

National Textile Center

FY 2003 (Year 12) Continuing Project Proposal

Project No.

C01-CL01.

Competency: **Chemistry**

Novel Textile Chemistry for Dense Gas Fluids

Project Team:

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Objective:

The objective of this proposed research is to investigate the utilization of novel reactions using dense gas fluids for durable finishing, morphology modification and coloration of textile fibers. The ultimate goal is to identify and develop new, environmentally benign *fiber-reactive* chemistry that utilizes the unique properties of dense gas fluids. It is our hypothesis that dense gas fluids have several unique characteristics that have yet to be fully explored for their potential applications in textile materials. Some of the more important of these include: 1) higher selectivity and higher reaction rates, 2) the ability to utilize reactive functional groups with few, if any, side reactions, and 3) the ability to precisely control a reaction by varying the reaction temperature and pressure.

Progress Statement:

Since the beginning of this research we have demonstrated that we are able to form covalent bonds between selected reactive groups and the functional groups in nylon, silk, wool and cotton fabrics in dense gas CO₂. We have installed a new in-line FTIR analysis system into an existing 300 mL high pressure reactor system and have been able to demonstrate loss of reactants, and formation of products in real time for a diazotization and coupling reaction. We have also identified a catalyst that promotes hydrolysis and silanation in dense gas CO₂, initiated a study of its mechanism and demonstrated diazotization in dense gas CO₂. Finally, with the team, M01-CL03, *Hybrid Polymer Layers for Fiber Surface Modification*, we are exploring the adaptation of a novel experimental approach for the modification of fiber surfaces using epoxide chemistry in dense gas CO₂ (DG CO₂).

Functional Group Synthesis:

Over the past year, we have completed an investigation of the utility of the vinylsulfonyl reactive group for covalent bond formation with wool and nylon fibers in dense gas fluids, and this work has been submitted for publication⁽¹⁾. Reaction with fibers possessing nucleophilic groups, such as the amino groups present in polyamide and wool fibers, is readily achieved via Michael addition-type covalent bond formation using functional groups such as vinyl sulphone (VS). We have now demonstrated that DG CO₂ can be used as a medium for covalent bond formation between primary aliphatic amino functional groups and a compound possessing a vinylsulfonyl reactive group. During this period (year 2) we have completed an investigation of the utility of the vinylsulfonyl reactive group for covalent bond formation with wool and nylon fibers in dense gas fluids, and this work has been submitted for publication⁽¹⁾. We have also demonstrated that, although fiber-reactive treatments of silk produced unsatisfactory reaction with the fiber, at least 95% reaction completion is possible with wool and nylon, depending on the reaction conditions. Note that these results present a new paradigm for durable treatments of these fibers, including both dyeing and finishing treatments such as water repellency and flame retardency. An interesting consideration is the potential to produce an anti-shrink agent for wool using a non-colored bi- (or tri- or tetra-) vinylsulfonyl functional reactive compound in DG-CO₂.

One of the most exciting new avenues that has emerged as a result of our dense gas fluids project is the ability to synthesize azo dyes within cotton fibers. This idea stemmed from a separate dense gas project involving dyestuff synthesis, in which azo dyes were synthesized in DG CO₂ and water, in the absence of mineral acid. This work was published very recently⁽²⁾, and is shown to facilitate a highly controlled synthesis with low or no electrolyte present, and no mineral acid that would conventionally require neutralization prior to discharge into receiving waters. The concept of diazotization and coupling within a fiber is, of course, not new. It is known as azoic dyeing. However, to our knowledge the formation of dyes within a fiber using diazotization and coupling in dense gas fluids has not been attempted previously. Using a one-pot synthesis, p-nitroaniline and N,N-diethylaniline were coupled using sodium nitrite in DG CO₂ in a 300 mL reactor. Also a very small amount of water (4 mL, less than 1.5% by volume) was added to facilitate formation of carbonic acid. The yield and purity of the azo synthesis was highly dependent on temperature and far less dependent on pressure of the DG CO₂ medium.

At 80 °C, greater than 90 % conversion to the dye was achieved. The synthesis data were employed as a basic method to perform an 'azoic' dyeing on cotton using DG CO₂. An initial, simplified approach was selected to show the proof of concept for diazotization and coupling in DG CO₂ within a fibre. A 100% plain weave scoured cotton was pre-treated with a solution of the sodium salt of a β-naphthol derivative and sodium nitrite, which is typical of the procedure used in conventional aqueous azoic dyeing. Hence, β-naphthol would act as the coupling component for the azo synthesis reaction. The treated fabric was loaded into the high pressure reactor and aniline and 4 mL of water were added. The reactor was sealed and pressure and temperature increased to the desired condition. The reaction was run for 20 minutes and then pressure was released slowly. After the dyeing procedure, the dry sample was removed and washed with water and wash and rub-fastness were determined. The colour strength of the dyeings was assessed using K/S at λ_{max} before and after the wash fastness test. Table I and Figure 1 show that although significant levels of dye were removed following washing, there was still a relatively high level of dye on the fibre.

Table I. Azoic Dye K/S data on dye uptake and fixation

Conditions	Rub fastness	Color Strength (K/S)	
		Before washing	After washing
860 psi @ 25°C	3	20.02	16.62
3000 psi @ 80°C	1	16.74	14.69



Figure 1. Image of 'azoic' dyeings on cotton using pressurized CO₂ (top: 3000 psi, 80 °C; bottom: 860 psi, 25 °C).

¹ N Punrattanasin, D Hinks, G A Montero, B Mead, and Nneka C Ubeka-Adams, Fibre-Reactive Dyeing of Nylon 6,6 and Wool in Supercritical Carbon Dioxide, Coloration Technology, *submitted*.

² J. Hooker, D. Hinks, G. Montero, and C. Conlee, Synthesis of N,N-diethyl-N-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}amine Via *in situ* Diazotisation and Coupling in Supercritical Carbon Dioxide, Coloration Technology, 118 (2002) 1.

Surface Modification:

Many fibers of interest contain active functional groups on their surfaces. Some, such as celluloses, contain reactive hydroxyls both on the surface and throughout the fiber structure. Others such as glass only have functional groups on the surface of the fibers. And on other fibers, such as polyesters, the surface functionality can be increased through the use of controlled hydrolysis. The objective of this focus area of the work is to study the use of dense gas fluid CO₂ as the reaction media for surface modification. However, with respect to characterizing the chemistry that occurs as well as the resulting surface modifications it was found that both the glass surface and cotton fabrics had many disadvantages. Therefore, we have employed highly polished silicon wafers (with Si-OH surfaces) and atomic force microscopy (AFM), electron spectroscopy for chemical analysis (ESCA), ellipsometry and static contact angle measurements extensively in this study. While the results obtained for wafers treated in dense gas CO₂ with chlorodimethyloctadecylsilane (CDMODS) and octadecyltrichlorosilane (OTS) have been discussed in detail in the 2002 annual report, the fact that the surface modification from dense gas CO₂ was complete in less than 60 minutes, while it took typically 24 hours to complete the process from toluene solution should be emphasized here. In addition, it should be noted that these results represent one of the first reports in the literature of the formation of these types of surface layers using reactions in dense gas CO₂.

In addition to the highly polished silicon wafers, CDMODS and OTS were applied using either dense gas CO₂ or an aprotic organic solvent (toluene) to cotton print cloth specimens. The resulting fabric surface coatings were characterized by wetting contact angle, ESCA and tensile testing. The ESCA binding energies of ~ 101 eV for the treated fabric samples clearly indicated the presence of Si-O-C bond formation. However, with both the toluene and dense gas treated samples significant tendering of the cotton fabric by the HCl produced from either the hydrolysis or direct silanation reaction or both was observed. The tenacity decreased by almost 50% in most of the treated fabric samples and severe discoloration was observed in some of the samples after oven drying.

In an effort to overcome this problem without needing to use scavengers in the system, the use of functional silanes of the general structure R_x-Si-OR'_(3-x), where R' = -CH₃ or -CH₂CH₃ was then investigated. As expected the methoxy and ethoxy silanes were found to be significantly less reactive towards both the wafer surface Si-OH and the cellulosic hydroxyls than the chlorosilanes. Consequently, the search for a catalyst that would be active in dense gas CO₂ was initiated using octadecyltrimethoxysilane (OTMS) and dimethylmethoxyoctadecylsilane (ODMMS) as the functional silanes. At least one compound, DLT-1, has been identified and the initial focus of this work has been on characterizing the chemistry of DLT-1 in dense gas CO₂. The reactions have been studied using the same approaches that were used to characterize the reactions of the chlorosilanes. Some of the pertinent results from these experiments are summarized in Table II.

Table II. Comparison of Contact Angle and Wetting Data for Treated Wafers and Fabrics

Treatment	Contact Angle, Si Wafer	Contact Angle, Cotton Fabric	Wetting Time, sec. Cotton Fabric
CDMODS	99±1	123±1	Did Not Wet
OTS	107±3	142±5	Did Not Wet
ODMMS	69	--	<2
ODMMS & DLT-1	55	--	<2
OTMS	87±3	--	30±35
OTMS & DLT-1	110	142±1	Did Not Wet

As the data in Table II clearly illustrates, the methoxy substituted silanes were significantly less reactive than the chlorosilanes. In addition, without the added catalyst, DLT-1, the reaction was very slow under the conditions employed. However, in the presence of DLT-1, the results obtained with OTMS were comparable to those previously reported for the chlorosilanes. Currently we are using FT-IR and NMR spectroscopy to characterize the hydrolysis and silanation reactions that occur with and without the presence of added DLT-1.

The next phase of our surface modification experiments includes extending our study to the epoxide group. This work has been initiated in conjunction with the surface modification research currently underway in another NTC project, M01-C103, *Hybrid Polymer Layers for Fiber Surface Modification*. In these experiments, polyfunctional epoxides are first deposited on a substrate using a solution technique, the epoxide is then reacted to form an anchoring layer for the subsequent reaction of selected surface modifiers. In our initially experiments, the objective was to determine if exposure to dense gas CO₂ had any significant effect on the subsequent epoxide chemistry. While the results from this phase of our work are preliminary at this time, both AFM micrographs and contact angle data suggest that exposure to dense gas CO₂, under the appropriate conditions can produce a significant effect on the surface morphology of the resulting layers.

Next Year's Goals:

1. Finalize, the method development of the in-line FTIR analysis system for study of reactions in DG-CO₂.
2. Demonstrate the scope of the new dense gas, azoic chemistry for multiple fibers and reaction conditions.
3. Begin to investigate the chemistry of at least one additional functional group with a strong focus on reactions with the cellulosic hydroxyls.
4. Re-design the experimental protocol for treating cotton fabrics with organosilanes; complete the study on the mechanism of catalytic action of DLT-1; initiate a detailed investigation of the chemistry of the epoxide functional group.

Approach:

The objective of this investigation is to investigate new chemistry that can be performed on textile substrates from dense gas CO₂. At N.C. State the focus is mainly on the synthesis of compounds that will react with the functional groups on fibers. However, we have expanded the scope slightly owing to the recent work on azoic dyeing in dense gases. This approach is new and requires significant resources to assess the scope of the methodology. Thus, a designed experiment is underway and will be completed during year 3 to assess the influence of key variables on levelness, dye yield, and fastness properties. Variables that will be assessed include temperature, pressure, stir rate, time, concentration and level of preparation of the fiber.

At Clemson the focus is on surface modification chemistry using existing reactive materials. While a number of functional groups have been identified for investigation, the initial focus of this phase of the work has been on silane chemistry because of their ready availability and extensive utilization in a wide variety of textile applications. One of the fundamental questions we are addressing is whether the surface coatings formed in dense gas CO₂ are structurally and chemically different than those formed from solution. A second fundamental question we are addressing concerns the effect of dense gas CO₂ as a reaction media on the chemistry of catalysts such as DLT-1 or functional groups such as epoxides.

Once the primary objective of covalent bond formation between fibers and organic molecules in dense gas fluids has been fully characterized the proposed research will then focus on the design of new textile chemical auxiliaries and processes for use in such media.

Outreach to Industry:

Dense gas fluids may represent the only reasonable process medium alternative to conventional textile wet processing. The activity in the patent and technical literature as well as numerous industrial inquires clearly demonstrate that dense gas fluid processes for textile applications is still a topic of considerable global interest. With the facilities in place at Clemson and N.C. State a key goal is the development of formal and informal industrial partnerships to explore the feasibility of extending the scope of our investigation. At the present time we have already established an informal partnership with a major chemical company and supplier.

New Resources Required:

At NCSU a new pump, pressurized addition vessel and sight glass are required: total cost \$7K.