Project Title: Fundamentals of Dye Diffusion Variance in Polyamide and Polyester Fibers

Project Number: S95-7

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Goals:

1. To create an understanding of the factors that control the temperature dependence of dye diffusion into synthetic fibers in sufficient detail to provide leads for developing dyeing methods and chemicals to completely eliminate dye streaks.

2. To develop chemical or physico-chemical approaches to eliminating dye variability in continuous filament synthetic yarns.

The first year of this project will be spent 1) improving our experimental capability for observing the properties we need to measure, 2) synthesizing appropriate molecular probes and potential chemical modifiers, and 3) implementing a state of the art theoretical and computational background. The second and third years of this project will use the technology developed during year 1, as described in the “Technical Approach” section.

Abstract:

We are in the early stages of reviewing the current literature, and assembling and testing new equipment and new methods for dye diffusion, dynamic mechanical, molecular modeling, and molecular probe studies. We are also strengthening our links with both industry and university collaborators. The literature reviews have revealed important and useful advances in both ESR and NMR probe methods, and have made us aware of the potential usefulness of fluorescent probe molecules in fluorescence quenching studies of molecular mobilities in solid polymers. Our contacts with other potential collaborators have been very encouraging.

Three novel fluorinated molecular probes have already been synthesized. Selected commercial dyes are being purified, and the synthesis of other types of molecular probes is in progress.

The polymer physics literature, some of which stems from current members of our group, has revealed new ideas about molecular motions in fiber-forming polymers which will be very helpful in our work.

Relevance to NTC Goals:

Streaks, and in particular dye streaks, have been a nagging and expensive problem in the textile industry for 50 years. Sufficient information is now available that foreign competitors could produce yarns which give no streaks, albeit with increased (but low cost) labor. The most desirable approach to eliminating streaks would be a chemical one, but none is known. By understanding the fundamental causes of dye variability, and developing chemical routes to eliminating it, this project will help maintain a level playing field for USA industries in the critical-dyed apparel and carpet markets.

Technical Approach:

Past work (mostly ours) and currently available physical chemical approaches to reducing dye variability tend to point in the same direction. This seems to support the general validity of the approaches but emphasizes the need for further confirmatory experimental data.

Fibers have a crystalline fraction which is hardly influenced by temperature or dyebath chemicals, and a noncrystalline fraction (A), which is strongly influenced by these factors. With increasing temperature, an increasing part of region A develops enough liquidlike mobility to permit dye diffusion. We call this process mobilization. The main difference between two like yarns which dye differently is the temperature dependence of mobilization, which is not well understood.

One way to eliminate streakiness would be to mobilize 100% of region A in all the competing yams before permitting any significant dye uptake. Physical-chemical methods to do this have already been reported, e.g. Bayer's Telon ST (R) process, and DuPont's Infinity (R) dyeing process.

Initial streakiness arising from different initial dye sorption rates will be made worse by the concentration dependence of the diffusion constant. In addition, dyes with high distribution coefficients will be unable to migrate from yarn to yarn in order to reduce these initial inequalities in dye uptake. The concentration dependence of the diffusion coefficient in ionic dyeing systems is not fully understood, but when the dye ion is a counter-ion, this concentration dependence can be reduced by appropriate ionic pre-treatments of the fiber.

We plan to improve the understanding of this mobilization process by combining computer modeling of diffusion in the noncrystalline regions, molecular probe diffusion studies, precise dye diffusion and dynamic mechanical measurements, and their comparison with the best available theories, including the newer theories of thermoreversible gels.

Based on the extension and improvement of the understanding thus generated, we will develop novel chemical approaches to control the polymer chain mobilization, and the rate of dyeing. This preferred approach differs from past methods that have focussed on preventing significant amounts of dye from penetrating the fiber until the non-crystalline region A is 100% mobilized.

Industry Outreach:

We have spent considerable effort organizing the industry connections for this project. We examined our status and capabilities and concluded that the main functions of collaboration with an industrial partner are to provide the project with 1) special nylon fiber samples, 2) assistance in the design and execution of specialized nuclear magnetic resonance (NMR) testing, 3) a place to test the ideas which come from our work and 4) a mechanism to make sure that the course we are following is going somewhere useful.

We have discussed our project with several potential industrial partners and selected one as the most likely to be involved initially, based on our understanding of their needs. In April we presented a seminar covering our most recent dye diffusion work at their main research facility and discussed future collaboration. This company wants to be involved, and will provide fiber, contacts and NMR experiments. However, the appropriate NMR expertise appears not to be readily available there. We are working with two of their R&D people and expect a fruitful collaboration, but we will need to get the NMR expertise elsewhere. We are now exploring collaborative NMR and ESR work with the Chemistry Departments at NCSU and UNC-Chapel Hill.

Current Progress:

Experimental resources:

We have begun to assemble the components for a dyebath monitoring system based on the latest technology developed by the new NTC Project S95-4. This system will be used for continuous monitoring and feedback control of dyeing experiments. In addition, we are also assembling dyeing systems of the type used by Grieder (J. Soc. Dyers. Colourists, pp 435-441, December 1974) for direct measurements of the dye diffusion coefficient, based on the rate of dye sorption by small fiber samples. This will require parallel sorption equilibrium studies. In addition, spectrophotometric microdensitometry of fiber cross sections is being carried out in the laboratories of a fiber manufacturer.

Probe synthesis and application:

One of our major goals is the synthesis of labeled dye molecules which can serve as molecular probes of the environments within fibers during dye diffusion and sorption processes. In particular, these probes will provide information about the molecular mobilities and the diffusion coefficients of the probe molecules within the fiber structure.

Our colleagues at Clemson are exploring the synthesis of ^{13}C labeled dyes and metal complex dyes as new probes for NMR studies. They are also investigating synthetic routes to stable free-radical dye probes for ESR studies, and to fluorescent probes for fluorescence-quenching studies of the molecular mobility of the fluorescent molecules in the fiber structure.

One of our current activities has been the preparation of fluorine (^{19}F) labeled azo dyes for molecular probe NMR studies. Three fluorinated acid dyes have been prepared, which are sodium 1-(2-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulfonate, sodium

1-(3-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulfonate, and sodium 1-(4-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulfonate. They were synthesized by the coupling of the corresponding diazotized aniline derivatives with sodium 2-hydroxy-6-naphthalenesulfonate, purified, and dried. Sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate (Crocein Orange G, Aldrich) is being purified. In addition, the corresponding acid dyes containing a methyl group will be synthesized.

We plan to use the fluorinated dyes in order to investigate their mobility in nylon fibers by using NMR spectroscopy. Also classical diffusion measurements for the dyes will be carried out to elucidate the effects of the position and kind of the substiuent. High-resolution solid-state ^{19}F-NMR spectroscopy of the sorption and diffusion of fluorine-containing aromatic molecules in polymeric media was reported recently (P. J. Toscano et al., J. Polym. Sci.: Part A: Polym. Chem., 31, 859 (1993)). ^{1}H NMR spectroscopy and pulsed-gradient NMR techniques also seem to hold promise as a means to probe the mobility of dyes in fibers and possibly also to monitor their intrafiber molecular environments.

Searches have been made of the recent literature on the ESR spin probe technique. New developments include the determination of translational diffusion coefficients using ESR imaging (e.g. J. Freed, Ann. Rev. Biophys. Biomol. Struct., 23, 1 (1994)), and monitoring of the bimodal distribution of the the ESR spectra of nitroxides to explore the penetration of solvents into polymeric materials (Ö. Pekcan and Y. Demir, J. Appl. Polym. Sci., 43, 2169 (1991) and Ö. Pekcan and Y. Demir, J. Appl. Polym. Sci., 49, 1877 (1993)). These papers indicate that modem ESR spin probe techniques provide powerful methods for investigating not only rotational diffusion but also translational diffusion in synthetic polymers and natural membranes. Freed and his co-workers have revealed interesting differences between the macroscopic and the microscopic ESR-based diffusion coefficients for molecular probes in different media.

The motional freedom of the polymer chains in the accessible regions of a polyamide fiber is known to be highly sensitive to the presence of water molecules. A study of the molecular motions of D_2O in dyed and undyed nylon-6,6 fibers is currently being carried out by ^{2}H NMR spectroscopy, via a collaboration with Dr. Edward Samulski and his graduate student Julie Hutchison at the Chemistry Department of the University of North Carolina at Chapel Hill.

Polymer physics:

We have also been reviewing literature in the areas of polymer physics which seem likely to help us to understand the liquidlike/solidlike transition which appears to control dye diffusion in fibers. In addition to the gel-like solidification process discussed in our original proposal, another credible mechanism has been uncovered. This is the "orientational crystallization" mechanism of Elyashevich (Advances in Polymer Science, 43, 205, 1982) which is based on Flory's liquid-crystal theory, rather than on thermoreversible gelation. We are studying these theories in detail to determine if the two mechanisms, which are based on fundamentally different assumptions, can be differentiated by experiments.

Molecular modeling:

We intend to model the structures and motions of nylon and PET chain segments in the non-crystalline regions of their fibers, where the dye molecules must reside. Hawthorne Davis' work, in which he observed the dynamical mechanical properties (DMP) of fibers in aqueous glycerol baths, showed that the activation energy of their DMP is very similar to the activation energy of dye diffusion in the fiber, and that the non-crystalline fraction of the fiber consists of a mobile, liquid-like phase, through which the dye could diffuse, together with a glassy, and presumably impenetrable, rigid phase. The relative ratio of the two non-crystalline environments was found to be temperature dependent. Recent X-ray diffraction observations and analyses of PET fibers by Wunderlich et al. also suggest the existence of two distinct non-crystalline phases, one completely disordered and amorphous and the other partially ordered.

We have in prior unrelated work modeled the behavior of single nylon and PET chain segments as they are confined to occupy cylinders with ever decreasing radii. Hopefully the information generated there will serve as a starting point for modeling a small non-crystalline portion of nylon and PET fibers containing at least 2 chain segments, with and without the presence of a dye molecule. A molecular dynamics simulation, as well as a brute force search of configurational space, may be utilized in the modeling.