substituting eq. (4) into eq. (1) we have

$$C_\infty = K_{To}(C_b)e^{-E/RT} \cdot K_S \tag{5}$$

The effect of carrier (phenol or phenylphenol) to the dye concentration is considered to be unimportant provided only a small amount of carrier being present, the $K_{To}(C_b)$ is a constant, therefore eq. (5) is

$$C_\infty = k_o{}' e^{-E/RT} \bullet K_S \tag{6}$$

The structural factor K_S in eq. (6) can be related to the mechanical properties of a fiber. Fukuda and Omen[6] studied the relation between the dyeing properties of fibers and films of poly(ethylene terephthalate) and their copolymer of poly(ethylene isophthalate) to their dynamic mechanical properties.

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Journal of Applied Polymer Science, Vol. 111, 189–193 (2009)

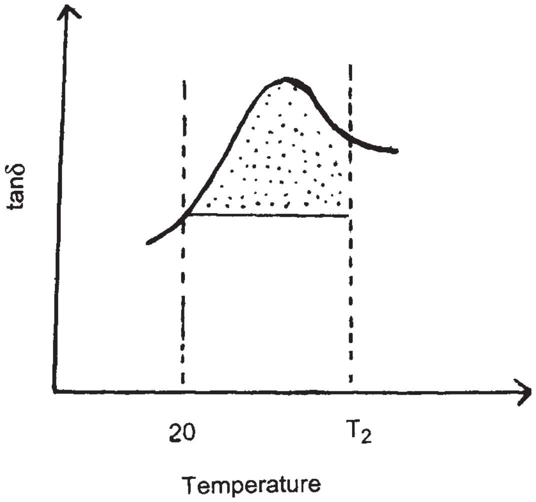

Figure 1 tan δ versus temperature. The dot area is the integration of tan δ from 20°C to T_2.

They found the color yield of a fiber to its loss tangent to be

$$\mathrm{CY} = k' \int_{20}^{T_2} (\tan\delta)_c \, dT \tag{7}$$

$$(\tan\delta)_c = (\tan\delta)_T - (\tan\delta)_{20} \tag{8}$$

The quantity (tan δ)$_c$ is a corrected value of tan δ at temperature T; k' is a constant, and T_2 is the upper integration limit which is characterized by the dye type and other dyeing conditions.

Walters et al.[7] worked on the dyeing properties of polyamide fibers with different glass transition temperatures. They considered the difference between the upper limit T_2 and mechanical transition temperature T_g to be equivalent to the dyeing temperature T_d and dyeing transition temperature T_g(dye), i.e.,

$$T_2 - T_g(\text{mechanical}) = T_d - T_g(\text{dye})$$

Therefore

$$T_2 = T_d - [T_g(\text{dye}) - T_g(\text{mechanical})] \tag{9}$$

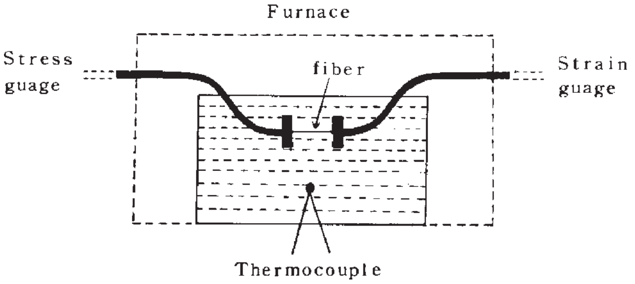

Figure 2 Cross-section of the modified bath for carrying out experiments in solution.

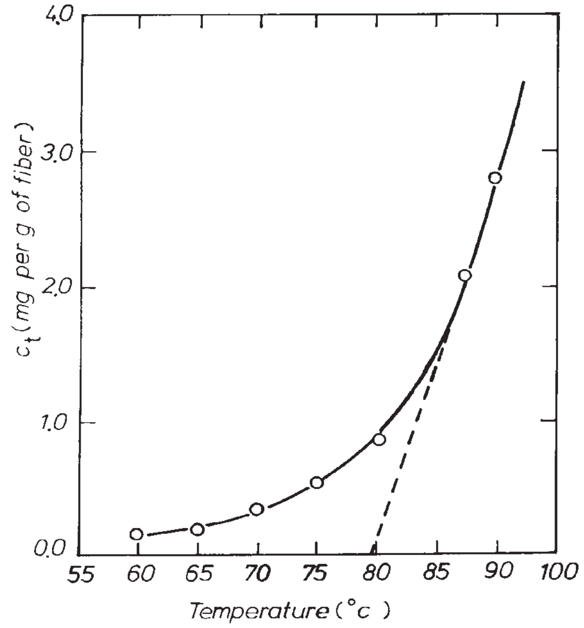

Figure 3 Dye uptake of acrylic fibers at various temperatures for dyeing time of 25 min in water.

The integration value in eq. (7), $\int_{20}^{T_2}$ (tan δ)$_c$ dT, is the area under tan δ versus temperature curve (Fig. 1), which is related to the total amount of free volume in the amorphous region of a fiber. It is a measure of structural factor K_S, therefore we put

$$K_S = k'' \int_{20}^{T_2} (\tan\delta)_c \, dT \tag{10}$$

where k'' is a constant. Substituting eq. (10) into eq. (6) we have

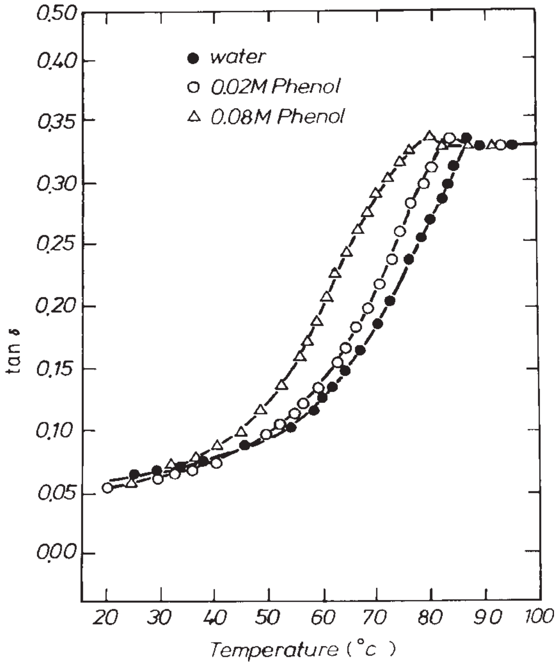

Figure 4 tan δ versus temperature in the presence or absence of phenol in water.

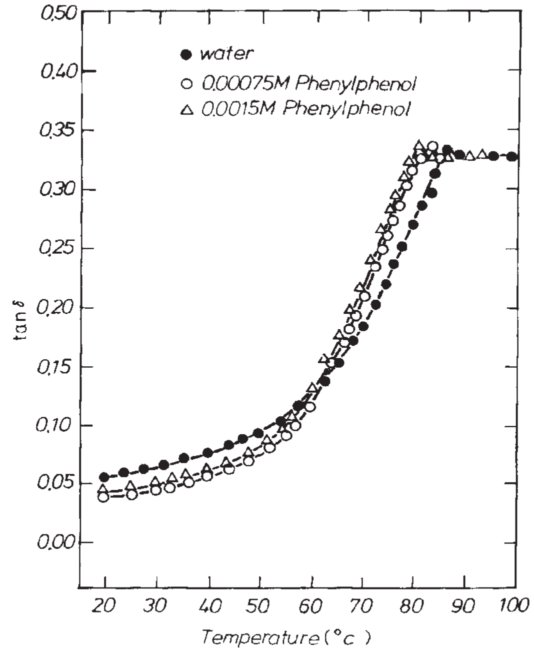

Figure 5 tan δ versus temperature in the presence or absence of phenylphenol in water.

$$C_\infty = k_0\, e^{-E/RT} \int_{20}^{T_2} (\tan\delta)_c\, dT \tag{11}$$

where

$$k_0 = k' \cdot k''$$

and

$$T_2 = T_d - [T_g(\text{dye}) - T_g(\text{mechanical})] \tag{12}$$

Equations (9) and (11) are the basic equations to characterize the dyeability of a fiber.

EXPERIMENTAL

Materials

A sample of Acrilan (Monsanto company, St. Louis, MO) continuous-filament (3 den) was used. It was scoured in a solution containing Dispersol VL (0.5 g/L) (ICI, London, UK) and trisodium phosphate (0.5 g/L) at 40°C for 150 min and washed until the pH value of the rinse water was constant. The dye was C. I. Green 4 (Malachite green) (ICI).[4] The commercial powder was extracted with hot distilled water and recrystallized several times until the product had the same extinction coefficient at the wavelength of maximum absorption in distilled water.

TABLE I
Mechanical Glass Transition Temperature of Acrylic Fiber in the Presence or Absence of Carrier in Solution

Water	86.5°C
0.00075M phenylphenol	83.5°C
0.0015M phenylphenol	81°C
0.02M phenol	83°C
0.08M phenol	79°C

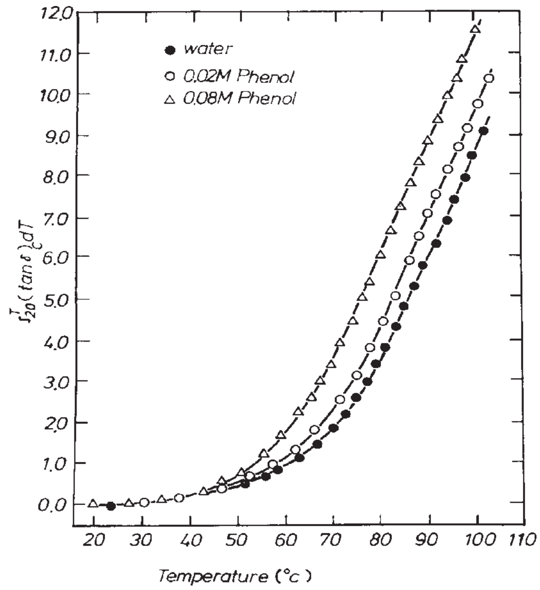

Figure 6 Structural parameter versus temperature in the presence or absence of phenol in water.

Pretreatment of fibers

To avoid the structural instability, the fibers were pretreated with the same solution at the dye bath (without dye) before dyeing or dynamic measurement. The temperature was kept at 95°C for 2 h.

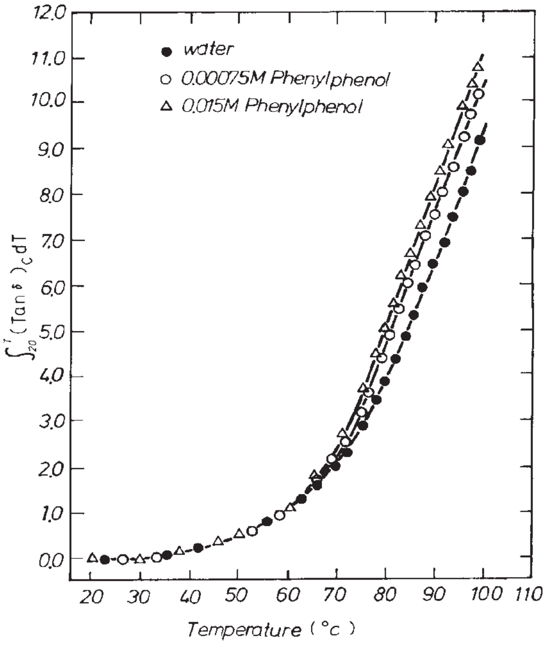

Figure 7 Structural parameter versus temperature in the presence or absence of phenylphenol in water.

TABLE II
Relationship Between the Dyeability, Structural Parameter, and Thermodynamic Parameter at $T = 80°C$

	0.00075*M* phenylphenol	0.0015*M* phenylphenol	0.02*M* phenol	0.08*M* phenol	Water
C_∞ (mg/g of fiber)	12.7	13.9	13.0	16.6	10.8
$\int_{20}^{87} (\tan\delta)_c\, dT$	6.41	6.95	6.52	8.33	5.36
$k = C_\infty / \int_{20}^{87} (\tan\delta)_c\, dT$	1.98	2.00	1.99	1.99	2.02

Dyeing and determination of maximum dye up-take

Dyeing were carried out in an infinite dyebath with various concentration of two carriers (phenol or phenylphenol) and three dyeing temperature (80, 85, and 90°C). The time for equilibrium dyeing was at least 40 h in water and 30 h in carrier solution. The pH of dye solution was controlled at 4.1–4.2 by carefully using acetic acid and sodium acetate aqueous solution (the sodium acetate was dissolved in water, then the acetic acid was added until the desired pH value was reached). After being dyed, the fibers were collected and washed with 50% aqueous methanol containing 5 g/L acetic acid until the washings were clear. The fibers were then dried in the vacuum oven overnight and kept in the desiccators. Before measuring the optical density by Unicam Spectrophotometer, the fibers were dissolved in 20% acetic DMF (dimethyl formaldehyde) solution and filtered.

Dynamic measurements

The dynamic loss tangent tan δ was evaluated by using Rheovibron DDV-III (A and D Orientec, Tokyo, Japan) at 11 cycle/min. The temperature was raised at an approximately constant rate of 2°C/min. To measure the true behavior of fiber in the solution of dye bath, the Rheovibron was slightly modified to suit the purpose.[10] This was done by bending the sample arms to the gauge (Fig. 2). The arms were checked with the normal arms. No difference in results was observed.

RESULTS AND DISCUSSION

Measurement of dyeing transition temperature

The dye uptake of acrylic fiber in water at eight various temperatures (60, 65, –, 85, 87.5, and 90°C) for a dyeing time of 25 min was taken. By plotting the uptake of dye against the dyeing temperature, the transition temperature could be located by extrapolating the curve to x-axis as shown in Figure 3. The dyeing transition temperature of acrylic fiber in water is found to be 79.5°C. Therefore, T_g(dye) is 79.5°C.

Measurement of mechanical transition temperature and structural parameter

The plot of loss tangent, tan δ, against temperature of the acrylic fiber in the presence or absence of carrier in solution (phenol or phenylphenol) is shown in Figures 4 and 5. The mechanical glass transition temperatures were listed in Table I. They are decreased with the presence of carrier and increase of carrier concentration. The purpose of using different carriers is to determine which one exhibiting more potential to swell the amorphous region of the fiber and allow the dye molecule to diffuse into the available dye sites and fixed. As seen in the table, it is obvious that the phenylphenol is more effective than the phenol.

Surprisingly, as seen in the graph, although the value of tan δ in the presence of carrier was much higher than that in pure water at temperature below T_g (mechanical), but it was nearly the same as that in water after the plateau being reached. From this, it was believed that the effect of carrier to swell the amorphous region of the acrylic fiber was less effective as temperature beyond T_g (mechanical). In another word, carrier was not required to achieve a high dyeability at high dyeing temperature. In case of carrier system, the mechanical transition temperature, as indicated by Gulrajani et al.,[8] could be related to dyeing transition temperature as

$$\begin{aligned}\Delta T_{\text{dye}} &= T_g(\text{mechanical}) - T_g(\text{dye}) \text{ in water}\\ &= T_g(\text{mechanical}) - T_g(\text{dye}) \text{ in carrier solution} \quad (13)\end{aligned}$$

TABLE III
Relationship between the Dyeability, Structural Parameter, and Thermodynamic Parameter at $T = 85°C$

	0.00075*M* phenylphenol	0.0015*M* phenylphenol	0.02*M* phenol	0.08*M* phenol	Water
C_∞ (mg/g of fiber)	15.0	16.0	15.0	18.8	12.7
$\int_{20}^{92} (\tan\delta)_c\, dT$	7.77	8.45	7.90	9.70	6.73
$k = C_\infty / \int_{20}^{92} (\tan\delta)_c\, dT$	1.93	1.90	1.90	1.91	1.88

TABLE IV
Relationship between the Dyeability, Structural Parameter, and Thermodynamic Parameter at $T = 90°C$

	0.00075*M* phenylphenol	0.0015*M* phenylphenol	0.02*M* phenol	0.08*M* phenol	Water
C_∞ (mg/g of fiber)	16.5	18.1	16.9	20.4	14.6
$\int_{20}^{97} (\tan \delta)_c \, dT$	9.15	9.95	9.26	11.1	8.10
$k = C_\infty / \int_{20}^{97} (\tan \delta)_c \, dT$	1.81	1.82	1.82	1.84	1.80

Therefore the integration upper limit T_2 in eq. (12) is

$$T_2 = T_d - (86.5 - 79.5) = T_d + 7 \qquad (14)$$

where T_d is the dyeing temperature.

The structural parameter, the integration value in eq. (7), could be obtained by integrating from Figures 4 or 5 and shown in Figures 6 or 7, respectively. As seen in the graphs, the shape of the structural parameter curve was similar to that in Figure 3 (dye uptake versus dyeing temperature curve).

Relationship between dyeability, structural parameter, and thermodynamic parameter

The data relating the equilibrium dye uptake (dyeability) of the acrylic fiber to the structural parameter with the presence or absence of carrier in solution were listed inTables II–IV. The thermodynamic parameter, $k = k_0 \, e^{-E/RT}$, which could be evaluated by eq. (11), was also calculated and listed in the tables. As seen in the tables, the order of equilibrium dye uptake C_∞ was

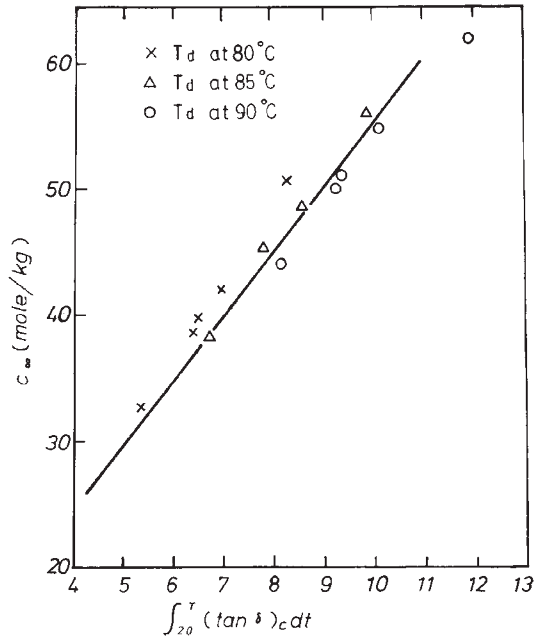

Figure 8 Relationship between C_∞ and the structural factor.

$$\underset{\text{phenol}}{0.08M} > \underset{\text{phenylphenol}}{0.0015M} > \underset{\text{phenol}}{0.02M} > \underset{\text{phenylphenol}}{0.00075M} > \text{water}$$

The thermodynamic parameter k as shown in the table was reasonably constant at the same dyeing temperature irrespectively to the variation of carriers and their concentrations. The k value was slightly decreased as dyeing temperature increased. Plot of log k versus reciprocal dyeing temperature, the activation energy of 2.4 kcal/mol was found (using the average value of k) (Fig. 8).

CONCLUSIONS

From the present studies of relating the dyeability to structural parameter and thermodynamic parameter, we could draw the following conclusions.

(a) The experimental results were considered to be reasonably good with respect to the proposed theoretical basis. The theory could be further extended to other dyeing systems, e.g., polyester with disperse dye.
(b) The equilibrium dye uptake is linearly related to the structural factor, $\int_{20}^{T} (\tan \delta)_c \, dT$, of the acrylic fiber with different carriers. The activation energy of 2.4 kcal/mol was obtained.
(c) The effect of carrier to swell the amorphous region of the acrylic fiber was less effective as temperature beyond T_g (mechanical).

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