The dyeing of polypropylene fibers in supercritical fluid

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Abstract Many attempts to use water dyeing polypropylene (PP) fibers have not resolved the undyeability of the fibers very successfully. Because of the success of dyeing polyester with disperser dyes in supercritical fluid many attempts to apply this technique to dyeing PP fibers have been made. This paper discusses the advantages and feasibility of dyeing PP in supercritical fluid instead of water. Approaches of dyeing PP fibers in supercritical fluid and the dyes used in supercritical fluids are also reviewed.

Keywords supercritical fluid, polypropylene fibers, dyeing

1. Introduction

The worldwide consumption of polyolefin fibers, mainly PP has grown rapidly in the polymer market since 1980s. The growing demand[1] for PP fibers can be explained by their several intrinsic, advantageous properties, namely easy process ability, low specific gravity, almost zero water adsorption, good chemical resistance, good antistatic character as well as wide availability and low cost.

PP fiber has a non-polar, aliphatic structure with its high crystallinity and high stereo-regularity which are responsible for the good physical properties of the material. PP fibers are difficult to dye since their structure does not contain dye sites to which certain kinds of dyes will bind. To improve the dyeability of PP fibers, the primary mission is to investigate the solvents capable of penetrating the PP structure so as to carry a dyestuff into the penetrated fibers. Since conventional dyeing medium---water does not resolve this successfully. Fiber modifications without deterioration of the positive characteristics of PP fibers have been tried to make conventional water-dyeing possible[2], but most of them have not been successful till now. The application of new polymer additives[3] changed the positive characteristics of PP fibers. The high cost of blending PP fibers with other fibers made the technology unsuitable for commercial use[4].

2. Dyeing PP fibers in supercritical fluid

In recent years, waterless dyeing that uses the supercritical fluid as an alternative solvent of water in conventional dyeing process has been gaining much interest in the textile industry.

The new process for dyeing textile fibers using supercritical carbon dioxide (SC-CO_2) instead of water was patented by Schollmeyer. This dyeing system has since been developed from laboratory scale using a 400 ml autoclave to a semi-technical scale[5,6]. The applications of SC-CO_2 to natural fibers such as cotton[7, 8] and wool[9] have been extended by investigators. Several investigators have attempted to dye cellulose fibers[10,11] in SC-CO_2 because of its large share on the market and their results suggested that further exploits are required. Bach et al.[12,13] investigated the pretreatment of polyethylene terephthalate (PET) by a heat-setting process before dyeing in SC-CO_2 and they[14,15] also reported the results of experiments with Uhde pilot plant by SC-CO_2. It was further reported PET was dyed with different dyes by this method successfully [16].

2.1 The advantages of the supercritical fluid as a medium for dyeing

The processes of dyeing of PP fibers in water and SC-CO_2 are respectively showed in Figure 1 and 2. Dyeing process of PP fibers by conventional method discharges much wastewater which is contaminated by various kinds of dispersing agents, surfactants and unused dye. It is very difficult to treat the wastewater containing many additives by conventional biological process.

Above critical points of CO_2 and N_2O, they have a high dissolving power for hydrophobic dyes[17,18]. The dyeings were carried out at temperatures of 110-130℃ and pressures between 260 and 300 bar. CO_2 as the dyeing medium should normally promote the diffusion of dyes into fibers without fiber modification. This was observed by measuring the melting point and the melting enthalpy of the fiber sat different pressures by differential-heat-flow calorimetry. CO_2 acts as a quasi-impurity by which the melting point of the fibers at 280 bar by comparison with air under atmospheric pressure[10]. The CO_2-dyestuff mixture penetrates very well into the fibers because of its low viscosity and high diffusion rate and afterwards pressure has to be decreased moderately so that the dyestuff remains in the material[19]. The excess dyestuff after depression is recovered as dry material and can be reused for further dyeing step.

The partition equilibria of the fiber/dye/ CO_2 system at fixed temperatures and pressures are therefore mainly responsible for the dye uptake the fibers. SC-CO_2 eliminates colored wastewater and high drying-energy costs associated with aqueous fibers dyeing and SC-CO_2 and becoming potentially attractive alternative.

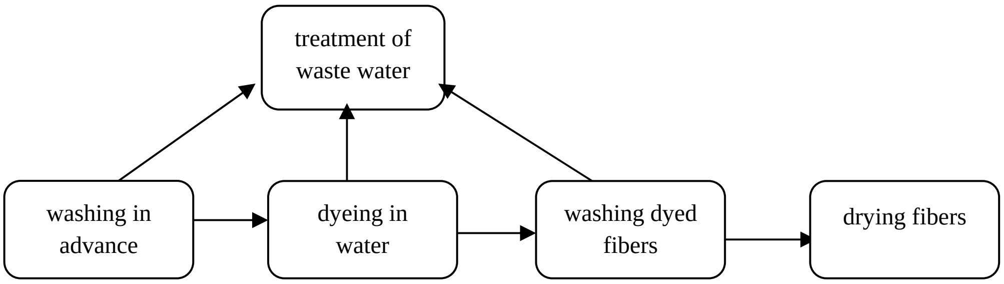


Fig. 1 The process of dyeing in water

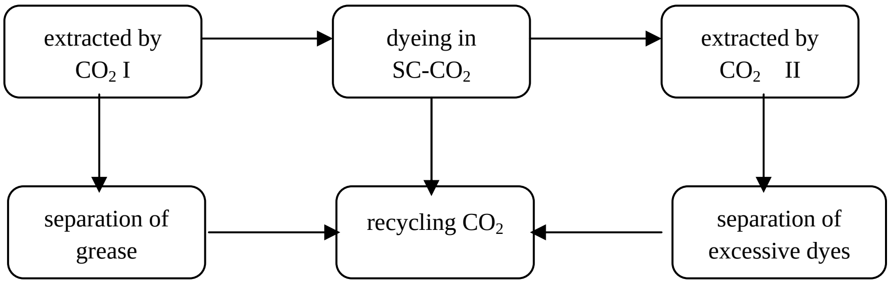
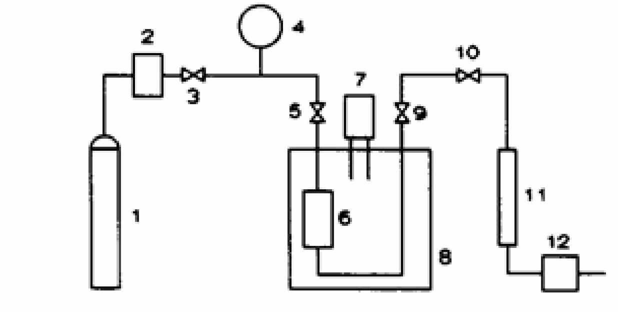


Fig. 2 The process of dyeing in SC-CO_2

2.2 Development of the dyeing PP fibers in supercritical fluid

Because of the success of dyeing polyester with disperser dyes in supercritical fluid many attempts to apply this technique to dyeing PP fibers have been made. Saus, Wolfgang and Schollmeyer applied SC-CO_2 dyeing technology to dyeing hydrophobic fibers in 1993. In recent years, the studies have become popular because of their good leveling results and greater economic efficiency.

The dyeing apparatus used in some experiments are shown in Figure 3. Fabric and dye are put in the container before dyeing. Then the apparatus is sealed and heated to a pre-selected dyeing temperature while CO_2 is pumped simultaneously to the settled pressure. The dyeing is maintained for some time and then the pressure is reduced step by step while the temperature is still maintained at dyeing temperature until the pressure is reduced to atmospheric pressure.

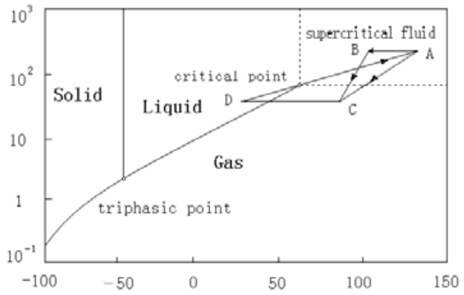


1. Liquid CO_2 2. Pump
3,5,9. Pressure-control valves 4. Manometer
6..Autoclave 7. Temperature sensor
8. Dyepot 10. Adjust valve

Fig. 3 Diagram of SC-CO_2 dyeing technology

Significant structure changes in PP fibers occur only when the material is not thermo-set or the processing temperature is near or above the heat-setting temperature. In SC-CO_2 dyeing process only the pressure and temperature need to be changed as shown in Figure 4.

Dyeing PP fibers with disperse dyes can be accomplished using a SC-CO_2 system because of the excellent compatibility of the dyes and CO_2. The decreasing value of birefringence caused by the diffusion of dye and CO_2 could make the polymer chain more mobile without damaging the fabric[20]. This was confirmed by wide-and small-angle X-ray scattering[21,22], differential thermal analyses (DTA) and stress-strain. Generally, the change in the crystal network of PP fibers is increased by the treatment in CO_2 in comparison with that in water and air [20].

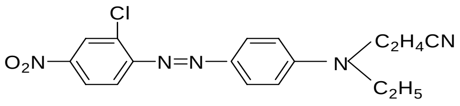


A extracted by CO_2 I and dyeing in SC-CO_2
B extracted by CO_2 II
C separation of grease D feed the dyes and CO_2

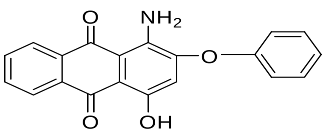
Fig. 4 Recycling of CO_2 in SC-CO_2 dyeing technology

Solubility of dye in SC-CO_2 is one of the most important parameters for dye selection and also for process temperature and pressure optimization. In order to utilize SC-CO_2 dyeing technology to industrial application, dye solubility must be high at conditions that can be realized in commercial dyeing machinery.

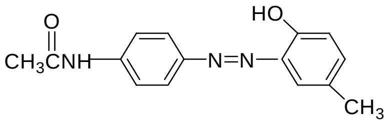
The diffusion and solubility of dye were strongly dependent on the properties of the dye itself. Bach et al.[23,24] dyed polyolefin fibers in SC-$CO_2$with disperse dyes which are showed in Figure 4. The dyeing temperature for PP fibers was 120℃, the pressure of CO_2 280 bar, the dye concentration 2%w.o.f.， the dyeing time 30min. They investigated the influence of the dye structures on the fastness of the dyed PP fibers.



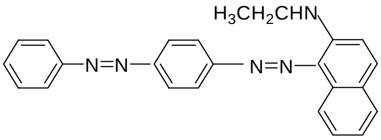
1.C.I. Disperse Red 50



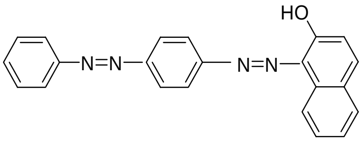
2. C. I. Disperse Red 60



3. C.I. Disperse Yellow 3



4. C.I.Solvent Red 19



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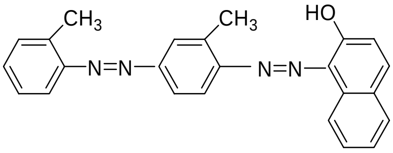

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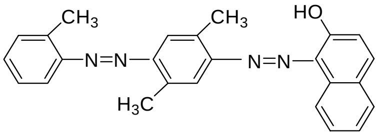
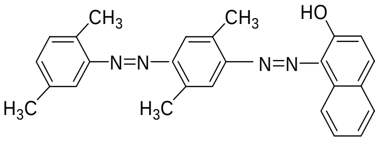


7. C.I. Solvent Red 26



8. C.I. Solvent 27

Fig. 4 Structures of disperse dyes used in the experiment of Bach et al.

In their research work the dye uptake of PP fibers was determined as example for Solvent Red 27 after respectively dyeing in SC-CO_2 at 280 bar 120 ℃ and in water under optimum conditions at 120 ℃.The results are presented in Table 1.

Table 1 Comparison of the Dye Uptake of PP Fibers after Dyeing in Water and SC-CO_2

Fibers	Dye Uptake （mg/g Fiber）	
	In CO_2	In H_2O
PP multifil	2.5	1.5
PP heavy-duty fiber	2.1	1.0

Because of the highly apolar character of the dyes with a naphthalene moiety, better grade of the sublimation-fastness was expected. The results in Table 2 and Table 3 showed that small dye molecules have very poor sublimation-fastness on all fibers tested.

Table 2 the sublimation-fastness of PP in SC-CO_2

Dye	PP multifil	PP heavy-duty fiber
4	4	4-5
5	4	4
6	4	3-4
7	3-4	4
8	3	4

Reflectance measurements showed that disperse azo dyes with a naphthalene moiety gave much deeper colors than benzoazo or anthraquinone dyes. The light- fastness and washing-fastness at 40℃ were both 5 grade for PP fibers dyed with most of the naphthylazo dyes. The color-fastnesses of the dyed fibers to sublimation in storage are in the range from 3 to 4.

Table 3 the Light-fastness of PP in SC-CO_2

Dye	PP multifil	PP heavy-duty fiber
1	1	3
3	>5	>5
4	2-3	2-3
5	5	5
6	5	5
7	5	5
8	5/5*	5/4*

Tataba, Isao[25] dyed PP fibers with two different disperse dyes in SC-CO_2 fluid. The partition coefficient (K) of dyes between polymer phase and SC-CO_2 phase was calculated from the equilibrium dye uptake and the solubilities of dyes. A linear relationship was found in the plots of the logK vs. logrF. The slope roughly depended on solvation of dye in SC-CO_2 for all polymer-dye systems.

Kikuchi, Keiichi et al.[26] reported that a PP fabric was dyed with Shikon (Lithospermum erythrorhizon) in SC-CO_2 at 110℃ and 20 MPa for

30 min. Color yield (K/S) value was 195. In the article of Cho, Sung Mi et al.[27] PP fibers and fabric were dyed with anthraquinone disperse dyes without any auxiliaries in SC-CO_2. The solvolysis of the dyes and dyeability of PP in SC-CO_2 were investigated. The results showed that high affinity of dyes for the fibers in SC-CO_2 dyeing system was very different from that in solvent dyeing with extremely small affinity of the dyes for the fibers.

Because some dyes can be used only for technical applications and not for clothing. Dyeing experiments with non-toxic dyes are in progress. It was therefore expected that other dyes with special chemical structures are needed to dye PP fibers to deep colors without any carriers.

Through all these process modifications, the main disadvantage of the very low light-fastness of PP fibers could not be overcome. For example, alkyaminoanthraquinone dyes with long aliphatic chains, which show good dyeing results and fastness properties when dyed in water[28], have low fastness on PP fibers when dyed in CO_2. The unacceptable low fastness properties of PP dyed by disperse dyes are the result of only a few dye-fiber interactions. Hence only dyes with a high hydrophobic characteristics, such as anthraquinone and disperse dyes with many methyl groups or long aliphatic chains, are suitable for increased dye-fiber interactions, based on Van der Waals or dispersion forces and maybe realize fastness properties. The exploitation of new dyes used in SC-CO_2 is important.

3. Summary

The normal dyeing process using water as solvent has disadvantages. Different agents have to be added for treatment of hydrophobic material, after dyeing a subsequent drying process with high energy consumption is necessary and large amounts of high loaded wastewater is produced. In contrast, dyeing by SC-CO_2 discharges much less wastewater. These results make new ways to dye PP fibers in SC-CO_2 and help to expand the application of supercritical dyeing technology.

The analysis indicated that if the limitation in the color fastness demand can be compromised, the process of dyeing in SC-CO_2 can show benefits in energy, time and even cost. Thus dyeing of PP fibers with the SC-CO_2 method is worth developing and can be applicable commercially.

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