

## Supercritical fluid dyeing of polycarbonate in carbon dioxide



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### ABSTRACT

In this work, the applicability of the supercritical CO<sub>2</sub> dyeing process on polycarbonate pellets was investigated by the use of two azo-disperse dyes; disperse red 1 (DR1) and disperse red 13 (DR13). Experiments were performed in the range of 100–300 bar and 40 °C–60 °C with 3–24 h of impregnation time. Dyeing took place in a high pressure vessel and kinetics was studied and explained. Impregnation efficiency on the polymer pellets was measured by UV–vis spectroscopy. The process was successfully applied and resulted in an entirely, equally deep-dyed polymer with excellent dyeing fixation. Arising from the different solubility and chemical structure of the dyes, their sorption kinetics was found to be different. Maximal dye uptake obtained with DR1 and DR13 were 0.010 wt% and 0.055 wt% respectively, with respect to the mass of the polymer. New solubility data for DR13 in supercritical CO<sub>2</sub> has also been measured and partition coefficients ( $K_c$ ) for the dyes between the fluid and the polymer phase were calculated.

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### 1. Introduction

Supercritical (sc.) fluid impregnation technique is used in several fields of the chemical industry. Most common examples are wood impregnation [1], sc. fluid deposition aerogel impregnation [2,3] and polymer dyeing [4].

The conventional dyeing of different natural products and polymers demands enormous amount of water, which contains at the end of the process large quantities of chemicals, salt and alkali [5]. This becomes a chemical waste, which is difficult to treat. By using a particular case of solute impregnation, the supercritical fluid dyeing (SFD), both the water consumption and the waste production can be eliminated. The sc. dyeing of textile yarns (such as cotton) and synthetic fibers (e.g. polyethyleneterephthalat (PET), polypropylene and aramides) have already been put into practice [5,6] and applied in the industry.

Dyes and pigments are conventionally incorporated into polycarbonate (PC) resins during their manufacture. This method suffers from two general drawbacks. First, the high melt viscosity of the resin makes it difficult to disperse the color uniformly and second, the high temperatures used in molding the resin exclude the use of thermally labile dyes. Processes invented to overcome these disadvantages consume high amount of organic solvent (contain-

ing carriers and surfactants) and hence an additional drying step has to be involved at the end of the dyeing process [7,8]. Our goal is to apply the SFD method for polycarbonate to overcome all the above mentioned drawbacks that conventional techniques have.

In the SFD process, a disperse dye is dissolved in a sc. fluid and by simultaneously contacting this solution with a polymer matrix in a high pressure vessel the dye penetrates into the polymer. Due to its feasible properties (it is nontoxic, nonflammable and relatively cheap) mostly scCO<sub>2</sub> is used as dyeing media. The dye uptake proceeds in four steps: (1) the dissolution of the dye in CO<sub>2</sub>, (2) dye transport to the material, (3) adsorption on the surface and finally (4) the diffusion of the dye into the matrix [4]. ScCO<sub>2</sub> dissolved in glassy polymers increases the diffusivities of additives in the polymer matrix because of its plasticization effect [9]. SFD is mainly controlled by diffusion, which is described by the Fick law [10]. Pressure, temperature, impregnation time, stirring and the amount of dye also influence the mass transport. The fluid phase has always to be saturated and cannot be exhausted by the uptake of the polymer during the impregnation. This is achieved by creating a saturated phase in the impregnation vessel with high excess of dye. Although the solubility of both, here applied dyes in scCO<sub>2</sub> is rather low [11], the high partition coefficient between the polymer and the fluid phase can drive the dye into the polymer matrix. As a result, the dye concentration in the applied polymer can be remarkably higher than in the dye bath [4]. Since CO<sub>2</sub> is a gas under ambient conditions its removal from the product is very easy, avoiding the cost intensive processes of drying or organic sol-

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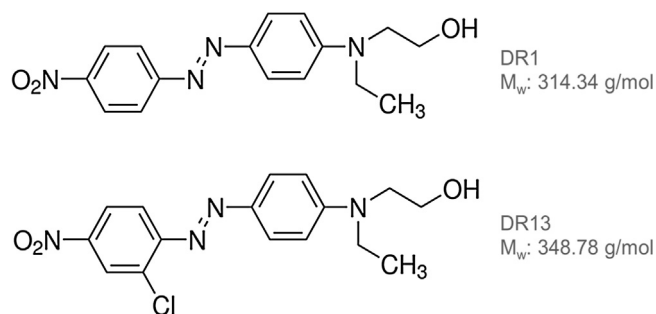


Fig. 1. Chemical structure of dyes DR1 and DR13.

vent removal. Its mild critical temperature (31.1 °C) enables also the use of thermal labile dyes. In the literature many commercially available disperse dyes suitable for scCO<sub>2</sub> dyeing are mentioned [4]. Although several polymers had already been colored by SFD [12], to our best knowledge, there is no detailed experimental data in the open literature on successful PC dyeing by SFD technique. However, the work of West et al. [13] should be noted who reported the dye impregnation of poly(methyl methacrylate) (PMMA) films with two disperse dyes. These authors achieved remarkable dye uptake (approx. 0.5 wt%) of the PMMA film at 40 °C and 91 bar. However, they could only achieve very poor coloring on PC sample at

these conditions. They mention, that by the use of disperse red 1 dyestuff PC samples were colored slightly pink contrary to PMMA's dark red color. Therefore, in that article the dyeing of PC turned out to be complicated which was explained by the relatively nonpolar environment [13].

## 2. Materials and methods

### 2.1. Prime materials and reagents

Disperse red 1 (*N*-Ethyl-*N*-(2-hydroxyethyl)-4-(4-nitrophenylazo)aniline) and disperse red 13 (2-[4-(2-Chloro-4-nitrophenylazo)-*N*-ethylphenylamino]ethanol), DR1 and DR13, respectively, were supplied from Sigma Aldrich. They are common chromophores for nonlinear optic (NLO) materials and only differ in one chlorine group (see Fig. 1). Since it is known that the presence of halogen groups increases the solubility in scCO<sub>2</sub> atmosphere [14], we suggested them to be appropriate for a comparison in their dyeing efficiency. Polycarbonate (LEXAN® resin 121) was kindly provided by Saudi Basic Industries Corporation (SABIC) in pelletized form with a diameter of approx. 1.5 mm and a length of 3 mm. Carbon dioxide was ordered from Linde Gas GmbH. and had a purity of 99.5%. Other reagents (e.g. cleaning ethanol and dichloromethane) were supplied from Sigma Aldrich and had a purity of >99.5%.

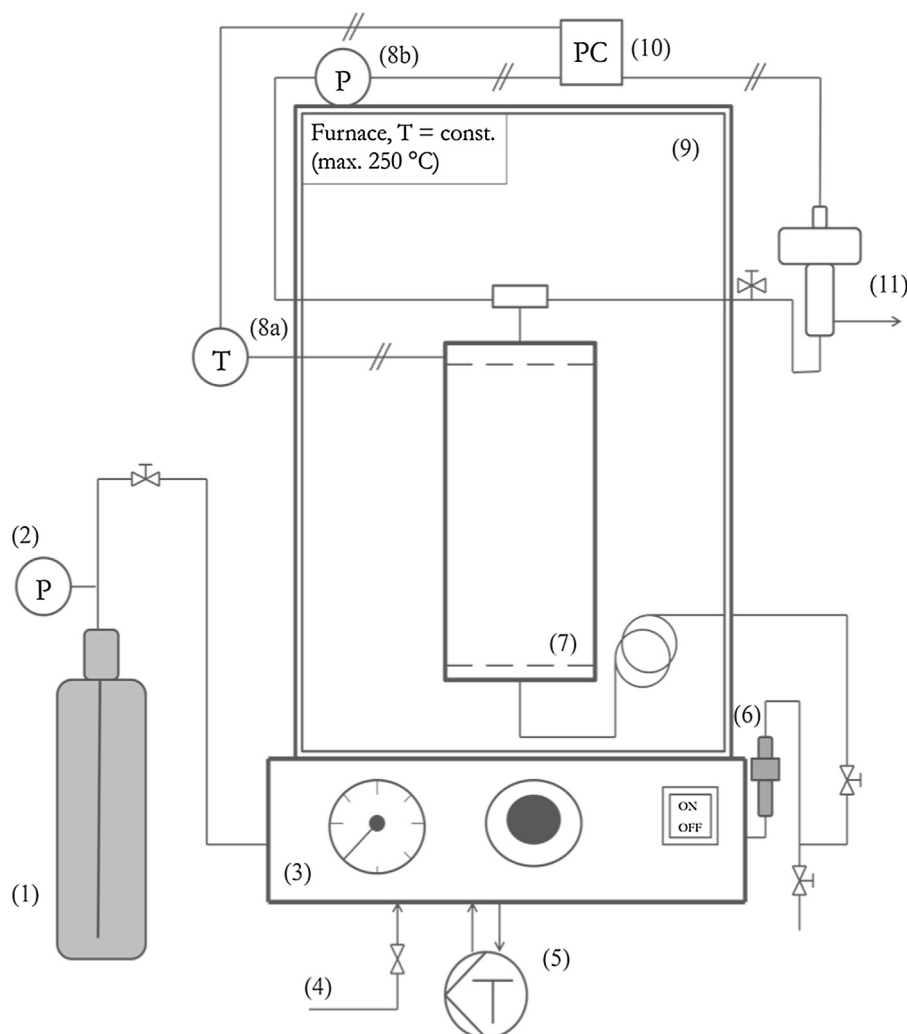


Fig. 2. Experimental SFD apparatus. Carbon dioxide cylinder (1), manometer (2), CO<sub>2</sub> liquid pump (3), pressurized air (4), recirculation cooling bath (5), check valve (6), high pressure vessel (7), temperature and pressure indicators (8a and 8b respectively), heating chamber (9), computer (10), metering valve (11).

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