TREATMENT OF TEXTILES IN CO_2 – POTENTIALITIES AND LIMITATIONS

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While dyeing of poly(ethylene terephthalate) (PETP) fibres in supercritical carbon dioxide is now on its way to be transferred into the textile finishing industry to check the economic efficiency and practicability in an upscaled plant, dyeing of natural fibres such as cotton is still a problem. Within the paper an overview is given about the international state-of-the-art of dyeing technical (aramides, polyolefin fibres, polybenzimidazole and others) and natural fibres (wool, viscose, silk) in carbon dioxide. The potentialities and limitations are discussed regarding the dyes and fibre structure and polarity but also methods are presented to improve the dye uptake of these fibres in carbon dioxide. Moreover a new field of application in our institute is the disinfection and sterilization of textiles for medical use in CO_2. While pure CO_2 has limited disinfecting properties, good results are obtained by adding very small amounts of co-solvents such as water and alcohol or CO_2-soluble disinfecting agents. The results are compared with conventional technologies such as water/alcohol- mixtures, peracetic acid and disinfecting agents in water.

INTRODUCTION

The problem of dyeing natural fibres in carbon dioxide arises from the inability of carbon dioxide to break hydrogen bonds to a conveniently high extent [1,2]. This seems to hinder the diffusion of dyes into the interior of highly hydrogen bond crosslinked fibres such as cotton and viscose [2] but also wool and silk. Furthermore, disperse dyes only show slight interactions with polar fibres, leading to inacceptably low fastness data, while reactive-, direct-, and acid dyes which are used in conventional water dyeing are nearly insoluble in supercritical carbon dioxide. As a result of all the disadvantages, in literature different methods have been described to overcome the limitations of the CO_2-dyeing process for natural fibres [3].
Another challenging field of application of CO_2 in textile industry is the disinfection and sterilization of e.g. medical textiles and clothes before use [4-6]. Up to now this process is carried out by a treatment with water steam. By adding peracetic acid to the steam the disinfecting effect can be increased [7]. Under these severe conditions the fibre damage is very high and as a result the lifetime of the textiles is very short.
In this paper the disinfection of textiles using liquid carbon dioxide at a pressure of 70 bar at 20 °C is presented and discussed [6]. The main advantages are that no corrosion on the disinfecting machine parts occur, the fibre damage is negligible and the textiles do not have to be dried after the process. For comparison also disinfecting experiments in water are carried out.

A transfer of the disinfecting process in liquid carbon dioxide into industry is possible because the machinery equipment needed is based on the dry cleaning process of textiles which is meanwhile commercially used in the USA [8]. In comparison to the processes at high pressures presented by other authors [9-13] the investment costs for such a machine are much lower because of the moderate temperatures and pressures.

MATERIALS AND METHODS

The dyeing experiments in supercritical carbon dioxide [14-16] as well as the disinfection tests [6] were carried out as described elsewhere.

RESULTS AND DISCUSSION

Dyeing of natural fibres in supercritical carbon dioxide

Dyeability with disperse dyes can be improved by impregnation of swelling and cross linking agents or fibre modification before dyeing or by adding polar co-solvents as presented in Figure 1.

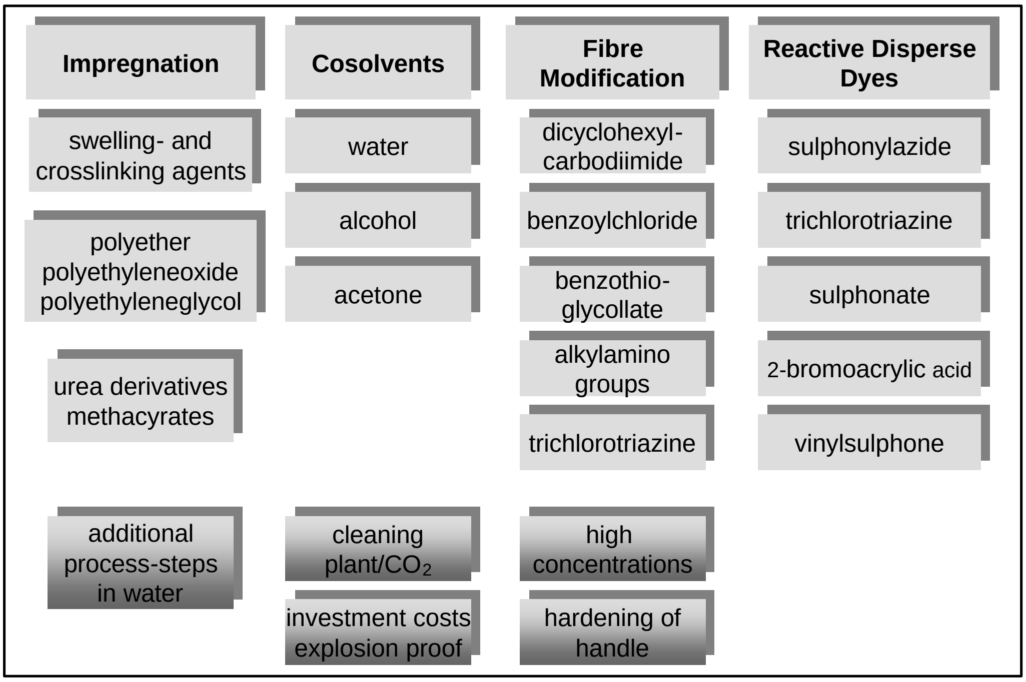

Figure 1 : Improving measures for dyeing of natural fibres in supercritical carbon dioxide

All the dyeing experiments on natural fibres described so far lose the main advantages of the water-free supercritical carbon dioxide dyeing because in all processes presented pre-treatment and in some cases after-cleaning of the dyed fibres has to be carried out in water or other solvents to remove the pre-impregnated substances from the fibre surface. This needs additional energy-consuming treatment and drying steps of the fibres which are not needed when they are conventionally dyed in water [3].

When substances are permanently fixed on the fibre surface, high concentrations of the modifying agent are needed to obtain convenient high colour depths. This leads to significant changes in the fibre properties of e.g. cotton which are unacceptable for most applications [3]. Moreover, when co-solvents are used, cleaning problems arise when the colour has to be changed because of the increased dye concentration in the fluid phase. In contrast to conventional CO_2 dyeing, the co-solvent has to be removed from the fibre after the process, which needs an additional drying step. For industrial applications, when organic solvents are used, the dyeing plant has to be explosion-safe and the co-solvent must be separated from the carbon dioxide after dyeing. Both will drastically increase the price of the plant [3].

As a result, other concepts have to be developed for the dyeing of natural fibres in supercritical carbon dioxide. One of the concepts which could overcome the disadvantages mentioned above is to modify CO_2-soluble disperse dyes with functional groups which are able to react with the fibre with the formation of a chemical bond (see Figure 1).

The reactive groups which have been determined up to now, their degree of fixation on cellulose and protein fibres and the fastness properties are summarized in Table 1 [3].

Table 1 : Influence of the reactive group on the colour yield and the fastness properties (mean values) after dyeing of natural fibres in supercritical CO_2 [3]

			Fastness Data		
Reactive Group	**Substrate**	**Colour Yield**	**Washing**	**Rubbing**	**Light**
Sulphonylazide	impregnated cotton	low	n.d.*	n.d.	n.d.*
1,3,5-Trichloro-2,4,6-triazine	cotton	low	1/3/5	5	4
	protein fibres	no fixation	-	-	-
SO_2X, X= Cl, Br, I, Acetate, Phenolate, NR_2-, Toluenesulfonate	-	-	-	-	-
	protein fibres	middle/high	5	n.d.	n.d.
2-Bromoacrylic acid ester or amide	cotton	middle/high	4-5	5	5
	protein fibres	middle/high	5	4-5	5
Vinylsulphone	cotton	middle/high	1-2	4-5	1-2
	protein fibres	middle/high	5	4-5	3-5

* not determined

Up to now, vinyl sulphone-containing disperse dyes are the most suitable dyes for dyeing amino groups containing fibres in supercritical carbon dioxide at moderate temperatures of not more than 120 °C at 300 bar without any fibre damage. For the dyeing of cellulose fibres, no concepts exist in literature which are suitable for commercialisation. Therefore, new ways have to be found which can overcome the existing limitations of supercritical carbon dioxide towards polar fibres, such as no breaking of hydrogen bonds, a low degree of swelling in the acidic CO_2 medium, activation of the reactive OH-bonds in cellulose by applying fibre-reactive dyes which form an alkali-stable chemical bond with cellulose at moderate dyeing temperatures of max. 130 °C [3].

Dyeing of high performance fibres in supercritical carbon dioxide

Another challenge is the dyeing of highly crystalline high-performance fibres such as m-, p-aramide and their copolymers in CO_2. Although some publications and patents in literature exist [17,18], the dyeing results obtained up to now are not very promising except for PPS and PEEK based on our own experiences [19]. Also in the presence of carriers known from the water dyeing of aramides, no convenient dye uptake up to 200 °C could be realized, showing that neither CO_2 nor the carrier has any influence on the T_g of the fibres [19].

Disinfection experiments in liquid carbon dioxide

To compare the efficiency of disinfecting agents in water and in liquid carbon dioxide experiments were carried out in both media at a fixed temperature of 20 °C. After disinfection the test materials were placed in sterile S1-Broth and cultivated for 24 h at 30 °C. After that the optical density of the broth was determined by measuring the UV/VIS-spectrum between 250 and 700 nm in difference to the sterile S1-Broth [20]. The higher the growth of the microorganism is, the higher is the turbidity of the broth by increasing the light scattering of the solution. This effect is reproducible and therefore valid to characterise the degree of disinfection.

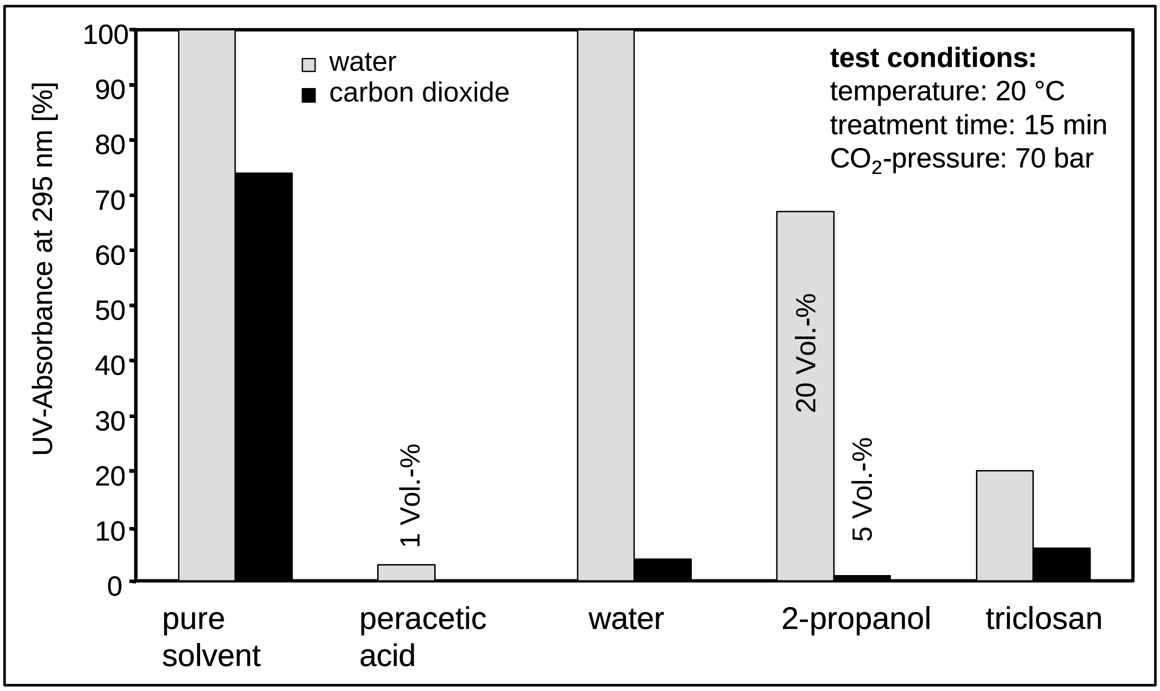

Figure 2 : Comparison of the disinfection effects in water and in liquid carbon dioxide

As expected, under the test conditions at 20 °C and a disinfecting time of 15 min pure water does not have any disinfecting properties, but by the addition of 1 vol.-% peracetic acid after a treatment time of 5 min a complete mortality of *E. coli* is observed as shown in Figure 2 [6]. In contrary to water, pure liquid carbon dioxide at 70 bar and 20 °C has a small disinfecting effect towards *E. coli* as presented in Figure 1. The absorption values obtained are comparable with those of the 15 min treatment in 2-propanol/water in Figure 1.

In liquid CO_2, water seems to be a highly efficient disinfecting agent. By wetting the fibre with water prior to the treatment in CO_2 the disinfecting effect is high. It can be assumed that in this case carbonic acid formed by water and CO_2 acts as the disinfecting agent. The acid decreases the pH mainly at the fibre surface, but also inside the microorganism under destruction caused by osmosis [6].
As in water, 2-propanol was also tested as disinfecting agent in liquid CO_2. In these experiments it can be seen that 5 vol.-% 2-propanol in CO_2 is sufficient for a complete mortality of *E. coli*. As shown in Figure 2 at this low concentration of co-solvent in comparison to water in the disinfecting process no growth of the microorganism could be detected subsequently [6].
Furthermore, from the results in Figure 2 it can be seen that Triclosan (Irgasan DP 300) is a very effective disinfecting agent not only in water but also in CO_2. The concentration in CO_2 seems to be high enough for a complete destruction of *E. coli*. One of the advantages of using Triclosan is that it does not undergo a chemical reaction during the disinfection process and remains unmodified if the temperature is lower than 40 °C [21]. Therefore it should be possible to separate the substance after the disinfection process and maybe to reuse it [6].

CONCLUSION

Due to the fact that cotton has a high market share of 37 % and PET of 35 %, another breakthrough of this technology would be if the dyeing of cotton could be realized in carbon dioxide. This would open the way for a “one-step” dyeing process of the most important PET/cotton blends. As already mentioned above this requires much more research based on new concepts and ideas to overcome the limitations of the dyeing of the fibre in CO_2. In this way the future will show if CO_2 dyeing technology will be suitable for the textile industry and to what extent it can be expanded for dyeing other fibres than PETP [3].
Another application which could have a potential for commercialisation is the sterilization and disinfection of textiles and related material in the medical field with carbon dioxide in the liquid and supercritical state. The first results using different disinfecting agents and co-solvents in CO_2 are very promising. This will be another main area of extensive research at DTNW in the future [3].

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