Supercritical Fluid Technology in Textile Processing: An Overview

Gerardo A. Montero,* Carl B. Smith, Walter A. Hendrix, and Donald L. Butcher

North Carolina State University (NCSU), College of Textiles, 2401 Research Drive, Raleigh, North Carolina 27695-8301

In light of environmental concerns, the textile industry has accelerated efforts to reduce or eliminate water consumption in all areas of yarn preparation, dyeing, and finishing. Supercritical fluid dyeing technology has the potential to accomplish this objective in many commercial textile applications around the world, both at present and in the future around the world. Increased interest in this technology has made a fundamental understanding of thermophysical (equilibrium solubility) and transport (kinetics) properties of such fluids and fluid mixtures necessary. Supercritical carbon dioxide (SC-CO$_2$) is one of the most environmentally acceptable solvents in use today, and textile processes using it have many advantages when compared to conventional aqueous processes.[1−4] Positive environmental effects range from drastically reduced water consumption to eliminating hazardous industrial effluent. Furthermore, economic benefits include increased productivity and energy savings. Successfully commercializing supercritical fluid CO$_2$ processing will improve the economics of dyeing and other textile chemical processes by eliminating water usage and wastewater discharges and increasing productivity by reducing processing times as well as required chemicals and auxiliaries and reducing energy consumption and air emissions. As a result, SC-CO$_2$ processing will be more rapid, more economical, and more environmentally friendly.[1]

Introduction

In the United States and Europe, many groups are investigating SC-CO$_2$ processing including Josef Jasper (Germany), Uhde Hochdrucktechnick GmbH (Germany), Ciba-Geigy (Basle, Switzerland), Ciba Specialty Chemicals (USA), Praxair (USA), Kherson Cotton Pape (USA), DTNW (Krefeld, Germany), Batelle National Institute (USA), Weatherly (USA), Obem (Germany), Separex (France), Chematur Ltd (U.K.), University of Leeds (U.K.), Clemson University (USA), and undoubtedly several others. Successful pilot plant machines have been publicly exhibited at ITMA '95 (Milan, Italy), Otemas 1997 (Osaka, Japan), and elsewhere for the past few years.[3,5,6]

Despite outstanding successes in this area and great potential, there is a lack of understanding of the importance of dyestuff solubility in SC-CO$_2$ to dyeing processes. In addition, there has been little study of the kinetics of dyeing processes or SC-CO$_2$ flow characteristics in porous (textile) substrates. In textile processing, especially dyeing, the evenness of application is critical, and methods and models used for dyeing in high viscosity noncompressible fluids (e.g. water) are not necessarily applicable. A fundamental understanding of these chemicophysical principles will allow process and equipment development groups (i.e. consortia) to overcome difficulties arising from effects such as solubilization of dyes in SC-CO$_2$, unfeasible time−temperature requirements, and so forth. This allows good control of the dyeing, once it begins, even though it may be expected to occur very rapidly. Accurate and precise hydrodynamic models of flow and kinetics will be valuable in designing machines, substrates, and processes.[6]

Because of its promise, a confidential program to develop a commercial process for dyeing polyester yarn packages in SC-CO$_2$ has been undertaken by researchers at the College of Textiles (COT) at North Carolina State University (NCSU).[2] A single-package, pilot-plant machine for dyeing polyester yarn packages using SC-CO$_2$ has been designed and fabricated under this program. On the basis of data gathered from experimental dyeing trials performed on this laboratory scale machine, the technical and economic feasibility of the SC-CO$_2$ dyeing process has been demonstrated.[1]

COT researchers undertook these studies not only to provide data for an economic comparison of SC-CO$_2$ dyeing with conventional aqueous dyeing technology but also to obtain information to evaluate commercial scale up. Rather than extrapolating entirely from laboratory work, this approach allows more realistic analysis of the capital and operating costs involved in such a process.[1,2] On the basis of the findings, a prototype supercritical fluid dyeing system capable of dyeing multiple, commercial-size polyester yarn packages has been built. This paper presents a summary of key results important to commercializing the SC-CO$_2$ polyester yarn package dyeing process.[1]

Solubility Studies of Disperse Dyes in SC-CO$_2$

Carbon dioxide (CO$_2$) is a inexpensive, nontoxic, nonflammable, environmentally friendly, and chemically inert gas under many conditions.[7] In an assembly of nonpolar molecules, CO$_2$ is a linear molecule with two symmetrical polar bonds.[8] CO$_2$ has no dipole moment (ranging in polarity near hexane and pentane), but its quadrupole is sufficiently strong to affect its thermodynamic properties. These properties are different from those of other nonpolar molecules of similar size and molecular weight, but without strong quadrupoles. Hyatt found that there were no significant differences

* To whom all correspondence should be addressed. Telephone: (919) 513-2832. Fax: (919) 513-1655. E-mail: gmontero@tx.ncsu.edu.
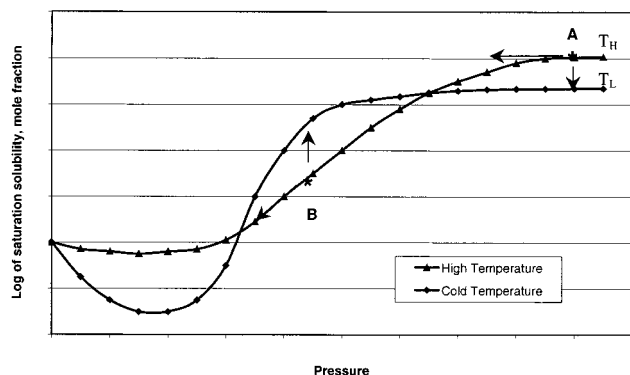
Figure 1. Qualitative representation of the solubility behavior of disperses dyes in SC-CO_2.

Figure 2. Solubility behavior of benzoic acid in SC-CO_2 at three different temperatures. (Copyright Butterworth-Heinemann; reproduced with permission from ref 9).

in polarity between liquid and supercritical phases of CO_2.[7]

In general, CO_2 displays the properties of a typical hydrocarbon solvent, such as toluene. However, for basic molecules, it provides more hydrogen-bonding basicity than hydrocarbon solvents. Beyond its critical point, CO_2 has unique properties. For example, SC-CO_2 exhibits densities and solvating powers similar to those of liquid solvents yet has extremely rapid diffusion characteristics and viscosity similar to those of a gas.

Since solubility is a function of solvent density for supercritical fluids, the behavior can be explained by examining the density behavior of a pure substance near the critical point. In this region a small increase in temperature causes a large reduction in density, and hence solubility. On the other hand, as the pressure is increased, the fluid density increases and eventually the equilibrium solubility of the solute increases with pressure. Increasing fluid density decreases the intermolecular mean distance, resulting in increased specific interactions between the solvent and solute.

The solubility behaviors of disperse dyes in SC-CO_2 are complex, as there are competitive pressure and temperature effects. This behavior is further complicated by the occurrence of a retrograde phenomenon or temperature inversion effect.[9]

Figure 1 shows qualitatively the dependence of disperse dye solubility on SC-CO_2 pressure and temperature. The actual point on its solubility plot where any particular dye is used in a commercial dyeing process depends on its properties such as molecular weight, heat of sublimation, melting point, and so forth. On a logarithmic plot of solubility (mole fraction) versus pressure, the plots of different isotherms are seen to cross. This temperature dependence is observed for all dyes studied in supercritical CO_2 by College of Textiles (NCSU) researchers, and indeed, it is observed for all solutes in supercritical fluids (Figure 2).[9] The relative location of the crossover "retrograde phenomenon" is observed for these dyes as solubility changes with temperature and pressure. If solubility is plotted as a function of carbon dioxide density, the crossover point will generally not be observed.[4]

Two competing effects can explain these intersection points shown in the temperature−pressure−solubility plots. In principle, temperature rise at constant pressure increases the sublimation pressure of the dye, but at the same time, the solvent density decreases. At low pressures, the decrease in solvent density dominates and the solubility of dyes decreases with increasing temperature. At higher pressures, the increase of sub-
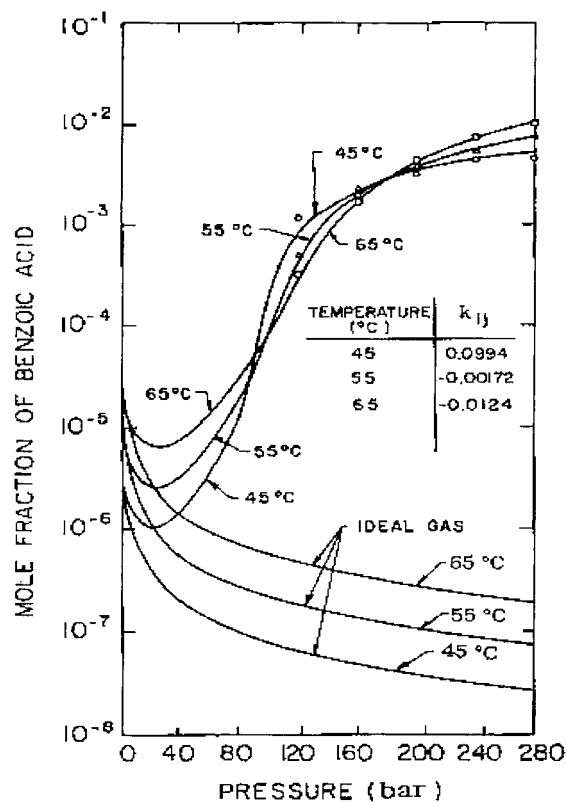
limation pressure with temperature overcompensates the decreases of solvent density. This point is further supported by the solubility versus density plots, where it is possible to observe that the solubility increases with rising temperature at constant CO_2 density, that is, as total pressure increases in the system.[4]

Density-Dependence or Temperature-Controllable Dyes. Referring to Figure 1, it may be observed that, if one is at relative point A on the curve for T_H (high temperature), the slope of the solubility as a function of SC-CO_2 pressure is approximately zero. In this case, a decrease in the pressure at constant temperature (i.e., in the direction of the left-hand pointing arrow) gives little or no decrease in dye solubility. On the other hand, a decrease in SC-CO_2 temperature (i.e., in the direction of the downward pointing arrow) results in decreased dye solubility. Point A corresponds to the case in which we have what is called a temperature-controllable dye.

Temperature-controllable dyes are those in which a controlled reduction in temperature will result in a controlled reduction of dye solubility, which causes the dye to partition favorably toward the fiber being dyed. The temperature remains above the glass transition temperature (T_g), the fiber dyeing temperature, at all times, and so the dye exhausts out of solution; it is sorbed into the fiber because the conditions are still favorable to dyestuff uptake. Figure 3 is a plot of saturation solubility as a function of pressure and temperature for Disperse Dye Blue 77, a temperature-controllable dye.[10,11]

On the other hand, lowering the pressure at a constant temperature (and therefore the density) via venting may not result in a significant reduction in solubility for a temperature-controlled dye until a point
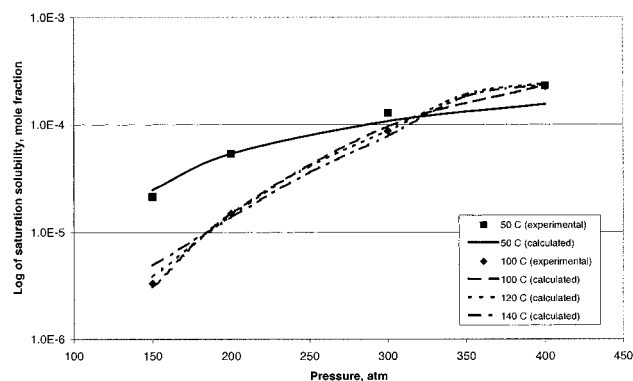
Figure 3. Saturation solubility of disperse dye Blue 77 in SC-CO_2 as a function of pressure. Comparison of predicted lines obtained by using an empirical correlation[23,24] versus experimental data.

Figure 4. Saturation solubility of disperse dye Blue 60 S in SC-CO_2 as a function of pressure. Comparison of predicted lines obtained by using an empirical correlation[23,24] versus experimental data.

on the solubility curve is reached where the solubility versus pressure slope is positive. At this point, the dye solubility drops rapidly with SC-CO_2 pressure (density) reduction and dye exhausts from the solution often at a rate that is too great to be sorbed into the fiber. When this circumstance occurs, dyestuff precipitates and a crocking (dye precipitated on the surface fiber) phenomenon occurs.[1,10]

Temperature-Dependence or Density-Controllable Dyes. Again referring to Figure 1, it may be noted that, if one is at relative point B on the curve for T_H, the solubility versus pressure slope is positive and the T_L curve lies above the T_H curve. In this case, a decrease in supercritical CO_2 temperature (i.e., in the direction of the upward pointing arrow) results in an increase in dye solubility. This circumstance may result in a "stripping" effect whereby dye actually desorbs from the fiber and into the solution. If a path is followed where the dye bath is cooled and then vented, crocking may occur because the dyeing rate will be too low as the dye exhausts out of solution (i.e., when the pressure/density decreases due to venting). Therefore, dyestuffs precipitate on the surface fiber rather than being sorbed into it.[1,10]

On the other hand, a decrease in SC-CO_2 pressure at constant temperature (i.e., in the direction of the arrow that follows the T_H curve) results in a decrease in CO_2 density and in dye solubility (point B in Figure 1). Density-controllable dyes are those for which a controlled reduction in density (effected by decreasing pressure at constant temperature) can result in a controlled reduction in dye solubility, which causes the dye to partition favorably toward the fiber that is being dyed. As the dye exhausts out of solution, it is sorbed into the fiber because the conditions are still favorable to dye uptake (i.e., $T_{dyeing} > T_g$).[1,10] Figure 4 is a plot of saturation solubility as a function of pressure and temperature for Disperse Dye Blue 60 S, a density-controllable dye.[11]

Solubility Behavior in Disperse Dyeing of Fibers. Poly(ethylene terephthalate) (PET) is the largest (by volume) man-made synthetic fiber produced in the world today. Since 1980, the market share of this fiber has increased from 47% to 56% of synthetics. The reasons for the tremendous production of this fiber include its useful properties, such as, durability, strength, stability during heat setting, abrasion resistance, and resistance to sunlight, acids, alkalis, and bleaches. These fibers also have very good crease recovery and
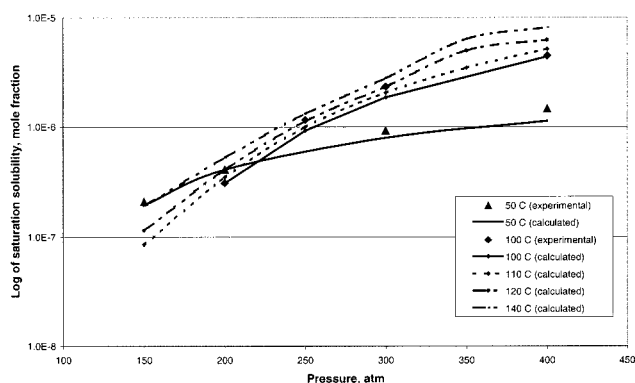
are durable to washing. Along with these characteristics, polyester also has many important uses including home furnishings, apparel fabrics, automotive interior fabrics, and carpeting.[12]

In the past, PET fibers were typically made through an ester exchange reaction between dimethyl terephthalate and ethylene glycol, followed by a condensation reaction. Today, PET is most often produced through the direct reaction of terephthalic acid with ethylene glycol. PET has a glass transition temperature (T_g) in air between 68 and 80 °C and a melting point temperature between 252 and 265 °C.[12,13] Solvents such as carbon dioxide offer a predominant advantage in applications to polymeric materials because CO_2 can plasticize the polymer, reducing its glass transition temperature to about 45−55 °C, which provides an ideal opportunity to impregnate the polymer matrix with solutes (dyes).[13,14]

The process whereby a dye partitions from the solution toward the polyester fiber is complex, depending not only on its solubility in the supercritical CO_2 but also on its affinity for the fiber, diffusion coefficient, and time at each particular set of conditions, that is, supercritical CO_2 temperature and density. Therefore, it may be suggested that there are depressurization paths other than the ones described above for points A and B in Figure 1, whereby crocking may be avoided. For example, from points A and B, one might follow paths that employ both cooling and pressure reduction (by venting) simultaneously. Furthermore, such paths might even be more advantageous, from the standpoint of reducing process time, than the depressurization paths described above for temperature-controllable and density-controllable dyes.[1,10]

The reasoning outlined above is based on comparison of dyeing behavior of certain disperse dyes at ~130 °C with that observed in previous saturation solubility studies at 50 and 100 °C.[11,15] For example, dyeing trials of Disperse Blue 77 at ~130 °C yield a higher concentration of dye in the fiber[15,16] (a maximum dyestuff uptake) without crocking problems when depressurizing by decreasing the SC-CO_2 density (venting) at a constant temperature at ~130 °C; that is, the dyeing behavior is density-controllable dye. These results are in marked contrast to those found at lower dyeing temperatures (50 and 110 °C), where the temperature must be decreased before venting in order to avoid crocking; that is, the dyeing behavior is temperature controllable.[1,15]

This change in dyeing process behavior with temperature increase for Disperse Dye Blue 77 may be explained as follows. Even though the saturation solubility is seen to increase very little between the range of 100 and 140 °C (see Figure 3), conditions are favorable at 130 °C for increased dye uptake: that is, the relative adsorption rate constant is higher.[15] This behavior occurs because, at higher temperatures, the polyester swells more, thereby allowing a greater amount of dye to migrate into the fiber.[15,16] Because of the adsorption rate constant, the dye is absorbed into the fiber as density is decreased rather than precipitating out on the fiber surface. Therefore, two distinct depressurization paths are observed for Dye Blue 77 whereby crocking may be avoided.[10]

At this point in the dyeing process development at the College of Textiles, NCSU, there is insufficient experimental dye solubility data at higher temperatures to determine with certainty the optimum depressurization paths for the temperature-controllable and density-controllable dyes that have been studied. However, there is sufficient data to explain the successful practices that have been described, any of which may or may not be optimum.[1,12]

It should be noted that the solubility behavior of dyes in SC-CO_2 might also be important to the levelness, or uniformity, of dyed textile materials. To date, SC-CO_2 dyeing processes have sought to maximize the amount of dye in solution at all times.[1] Such an approach might not be the optimum in terms of achieving a level dyeing in the minimum time. Instead, another approach might involve careful control of the SC-CO_2 density and temperature or use of a specific dye-dosing strategy, either of which could ensure that the dye concentration is favorable at all times to rapid equilibrium for dye uptake by the fiber.[17] Under these circumstances, unleveled dyeing problems, such as shading and streaking, might be minimized, with consequently less time at the dyeing temperature required for correction of the uniformity problems.[16,18,19]

Affinities Studies of Disperse Dyes in SC-CO_2

During the dyeing process development activities, College of Textiles, NCSU, researchers observed not only previously described dye solubility behavior for SC-CO_2 but also affinity effects for polyester fiber that are considered important. Even though these investigations are only at a preliminary stage, some significant findings have resulted.[15]

General Mechanisms for Levelness. In general terms, there are two fundamental mechanisms that contribute to level dyeing. One is the initial sorption of dye into the fiber, and the other is the migration of dye molecules after initial surface sorption on the fiber; that is, equilibrium desorption and resorption of dyes. Initial sorption of dye consists of the following steps: (1) establishment of equilibrium between associated molecular dye and single molecules of dye in solution (CO_2); (2) external diffusion of individual molecules of dye and CO_2 to the diffusion boundary layer at the fiber surface (immediate vicinity of the internal fiber surface); (3) diffusion of individual molecules of dye through the boundary/interface layer to the fiber surface; (4) adsorption of the molecules of dye at the fiber surface; and (5) internal diffusion of the molecules of dye into the fiber interior.

The migration mechanism consists of a reversal of the five steps outlined above for initial sorption at one fiber site followed by the reoccurrence of steps 2−5 at a different fiber site.[5,16]

Each of the steps in both mechanisms can influence the levelness of dyeings. An initial level sorption will lead to a level dyeing. On the other hand, an unleveled sorption may be subsequently made level if sufficient migration takes place. These two fundamental mechanisms can be controlled by physical properties of the dyes and also with dyeing process parameters such as SC-CO_2 flow rate, temperature, dyeing time, rate of diffusion, and so forth.[5]

Equilibrium in Disperse Dyeing. The basic model for disperse dyeing used is a first-order kinetics:

$$\frac{dC^f}{dt} = k_a C^s - k_d C^f \tag{1}$$

where

C^f = concentration of dye in fiber

C^s = concentration in solution

k_a = adsorption rate constant

k_d = desorption rate constant

t = time

Also Nernst thermodynamics,

$$K_{eq} = \frac{k_a}{k_d} = \frac{C_\infty^f}{C_\infty^s} \tag{2}$$

where K_{eq} is defined as the equilibrium partition coefficient when time (t) approaches infinity and C_∞^f and C_∞^s do not change with time. From this we see that, to get level dyeing, we can use either of two (2) approaches: (1) Wait a long period of time. (2) Ensure that each element of the package is exposed to the same solution concentration (C^s for the same time).

The times required for approach 1 could be over 60 min, which is excessive. Therefore, the focus by COT researchers was on alternative 2.[16]

To achieve alternative 2, even flow throughout the package, among other things, must be assured.[16]

Affinity Behavior in Disperse Dyeing. In a conventional aqueous dyeing, the process of the dye transporting from solution into the fiber is an exothermic reaction. It is assumed that, in a CO_2 medium, the same behavior would exist. This behavior was confirmed by the thermodynamic analysis of the affinity data obtained in previous sttudies.[15]

Therefore, analysis of the affinity data obtained was conducted, and a variety of factors were considered.[15] The density of the CO_2 was examined along with any crossover between increasing solvent power of the CO_2 due to the density versus temperature. The importance of these factors is based on the fact that K_{eq} depends on the equilibrium concentration of dye in solution. Therefore, if the dye is more soluble at a given density or temperature, it is expected that K_{eq} decreases. This again brings up the balance that must be considered between the solubility of the dye in CO_2 and the affinity of the dye for the CO_2 versus the polyester fiber.[15]

Several definite trends exist among the disperse dyes evaluated for the affinity study. First, if pressure is held constant, the value of K_{eq} decreases with increasing temperature. This behavior is consistent with what is observed in an aqueous dyeing environment, and is expected here because the dyeing process is an exothermic reaction.

In addition, increased solubility appears to cause a decrease in affinity. This trend was observed for the disperse dyes studied. This behavior is observed by the fact that K_{eq} is the ratio of the equilibrium solubility (concentration) of the dye in the fiber to the equilibrium solubility (concentration) of the dye in solution. Therefore, if a dye has a higher solubility in CO_2, it should have a high value of C_∞^s and a low value of K_{eq}. Finally, the overall differences in the value of K_{eq} for a given dye were higher for a dye with lower solubility. This dependence of K_{eq} on solubility as well as density has important implications for the dyeing of polyester in SC-CO_2.[15]

Solely on the basis of the affinity data obtained,[15] the optimum temperature and pressure to use in a dyeing pilot plant machine for dyeing polyester fiber in SC-CO_2 would correspond to the pressure and temperature giving the highest value of K_{eq}. This is because the highest value of K_{eq} would give the highest percent exhaustion (%E). The maximum value of K_{eq} varied for the three dyes studied but was between 200 and 250 atm and between 70 and 90 °C. Therefore, depending on the dye, the best temperature and pressure are expected to be in this range.[15]

However, several other factors must be considered. First, the solubility of the dyes in SC-CO_2 is an important factor. Because the vessel containing the dye will be in one part of the dyeing machine while the dyeing vessel is elsewhere, the solubility will be the transport mechanism for the dye. Thus, solubility and affinity data are both very important. Therefore, it is necessary to evaluate the optimum temperature and pressure solely on the basis of the solubility data and then to make adjustments according to the affinity results.

In addition to the solubility results, it is also important to consider the liquor ratio (L) that will be used, as percent exhaustion depends on this value. In the lab experiments, the liquor ratio varied from 5 to 10 g of CO_2/g of fiber depending on the density of the CO_2. In the pilot plant machine, the liquor ratio will vary from 10 to 20 depending on the density of the CO_2 and the size of the package used.[15] Because percent exhaustion is $K_{eq}/(K_{eq} + L)$, if L is very large, K_{eq} will be a small consideration. On the other hand, if L is small, K will be a larger factor. Therefore, it will be necessary to evaluate the importance of K_{eq} for a dyeing on the basis of the liquor ratio used. Also, L is important in terms of the ability to dissolve dye. If L is large, there will be sufficient SC-CO_2 to dissolve dye. Thus, changing the CO_2 density, and therefore L, is an added degree of control for dyeing.[15]

Relative Rate Constant for the Dyeing Process. The dyeing process being considered is dye$_{solute}\rightarrow$ dye$_{solution}\leftrightarrow$ dye$_{fiber}$, where the rate of dyeing is controlled by the adsorption rate constant, k_a. This rate constant depends on time, dyeing temperature, the dye used, the type of fiber, and circulation in the bath. To determine k_a, the Kubella−Munk K/S value for each dyed fiber sample was determined. This parameter is proportional to dye concentration and is calculated from

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \tag{3}$$

where R is the reflectance and has a value between 0 and 1.

The adsorption rate constant, k_a, was estimated in a fairly simple method using the following equation:

$$\frac{dc^f}{dt} = k_a C^s - k_d C^f \tag{4}$$

where dc^f is the change in concentration of dye in the fiber, dt is the change in time, k_a is the adsorption rate constant, C^s is the concentration of dye in solution, and k_d is the desorption rate constant.

Assuming that as $t \rightarrow 0$, $C^f \rightarrow 0$, so

$$\frac{dc^f}{dt} = k_a C^s \tag{5}$$

and furthermore, when the time of the experiment is short,

$$\frac{\Delta c^f}{dt} \approx \frac{dc^f}{dt} = k_a C^s \tag{6}$$

Since C^f at $t = 0$ is 0, this is

$$\frac{C^f}{t} = k_a C^s \tag{7}$$

Also, since solubility varies with temperature, C^s is not the same for all experiments at all temperatures, so

$$k_a \approx \frac{C^f(t)}{C^s t} \tag{8}$$

Furthermore, C^f is proportional to K/S, so

$$k_a(\text{relative}) \approx \frac{(K/S)}{C^s t} \tag{9}$$

The values of the concentration in solution are obtained from the solubility data from previous studies.[15] These k_a's are qualitative and relative, but still the information, though not quantitative, is useful in estimating the best conditions for starting out on pilot plant experiments. The dimensions for k_a are inverse time due to the fact that first-order rate kinetics were used.

The adsorption rate constant defines the operational factors such as the length of the dye cycles and the bath turnovers required per minute, for a dyeing process.[15,16]

New Strategies for Supercritical Fluid Dyeing Processes

The research summarized by this paper represents a significant advance in obtaining the knowledge required to commercialize a process to dye polyester yarn packages in SC-CO_2. However, there remains much work to be planned and conducted in this area by using supercritical fluids as a novel textile technology. There are two promising areas of research that are being pursued by researchers at the College of Textiles at NCSU.

First, researchers have developed package flow empirical models based on solution of the governing differential equations for radial and axial flow modes in yarn packages. These empirical models are broadly applicable to other processing situations.[20,21] Combining these flow models with the first-order diffusion and reaction kinetics for mass transport of exhaustable materials (e.g. dyes) from the SC-CO_2 into textile substrates will provide a useful tool for analyzing and mitigating the occurrence of levelness problems related with package dyeing at optimum CO_2 flow rates.[20] The COT package flow models include the effect of important characteristics of the fluid (e.g. viscosity) and the ability to model packages of varying permeability (e.g. radial, axial, hard spots, and hard ends of yarn packages), using finite element solutions of the equations. The theoretical results obatined from the empirical models to date show encouraging compatiblity with very extensive pilot plant data. These are beginning to lead us to a sound fundamental knowledge of SC-CO_2 thermophysical properties and transport principles, which facilitates process and equipment design.[20,21]

Second, both saturation solubility and affinity in a supercritical fluid are critical thermophysical properties that must be understood and modeled to effectively commercialize supercritical fluid dyeing processes and equipment. In particular, the temperature and pressure (and, therefore, density) dependence of disperse dyes' solubility and affinity must be accurately understood. To accomplish this final objective, it is necessary to investigate a wide variety of disperse dyes, some of which may have been used for aqueous dyeing and some of which perhaps are not suitable for use in water but might be useful in SC-CO_2. These selected materials, in combination with newly syhthesized dyes, should be evaluated to develop a fundamental understanding of application properties in SC-CO_2, including saturation solubility, affinity, leveling properties, fastness, strike temperature, dyeing (sorption/desorption) rate constants, equilibrium distribution coefficient, standard affinity, enthalpy of dyeing, and other thermodynamic properties as may be determinable (e.g. entropy of dyeing).[6]

Synthesis and characterization of the chemical structure and physical properties of many exhaustable textile additives (e.g. dyes) for batch/exhaust and their applications in SC-CO_2 are needed. This work would include a focus on specific chemical groups in dyes and other textiles auxiliares and their effect on saturation solubility and affinity in SC-CO_2 processing. Development of empirical models to predict appropiate dye candidates for SC-CO_2 dyeing would allow process developers to avoid extensive solubility of dyestuffs. The focus of this research would be to enhance the knowledge about structure−solubility relationships for dyes and other textile processing chemicals in supercritical carbon dioxide.[11,15] This novel approach should open up new opportunities for the supercritical fluid processing of textiles that may prove to be a highly beneficial path of progess for the textile industry in this textile dyeing in this milennium.[22]

Acknowledgment

Literature Cited

(1) Smith, C. B.; Montero, G. A.; Hendrix, W. A. U.S. Patent 6,048,369, 2000.

(2) *The Alumni Magazine of North Carolina State University, College of Textiles*, Raleigh, NC, 1999, autumn, 12−13.

(3) Back, E.; Cleve, E.; Schollmeyer, E.; Bork, M.; Körner, P. Experience with the Uhde CO_2-dyeing plant on technical scale. Part 1: Optimization steps of the pilot plant and first dyeing results. *Mellian Int.* **1998**, *3*, 192−194.

(4) Tessari, F.; Devetta, L.; Guarise, G. B.; Bertucco, A. Impregnation of Polyester Fibers in Supercritical Carbon Dioxide. CISF 99 Fifth Conference on Supercritical Fluids and their Applications, Garda, Verona, Italy, June 13−16, 1999, pp 441−448.

(5) Wang, X.; Bide, M. Factors Affecting the Levelness of Dyeing in Reused Acid Dye-baths for Nylon. *Textile Chem. Colorist* **1998**, April *30* (4), 45−52.

(6) Smith, C. B.; Montero, G. A.; Hendrix, W. A. Supercritical Fluid Carbon Dioxide (SC-CO_2) Processing Study; National Textile Center. Year 8−Proposal; 1999; No. C99−S01.

(7) Haytt, J. A. Liquid and Supercritical Carbon Dioxide as Organic Solvents. *J. Org. Chem.* **1984**, *49*, 5097−5101.

(8) Gutkowski, K.; et al. Solubility of Solid in Near-Critical Fluids V. CHI_3 in Ethane and Carbon Dioxide. *J. Chem. Thermodyn.* **1997**, *29*, 1077−1086.

(9) McHugh, M.; Krukonis, V. Supercritical Fluid Extraction, 2nd ed.; Butterworth-Heinemann: Boston, MA, 1994.

(10) Montero, G. A.; Smith, C. B. General Solubility Behavior of Solids and Specific Trends for Disperse Dyes in Supercritical CO_2 (SC-CO_2). Confidential Research Note, College of Textiles, North Carolina State University, Raleigh, NC, October 1998.

(11) Draper, S. L.; Montero, G. A.; Smith, B.; Beck, K. Solubility Relationships for Disperse Dyes in Supercritical Carbon Dioxide. *Dyes Pigments* **2000**, *45*, 177−183.

(12) Hatch, K. L. *Textile Science*, West Publishing Company: Minneapolis, MN, 1999.

(13) Drews, M. J.; Jordan, C. The effect of Supercritical CO_2 Dyeing Conditions on the Morphology of Polyester Fibers. *Textile Chem. Colorist* **1998**, *30*, 6, 13−20.

(14) Drews, M. J.; Jordan, C. The effect of Supercritical Carbon Dioxide Dyeing Conditions on the Morphology of Poly(Ethylene Terephthalate) Fibers. *The Magazine of the Textile Dyeing, Printing, and Finishing Industry, AATCC* **1995**, 261−267.

(15) Marlowe, T. L. Solubilities and Affinities of Disperse Dyes in Supercritical Carbon Dioxide. Master Thesis, College of Textiles, North Carolina State University, Raleigh, NC, May 1997.

(16) Montero, G. A.; Butcher, D. L.; Hendrix, W. A. Controlling the Mechanism of Dye Migration in Supercritical CO_2 Dyeing Processes. Effect of Dye-Bath Flow and Bath Turns on Dyeing Uniformity. Confidential Research Note, College of Textiles, North Carolina State University, Raleigh, NC, December 1999.

(17) Hendrix, W. A.; Montero, G. A.; Brent, C. B.; Butcher, D. L. Method for Introducing Dyes and Other Chemicals into a Textile Treatment System. U.S. Patent Application Serial No. 09/482,371 (NCSU Ref. No. 99-68). College of Textiles, North Carolina Sate University, Raleigh, NC, October 1998.

(18) Brent, C. B. Solubility Behavior of Temperature-Controllable and Density Controllable dyes in SCF-CO_2. Confidential Technical Note, College of Textiles, North Carolina Sate University, Raleigh, NC, September 1998.

(19) Montero, G. A.; Brent, C. B. General Solubility Behavior of Solids and Specific Trends for Disperse Dyes in Supercritical CO_2. Confidential Research Note, College of Textiles, North Carolina Sate University, Raleigh, NC, July 1999.

(20) Shannon, J. B. Development and evaluation of a Darcy Flow Model for Supercritical Fluid Flow through Polyester Yarn Packages. Master Thesis, College of Textiles, North Carolina State University, Raleigh, NC, 1999.

(21) Shannon, B.; Hendrix, W.; Smith, B.; Montero, G. Modeling of Supercritical Fluid Flow Through a Yarn Package. CISF 99 Fifth Conference on Supercritical Fluids and their Applications, Garda, Verona, Italy, June 13−16, 1999; pp 419−426.

(22) Holme, I. New Dyes for Supercritical Fluid Dyeing. The 79th World Conference of the Textile Institute. International Dyer, May 1999, pp 27 and 30.

(23) Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilstone, G. F. Solubilities of Solids and Liquids of Low Volatility in Supercritical Carbon Dioxide. *J. Phys. Chem. Ref. Data* **1991**, *20*, 4, 713−756.

(24) Özcan, A. S.; Clifford, A. A.; Bartle, K. D.; Lewis, D. M. Solubility of Disperse Dyes in Supercritical Carbon Dioxide. *J. Chem. Eng. Data* **1997**, *42*, 590−592.