Evaluation of the Utilization of Supercritical Fluid Technology for Analytical, Process and Environmental Applications in Textiles

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Goals Statement:

Regulatory compliance and the need to develop more environmentally friendly processes are two of the most important issues facing the Textile Industry today . This research directly addresses both of these issues as they apply to the analysis and processing of fibers, yarns and textiles. The major goal of the analytical component of this research is the elimination or severe reduction of the use of organic solvents in many routine environmental, OSHA and QC procedures utilized in textile and fiber plants by developing alternative supercritical CO_2 supercritical fluid extraction (SFE) methods. As a process medium, supercritical CO_2 offers many potential environmental benefits; it is non-toxic, it is low cost and it is recyclable and as illustrated by the example of disperse dyeing of PET, processing with supercritical CO_2 often generates no waste effluent stream. The goal of this aspect of this work focuses on exploring the use of non-toxic supercritical carbon dioxide as a process technology in the Textile Industry, especially for dyeing and finishing and the extraction and recovery of specific components from mixed solid waste streams such as carpet.

Abstract:

This report describes the NTC research effort to evaluate the use of supercritical fluid technology for analytical and process and applications in Textiles. The focus of the analytical studies reported here is the demonstration of the utility of SFE methods and also to answer fundamental questions concerning the SCF extraction mechanism to allow SFE to gain more rapid and widespread acceptance. In the work reported in the SFE of Cellulosics section, the analytical focus of the research was on the SFE of raw cotton and cotton fabric knitted and treated at NC State and includes an extensive study of the extraction of natural cotton waxes. In the section SFE of fiber Finishes, one of the principal objectives of the research reported here is the use of SFE with CO_2 as an alternative to Soxhlet extraction for the QC analysis of fiber finishes. The samples employed in this phase of the research included commercial poly(ethylene terephthalate) (PET) filament yarn, BCF nylon yarn and polypropylene staple fiber. The SFE experiments were carried out on four different commercial instruments. Based on the results obtained from this work to-date, it would appear that SFE can be successfully used to replace Soxhlet extractions for a wide range of textile and fiber applications. For the process oriented aspects of this research, the goals and objectives of this project are more global in the sense that they are represented by the two extremes of transport into the fiber as in dyeing, and transport out of the fiber as in the process dissolution and extraction of the fiber itself. In the section Process Scale Extractions, the focus of this work reported here is on the solubilization, separation and recovery of individual components from complex textile structures such as carpets with the initial emphasis on the polypropylene carpet backing. In this study, in order to relate the extraction yields to measurable parameters such as melt flow index and molecular weight, as well as polymer internal structure, various polypropylene samples from different sources were studied. Finally, in the section SCF Dyeing Studies, the initial results from a study designed to identify and characterize any changes in PET fiber properties and morphology that occurred under model supercritical CO_2 dyeing conditions are reported.

Research Summary:

SFE of Cellulosics

The analytical focus of the cellulosic research was on the SFE of raw cotton and cotton fabric knitted and treated at NC State. The knitting oils and waxes used were obtained and large samples of the fabric in the grey, scoured and bleached forms were prepared.

Samples of the grey fabric were initially used for the majority of both Soxhlet and SFE experiments, since they contain a larger quantity of synthetic oils and waxes as well as the inherent cotton waxes. Initial extractions on an HP SFE instrument at 75 °C and various pressures resulted in weight losses ranging from 0.86-0.94 wt%. Recoveries, however were approximately 50% less than the weight losses. Weight losses on the cotton knit extracted by Soxhlet averaged 0.75% which was slightly lower, but comparable, to the SFE results. The reproducibility and accuracy of the Soxhlet method was found to be very poor when additional samples of the grey fabric as well as the scoured and bleached knits were extracted. Weight loss determinations for the scoured and bleached knits were actually observed to be equal to and higher (2.43 wt% and 1.11 wt% average respectively) than for the grey knit (1.11 wt% average).

To determine the cause of the poor results, the Soxhlet procedure was reviewed and the most obvious potential sources of error were further investigated. These were 1) the cellulose thimbles which serve as sample holders during the extraction and 2) variations in weighing due to moisture regain of the samples. Some of the cellulose thimbles were found to have material that could be extracted by 1,1,1- trichloroethane (1,1,1-TCE, the standard solvent for cotton extractions). To eliminate this variable, the cellulose thimbles were eliminated or replaced by glass thimbles. Both of these alternatives have proven acceptable in several sets of experiments.

The second variable which contributed to poor Soxhlet results was a much larger than expected uncertainty in the sample weight measurements. This was also a problem for SFE weight loss determinations. The main source of variation was found to be the level of moisture retained by the cotton. Moisture is mainly affected by the amount of time the samples are allowed to dry and the conditions under which they are cooled before weighing. A drying time of 48 hours at 100 °C and cooling in a sealed vacuum desiccator has been found to acceptably remove moisture and reduce error. Since 48 hours is excessively long, a method using a vacuum oven has been developed reducing the drying/cooling time to 4.5 hours. This is the method currently being used. Reproducibility of both the Soxhlet and SFE determinations has significantly improved with these modifications and a much higher level of confidence in the data obtained has resulted. Samples extracted without thimbles and using a 48 hour drying cycle resulted in the following weight losses for the grey, scoured and bleached fabrics:

Fabric	Weight Loss, %
Grey	0.83 ± 0.04
Scoured	0.74 ± 0.02
Bleached	0.46 ± 0.06

To determine the optimum conditions for supercritical extraction of the synthetic oils and waxes as well as the natural cotton waxes , samples of the bleached knit were extracted by Soxhlet to remove the 0.46% extractables and then spiked with solutions of methylene chloride that contained either 1% paraffin wax or knitting oil. Supercritical extractions of these samples indicated that both materials were completely extracted at 75 °C and 353 ATM for 25 minutes using 1,1,1-TCE as the trap rinse solvent.

Since there was no readily available source of cotton wax, unprocessed cotton fiber was obtained and extracted similarly. Several sets of conditions were attempted but, at best, only 50% of the Soxhlet weight loss was obtained using SFE. Extractions were completed under several conditions that provided the same solubility parameter as the 1,1,1-TCE, but weight losses were still only 50% of the Soxhlet values. Even at 670 ATM and 85 °C, the weight losses observed were still less than from Soxhlet extractions.

This has led to an extensive study of the extraction of natural cotton waxes. Comparative analysis by standard FTIR showed no differences in the composition of the extracts obtained from Soxhlet and SFE methods. Differential Scanning Calorimetry indicated that the melting range of the natural cotton wax was 42-85 °C. Based on this information, it was suspected that the temperature during the supercritical extraction may significantly affect the amount of material removed. Literature references also indicated that the wax contains a very wide variety of components including long chain (C_{18} and above) alkanes, alcohols, acids, esters and steroids.

To determine the optimum condition(s) for extraction of all of these materials, a two part experimental design was completed. A total of eighteen sets of conditions simultaneously varying temperature and pressure were evaluated. Three temperatures (40, 65 and 90 °C) and six pressure settings (200, 325, 450, 525, 600 and 670 ATM) were selected. Extraction time was held constant at 60 minutes. Each extraction was done in duplicate and the extract was collected in four fractions, each representing a 15 minute extraction period. Statistical analysis of the resulting weight loss data indicated that the most significant factor was the extraction temperature, i.e., the higher temperatures (65 and 90 °C) gave greater weight losses. This is thought to be a result of softening of the waxes which may promote better solubility in the CO_2. A surface graph of the data showed that at pressures of 325 and 425 atm and 65 °C the highest weight losses were observed (0.68%). The second highest weight loss, 0.62 wt%, was observed at 325 atm and 90 °C.

Based on these results additional extractions have been completed on the cotton fiber at 90 °C and using a pressure gradient from 200-670 ATM. Samples for Soxhlet extractions were dried simultaneously and extracted by 1,1,1-TCE. Soxhlet weight loss was 0.80% and supercritical weight loss averaged 0.81%. Weight recoveries for the supercritical extractions averaged 0.83 wt%. A second set of experiments to confirm these results are in progress. In addition, microscopic FTIR and HPLC analysis of the extracts from the designed experiments, as well as the pressure gradient and 90 °C conditions will be carried out. The resulting information will aid in determining if both the Soxhlet and supercritical extractions remove the same components. Samples of the cotton fiber have also been forwarded to Clemson for scanning electron microscope analysis to see if the surface of the fiber is affected differently by the two extraction techniques. If the above data are confirmed, the original grey, scoured, and bleached cotton knits will be extracted to validate the method. Near-infrared spectroscopic analysis of the extracts will be evaluated as a more rapid means for quantitating the materials removed from the fibers.

SFE of Fiber Finishes

At the present time, almost all of the analytical schemes used in fiber and textile fabrics analysis involve Soxhlet extraction and the use of significant quantities of organic solvents. Typical examples of these procedures are the American Association Of Textile Chemist and Colorists AATCC Test Method 94-1992 and ASTM Method D 2257-89. Since many of these schemes are gravimetric methods, 100-200 ml of waste solvent are produced with each determination. Both environmental and safety concerns have resulted in an increase in the interest in the development of alternative analytical methods which would significantly reduce the use of these solvents. The principal objective of the research reported here is to demonstrate the use of SFE with CO_2 as an alternative to Soxhlet extraction. The samples employed in this phase of the research included commercial poly(ethylene terephthalate) (PET) filament yarn, BCF nylon yarn and polypropylene staple fiber. The SFE experiments were carried out on Dionex, Hewlett Packard, ISCO and Suprex extraction instrumentation. Finish analysis by SFE was done by both gravimetric sample weight loss and gravimetric finish recovery after extraction with unmodified supercritical CO_2. The SFE results were compared to those obtained using conventional Soxhlet extraction with Freon, 1,1,1-trichloroethane (1,1,1-TCE) and Pet ether.

Experimental Protocol:

All of the fiber and yarn samples employed in this work were obtained from commercial sources and included five different polyester (PET) yarns (PET, A-E), two nylon yarns (Nylon, A-B) and four polypropylene staple samples (A-D). With the exception of the polypropylene staple fiber, all of the Soxhlet extraction data were provided with the commercial samples. The nylon samples were Soxhlet extracted with petroleum ether and finish levels determined by weight recovery. The PET samples were Soxhlet extracted with 1,1,1-TCE and finish levels determined by weight loss. The PP sample was Soxhlet extracted for 4 hours with Freon and the percent finish determined by both gravimetric weight loss and recovery.

The supercritical fluid extraction instrumentation employed in this work included a Dionex 703M, a Hewlett Packard 7680A, a Suprex Prepmaster™ equipped with an AccuTrap™ and automated variable restrictor and an ISCO SFX 2-10 with a Model 100 DX pump. The general extraction conditions used were dependent on the sample and Soxhlet extraction conditions. The SFE CO_2 used was SFC/SFE and Analytical grades obtained from Air Products and Scott Specialty Gases. No CO_2 modifiers were employed in this study.

All of the PET samples were extracted at 75 ^{o}C and 680 ATM. In the Dionex 703M, 7.5 and 10 ml extraction cells were used. Approximately 2.5 g of yarn were weighed and inserted into the appropriate cell. The cell was mounted in the extractor oven and the temperature raised to 75 ^{o}C. For the majority of this work, 1,200 ml-min^{-1} restrictors maintained at a temperature of 150 ^{o}C were used. Since percent finish was determined by weight loss from the fiber, dry trapping was used. Once the sample came to temperature in the oven, the pressure was manually ramped to 680 ATM over a 5 minute period followed by an additional 20 minute extraction period at 680 ATM. The samples were then removed from the extraction cell, placed in a dessicator overnight to allow for the outgassing of any dissolved CO_2 and then reweighed to determine the gravimetric weight loss.

In the ISCO SFX 2-10, 9.2 ml extraction cells were used. Approximately 2.5 g of PET yarn were weighed and inserted into the cell. The cell was mounted in the extractor oven at 75 ^{o}C. For the majority of this work, 18 cm 50 µm ID fused silica restrictors maintained at room temperature were used. With these restrictors, at 680 ATM, the average compressed CO_2 flow rate was ≈ 3.5 ml-min^{-1}. Since percent finish was determined by weight loss from the fiber, dry trapping was used. Once the sample came to temperature in the oven it was extracted under static conditions for 2 minutes at 136 ATM. The pressure program then ramped the cell to 680 ATM in 9 steps over a 10 minute period. The sample was then extracted for an additional 10-12 minutes under dynamic conditions. The extracted samples were then treated the same as those from the Dionex 703M.

All of the nylon samples were extracted with the Hewlett Packard 7680A at 40 ^{o}C using 7.0 ml extraction cells. Approximately 2.0 g of yarn were weighed and inserted into the cell. The cell was mounted in the extractor oven and the temperature raised to 40 ^{o}C. For the majority of this work the HP variable restrictor was set to a compressed CO_2 flow of 1 ml-min^{-1} and a temperature of 45 °C. Once the sample came to temperature in the oven, the pressure was automatically ramped to 300 ATM with a subsequent 2 minute static extraction followed by an additional 30 minute dynamic extraction period. The restrictor flow was decompressed onto an HP trap with the ODS packing maintained at 25 °C. After completion of the extraction step, the trap temperature was raised to 30 °C and the contents of the trap were automatically rinsed into three pre-weighed collection vials with 1 ml of methylene chloride each. The solvent was then evaporated from the vials in an oven at 80 °C and the weight recovery determined by gravimetric analysis.

The four PP staple samples were all extracted at 40 °C and 300 ATM in the HP 7680A, and one of them, (A-1), in both the HP and Suprex instrumentation. The experimental conditions and procedure used in the HP 7680A for the extraction of the PP staple were identical to those used for the nylon samples. For the Suprex Prepmaster™ extractions of the PP, approximately 2.0 g of staple were weighed and inserted into a 10 ml cell. The cell was mounted in the extractor oven and the temperature raised to 40 °C. For the majority of this work the Suprex variable restrictor was also set to a compressed CO_2 flow of 1 ml-min^{-1} with the restrictor at 50 °C. Once the sample came to temperature in the oven, the pressure was automatically ramped to 300 ATM with a subsequent 3 minute static extraction followed by an additional 45 minute dynamic extraction period. The restrictor flow was decompressed onto the AccuTrap™ trap with deactivated fused silica packing maintained at 5 °C. After completion of the extraction step, the trap temperature was raised to 30 °C and the contents of the trap were rinsed into 2 pre-weighed collection vials with a total of 3 ml of methylene chloride. The solvent was then evaporated from the vials in an oven at 80 °C and the weight recovery determined by gravimetric analysis.

When accompanied by a standard deviation, all of the SFE data reported in this work represent a minimum of three determinations. All of the Soxhlet extraction data represent duplicate determinations.

Summary of Results

In the first phase of this research into the use of SFE for the analysis of fiber spin finishes, a spunbond PET fabric substrate which is manufactured without a fiber finish was employed and treated with the components of a model PET fiber spin finish (1). The finish components studied included a fatty acid ester lubricant, a linear EO/PO alcohol emulsifying agent and an ethoxylated phosphate ester salt antistat. In these experiments, weighed spunbond fabric samples were treated with the butyl stearate to a finish level of 1-3% on the weight of the fiber by a solvent evaporation technique. The SFE extraction efficiency was determined by gravimetric analysis and SFC. For this work, the initial temperature and density SFE extraction conditions used were determined by using fabric samples spiked with butyl stearate and by mimicking the results obtained from Freon Soxhlet extractions. However, the qualitative and quantitative data reported also showed that the SFE data were strongly affected by the extraction conditions chosen and that further experimentation would be necessary in order to better define the observed effects.

When a fiber such as PET is Soxhlet extracted the only experimental variables which need to be chosen are the solvent itself and the extraction time. In this case, the extraction temperature and solvating power of the solvent become constants once the solvent is chosen. On the other hand with SFE, because the solvating power of the supercritical CO_2 is a function of its density, as previously shown, the choice of solvating power becomes an important variable which must be addressed. In addition, the temperature range available (above the lower limit temperature of ≈35 °C required to achieve the supercritical state) to the analyst is restricted only by the instrumentation employed. After the initial SFE studies were completed, the supercritical fluid extraction temperature was chosen based on the boiling points of the Soxhlet solvents, 75 °C for 1,1,1-TCE and 40 °C for Freon and petroleum ether. In addition, the choice of extraction pressure was based on the Hildebrand solubility parameter (δ). For the solvents of interest here, the δ values in Hildebrand units are; 8.5 for 1,1,1-TCE , 7.3 for Freon and ≈7.6 for petroleum ether, which corresponds to supercritical CO2 pressures of 680 ATM at 75 °C for the PET samples and 300 ATM at 40 °C for the nylon and PP samples. In addition, based on earlier work, extraction times and restrictor flows were chosen to yield at least four supercritical CO_2 swept cell volumes. Any other instrument specific instrumental parameters such as restrictor or trap temperatures were set empirically.

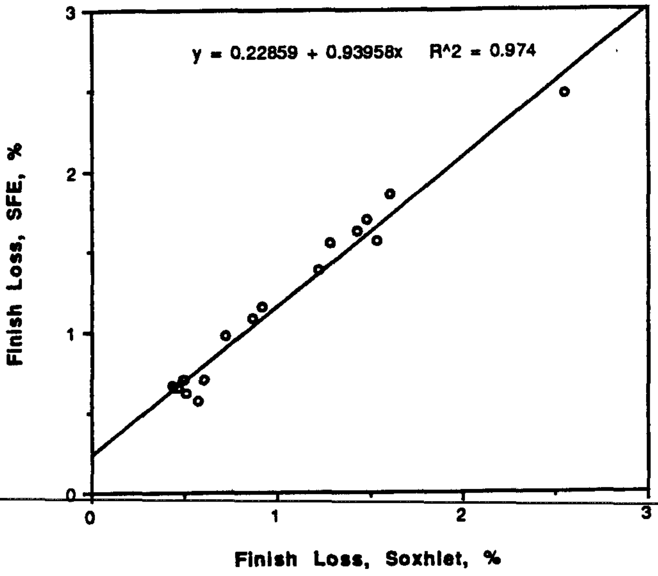
Whether the supercritical extraction efficiency was based on gravimetric weight loss or gravimetric finish recovery, was determined by the standard Soxhlet procedure for that sample. For the PET samples, the Soxhlet data represent weight loss data and consequently the SFE data are presented as weight loss results. On the other hand, the nylon Soxhlet data represent weight recovery results as are the corresponding SFE data. Since only the PP Soxhlet extractions were done at Clemson, only these experiments are compared on both a weight loss and recovery basis.

The results obtained from the SFE of the PET fiber samples using the Dionex 703M instrumentation at 75 °C and 680 ATM and the corresponding 1,1,1-TCE Soxhlet extraction data are summarized in Table I.

Table I. Comparison of PET Yarn Data From SFE at 680 ATM and 75 °C and 1,1,1-TCE Soxhlet Extraction

	Weight Loss, %	
Sample	Dionex 703M	TCE Soxhlet
A-1	1.09±0.07	0.86
A-2	0.98±0.09	0.72
B-1	1.85±0.10	1.60
C-1	0.57±0.07	0.57
C-2	0.70±0.02	0.60
C-3	0.62±0.04	0.51
C-4	0.67±0.03	0.44
C-5	0.66±0.04	0.47
C-7	0.66±0.05	0.45
C-8	0.70±0.07	0.49
C-9	0.70±0.07	0.50
D-1	1.55±0.11	1.28
D-2	1.70±0.11	1.48
D-3	1.57±0.19	1.53
D-4	1.62±0.10	1.43
D-5	2.48	2.55
E-1	1.16±0.06	0.92
E-2	1.39±0.09	1.22

Figure 1. PET SFE Finish Loss as a Function of 1,1,1-TCE Soxhlet Finish Loss Data



From the data summarized in Table I., it is clear that the SFE data correlate very well with the 1,1,1-TCE Soxhlet extraction results for these samples. This is further illustrated in Figure 1., where the SFE results are plotted versus the Soxhlet data. Also, based on these data it would appear that two samples would need to have finish levels greater than 0.2% apart in order to confidently distinguish between them by SFE under these conditions. By these criteria and using SFE, A-1 and A-2 have the same finish level, all of set C are the same, D-1 through D-4 are the same and different from D-5 and E-1 has less finish than E-2.

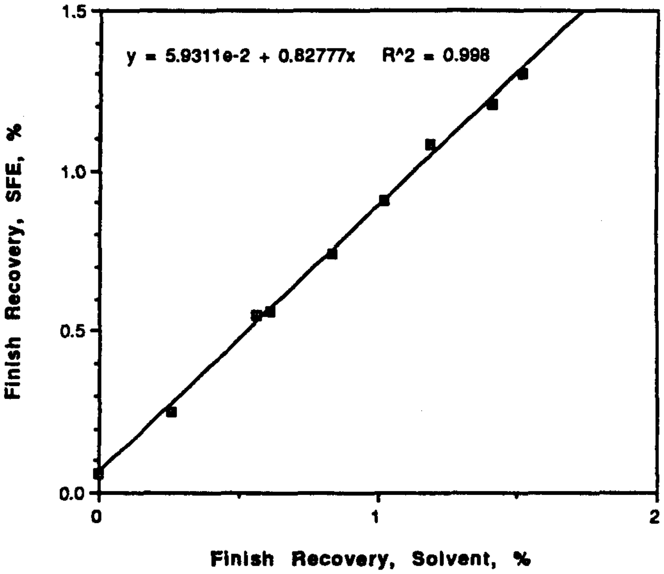
One additional observation that needs to be explained concerning the data presented in Table I. is the fact that, with the exception of sample D-5, the SFE gravimetric weight loss data is 0.1 to 0.2% higher than the corresponding Soxhlet data. If it is assumed that, at 680ATM and 75 °C, supercritical CO_2 is able to remove all of the same finish components as a 1,1,1-TCE Soxhlet extraction, then the supercritical CO_2 must be removing additional components from the PET itself. Prior work at Clemson, as well as other studies, have clearly demonstrated that both supercritical CO_2 as well as 1,1,1-TCE extract measurable quantities of oligomer and other low molecular weight species from PET. Therefore, the data in Table I. suggest that even though the calculated δ for supercritical CO_2 under the conditions employed for the PET SFE is less than that of 1,1,1-TCE, the supercritical CO_2 removes more oligomer at this density.

The SFE results from the two sets of nylon yarns with different finishes using the HP 7680A instrumentation at 40 °C and 300 ATM compared to the corresponding petroleum ether Soxhlet data are summarized in Table II and presented in graphic form in Figure 2.

Table II. Comparison of Nylon Yarn Data From SFE at 300 ATM and Pet Ether Soxhlet Extraction

	Finish Recovery, %	
Sample	HP 7680A	Pet Ether Soxhlet
A-1	1.27±0.06	1.52
A-2	0.88±0.04	1.02
A-3	0.76	0.82
A-4	0.55±0.01	0.56
A-5	0.25±0.04	0.26
B-1	1.21±0.05	1.41
B-2	1.06±0.05	1.19
B-3	0.90±0.03	1.01
B-1	0.74±0.02	0.83
B-1	0.55±0.02	0.61

Figure 2. Nylon SFE Finish Recovery as a Function of Pet Ether Soxhlet Finish Recovery Data



From the data summarized in Table II. and illustrated in Figure 2., as with the PET samples, it is clear that the SFE data correlate very well with the petroleum ether Soxhlet extraction results for both of these nylon yarn samples. However, based on these data, it would appear that two samples with finish levels less than 0.2% apart could be distinguished between by SFE under these conditions.

In contrast to what was observed with the PET weight loss SFE data in Table I., the SFE gravimetric weight recovery data for the nylon yarn samples was found to be 0.1 to 0.2% lower than the corresponding Soxhlet data. These results would suggest that at 300 ATM and 40 °C either supercritical CO_2 is not able to remove all of the same finish components as a petroleum ether Soxhlet extraction, or, the supercritical CO_2 must not be removing additional components from the nylon fiber itself. At the present time, further investigation is required in order to distinguish between these two possible explanations for this observation. In either case, the correlation observed for the data in Table II. between the SFE and Soxhlet results adds further support to the concept of using SFE as a replacement for Soxhlet extraction for quantitative finish analysis.

The SFE results from the PP staple samples using the HP 7680A instrumentation at 40 ^{o}C and 300 ATM and the corresponding Freon Soxhlet data are summarized in Table III. To date these samples represent the only commercial samples where a significant difference has been observed between the absolute % finish values from SFE and Soxhlet data. However, even for these samples there is a good correlation between the two methods for determining the relative finish level. The results of some preliminary experiments suggest that a major cause of the discrepancy observed between the SFE and Soxhlet results in this case may be due to low molecular weight material extracted from the PP by Soxhlet but not SFE under the conditions employed. Finally, when PP sample A-1 was extracted with the Suprex instrumentation the gravimetric finish recoveries was found to be 0.46±0.02%. As with the ISCO and Dionex PET data reported earlier, the SFE results for this PP staple sample are statistically indistinguishable between the two instruments.

Table III. Comparison of Polypropylene Staple Fiber Data From SFE at 300 ATM and Freon Soxhlet Extraction

	Finish Recovery, %	
Sample	HP 7680A	Freon Soxhlet
A-1	0.52±0.06	0.82
B-1	0.57±0.03	0.73±0.10
C-1	1.56±0.07	2.09±0.62
D-1	1.72±0.05	2.52±0.17

Based on the results obtained from this work to-date, it would appear that SFE can be successfully used to replace Soxhlet extractions for a wide range of textile and fiber applications. In addition to reducing or eliminating organic solvent consumption, these data show that SFE also significantly reduces the time required for a gravimetric finish analysis. The finish extraction work currently in progress has as its focus a more detailed understanding of the extraction mechanism. Several temperature, pressure time studies have been initiated in order answer some of the questions raised from the results of these experiments and also to establish a more fundamental basis for proposing a standard SFE extraction method.

Process Scale Extractions

The focus of this work was on the solubilization, separation and recovery of individual components from complex textile structures such as carpets. The feasibility of dissolution in CO_2 of polypropylene and nylon in a batch process has been demonstrated in earlier work. The present efforts were directed toward the use of continuous processes in polymer recovery with the aim of generating the appropriate experimental data to determine the optimum conditions for such processes.

The initial experiments were conducted on the use of supercritical fluids as solvents for the separation and recovery of the polypropylene split film primary carpet backing. In these experiments, supercritical CO_2 over the temperature range 180-220 °C and supercritical propane at 95 °C and pressures from 2,000-6,000 psia were utilized. Highest yields of extracts were obtained with supercritical propane at 6,000 psia.

Characterization of the extracted materials from supercritical propane was made using DSC and FT-IR. Comparison of 4,000 and 6,000 psia extractions revealed that the higher pressure resulted in a greater amount of extracted material in a given time. The DSC analysis of the original isotactic polypropylene film resulted in the melting point of 165 °C. In contrast to the 4,000 psia extractions which did not reveal any material with a melting point close to that of polypropylene, the 6000 psia runs yielded a substance with a melting point of $\approx$158 °C. This lower T_{mp} may represent oligomer or low molecular weight polypropylene extracted as a result of fractionation.

Attempts were made to perform experiments with supercritical propane at higher temperatures and pressures to possibly obtain even greater yields of extracted material. However, a great deal of difficulty with the apparatus was experienced with plugging of the lines and it was decided to concentrate the subsequent experiments on CO_2 extractions.

In order to relate the extraction yields to measurable parameters such as melt flow index and molecular weight, as well as polymer internal structure, various polypropylene samples from different sources were studied. As expected, atactic polypropylene which does not have a well defined melting point and has an amorphous internal structure appears to be the easiest to extract. A specimen of atactic polypropylene was successfully extracted at only 80 °C and a pressure of 6,500 psia the extract characterized by FT-IR. The melt flow index of this material could not be measured under standard test conditions because the MFI of this material was higher than the upper MFI range of the instrument. A commercial sample of isotactic polypropylene with a nominal MFI of 440 and wt. avg. M_W of 90,000 yielded extracts at 190 and 200 °C and 9,500 psia. Further experiments on these samples are in progress with the objective of determining the average solubilities of the different PP materials.

SCF Dyeing Studies

The conventional method of dyeing poly(ethylene terephthalate) (PET) fiber is with an aqueous dye liquor consisting of water, disperse dye, dispersing agents, and other auxiliaries which are needed to enhance the efficiency of the dyeing process. After dyeing, residual chemicals remain in the water and, consequently, add to the cost and complexity of treating the effluent stream. The cost of waste water treatment and the value of water as a raw material are both becoming more serious concerns to the dyeing industry. As a result, recently, there has been renewed interest in exploring approaches to the dyeing and coloration of textiles which involve the replacement of water as the dye transport medium. In one such approach, Ciba-Geigy Ltd., in conjunction with the German Center for Textile Research Northwest and equipment manufacturer Joseph Jaspers GmbH and Co., have developed a dyeing method and a line of dyes for use with supercritical carbon dioxide as a replacement for water as a dyeing medium.

Dyeing with supercritical carbon dioxide was developed to completely avoid the use of water during dyeing, thereby, creating no pollution. This novel technique offers other potential advantages including.

- less energy is used to heat the dye liquor,
- drying is not required after dyeing,
- carbon dioxide is recycled in the process,
- no auxiliary agents are used in the process,
- and, residual dyestuff is recovered in a reusable form.

These potential advantages of this process have even warranted the introduction of pilot scale commercial equipment in Europe.

However, very little has been published about the effects, if any, supercritical CO_2 dyeing may have on either fiber morphology or fiber properties. The NTC research into the use of supercritical CO_2 for analytical applications at Clemson has indicated that the PET fiber structure could be affected under the conditions typically used in supercritical dyeing. Thus, the principal objective of this study into SCF disperse dyeing was to identify and characterize any changes in PET fiber properties and morphology that occurred under model supercritical CO_2 dyeing conditions. This analysis was considered to be a necessary, integral step, into further research involving supercritical fluid dyeing with carbon dioxide. Clearly, if the fiber properties are adversely affected as a result of morphological changes, the potential future commercial use of CO_2 as a dyeing medium would be severely limited. On the other hand, morphological changes which led to improved properties would add value to supercritical dyed textile materials.

For this study, commercially available regular and micro denier PET, POY and fully drawn, filament yarns were used. The PET yarn samples were wound on bobbins under controlled tension and then exposed to supercritical CO_2 under conditions representing a typical supercritical CO_2 dye cycle. The control samples were obtained by exposing the yarns to a similar cycle in an aqueous dye bath in the Launder-ometer™ as well as a heat only cycle in the supercritical fluid cell. Tensile properties, optical birefringence, modulated differential scanning calorimetry, dynamic mechanical thermal analysis and scanning electron microscopy were the techniques chosen to characterize fiber morphology and properties. The preliminary results from this study clearly show that exposure to supercritical CO_2 does have an effect on the fiber morphology. However, until all of the data are fully analyzed, the significance of the observed effects cannot be ascertained and additional experiments are in progress to more fully characterize the observed changes in fiber properties.