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Effect of chemical oxidation treatment on dyeability of polypropylene

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Abstract

In present work, drawn continuous filament (CF) of polypropylene (knitted fabric form) is oxidized in $KClO_3 + H_2SO_4$ mixture. The oxidized samples dyed with different types of dyes (Metal Complex, Basic, Disperse) show considerable improvements in their dyeabilities.

Light fastness properties of used dyes on treated polypropylene (PP) are poor to moderate. But washing and rubbing fastness properties are good and acceptable.

FTIR Spectroscopy of oxidized samples confirms the presence of polar groups mainly (−OH) while electron microscopy (SEM) shows some physical changes on the surface. Physical properties measurements show reduction in tenacity and tensile strain values of oxidized samples in comparison with untreated ones.

Keywords: Chemical oxidation; Polypropylene; Improve dyeability

1. Introduction

Polypropylene is one of the important members of olefin polymers, which have become of great commercial importance because of their low cost coupled with their many attractive physical and chemical properties [1–3]. Polypropylene (PP) as a saturated hydrocarbon has a low surface energy and is classified as nonspecific adsorbent. This leads to its poor wetabillity by water and to very low adsorptive and adhesive properties to polar liquids. Practical aspects of this problem are well known in the printing industry [4].

Polypropylene cannot be dyed with common methods because of high crystallinity and non-polar aliphatic structure, which does not contain any reactive site in the molecule [1,5]. PP fiber is highly crystalline and only about one-third of the total volume may be accessible to dyes, thus making coloration in full depth difficult to achieve. The main difficulty, however, arises from the absence of sites where hydrogen bonding or electrostatic attraction can operate. Attraction between dye and substrate is limited to non-polar van der waals'

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forces and, in the absence of ring structures in the fiber molecules, these forces are likely to be weak [6].

Most of polypropylene is dyed now, and will be dyed in the future, by the mass pigmentation method. The fibers dyed with pigments exhibit high fastness properties, cause no wastewater problems, are relatively cheap and have become accepted in the marketplace. Nevertheless, from the purely colouristic point of view, such fibers do not represent textile materials of full value since, they cannot be dyed in blend and flexible matching of hues in dye house is impossible [1].

A great amount of research effort has been expended on making PP dyeable, because good dye ability is essential for widespread commercial acceptance of any textile fiber [7]. Successful coloration will probably depend on modification of the fiber such as bulk copolymerisation, grafting, oxidation and so on [1,6–10]. Besides mass coloration to limiting shades, coloration of PP even after modification has remained a problem for decades [11].

One of the modification methods for making polypropylene dyeable is oxidation. The oxidation of PP in solid phase is done in the reactions with ozone, γ-initiated, corona method, and UV ray or with chemical oxidizing mixture such as $K_2Cr_2O_7 + H_2SO_4$ [1,12–14]. Because of the presence of tertiary carbons and unsaturated sites in polypropylene (PP), its oxidation potential is greatly enhanced. The oxidation of PP leads to the formation of oxygen-containing groups, which greatly affect the surface polarity, and the adhesion properties of the polymer [13].

2. Experimental

2.1. Materials

Potassium chlorate, sulphuric acid (98%), carbon tetrachloride and acetone were obtained from Panreac (Co. Ltd.).

The following dye classes were used (Fig. 1): Maxilon Blue GRL (C.I. Basic Blue 41), Irgalan Yellow 2GL (C.I. Acid Yellow 59), Terasil Brilliant Red FB (C.I. Disperse Red 60). All of them were supplied by Ciba (Co. Ltd.).

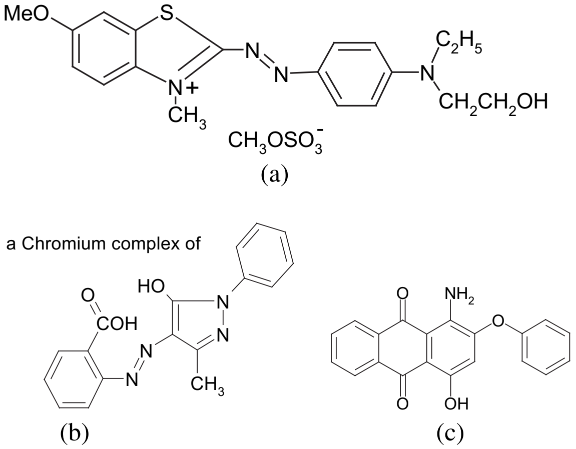


Fig. 1. Structures of dyes: (a) C.I. Basic Blue 41 (b) C.I. Acid Yellow 59 (c) C.I. Disperse Red 60.

2.2. Preparation of samples

Continuous polypropylene filament (2000 dtex, 117 monofilaments) was supplied by IranRisee (Co. Ltd.). Filaments were knitted into fabric form and samples of 2 g were prepared. Each sample was immersed in carbon tetrachloride for 24 h and then washed with acetone three times and dried in room temperature.

2.3. Oxidation

Oxidizing mixture was prepared from sulphuric acid (82%) and potassium chlorate (5 g/l). Samples were immersed in oxidizing mixtures at room temperature in Landro-meter. After oxidation the samples were immersed in sodium carbonate solution and washed with tap water for about 10 min.

2.4. Dyeing

The exhaustion dyeing method was adopted using a laboratory apparatus Linitest Hanau. The liquor ratio was 40:1, the bath acidity was pH 5.5 (acetic acid) and the dye concentration was 2% o.w.f. Oxidized and controlled (non-oxidized) samples (2 g) were entered into dyebath at 35 °C and the temperature raised to 100 °C over 40 min

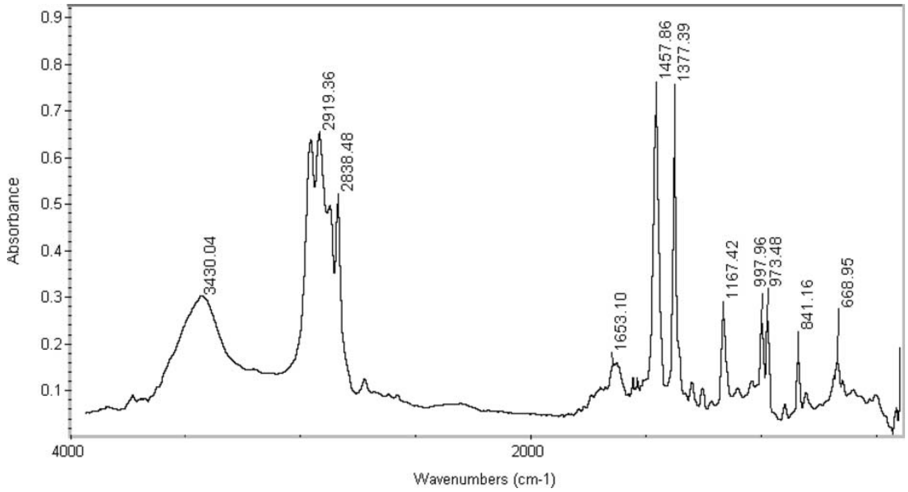


Fig. 2. FTIR spectrum of oxidized PP.

with continuous stirring. The temperature of the dyebath was held at 100 °C for an additional 60 min to complete the dyeing. The samples were removed from the dyebath, rinsed with water and treated in a soaping bath (1.5 g/l nonionic surfactant, liquor ratio 30:1, at 50 °C, for 15 min). The samples were then rinsed with water and dried.

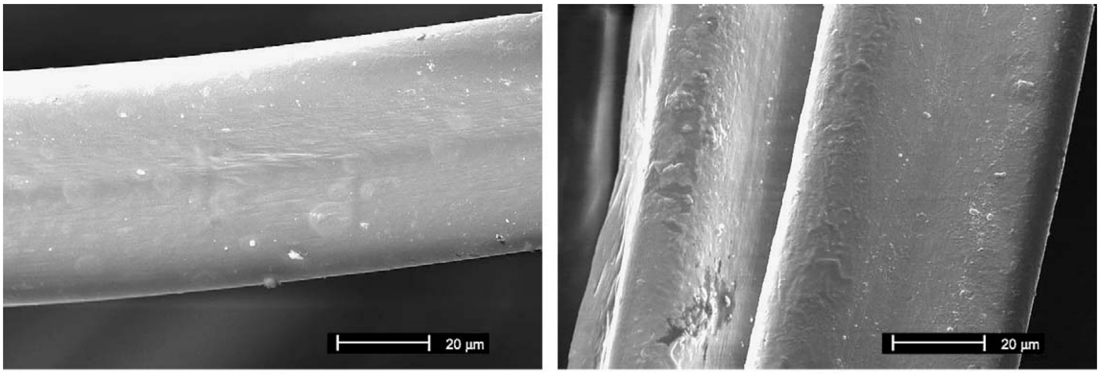
2.5. Measurements and standards

Percentage of dye exhaustion on the fiber was calculated by measuring the absorbance of the dyebath at the beginning and after dyeing using Jenway spectrophotometer. K/S (absorption to scattering coefficient) values of dyed samples were calculated by measuring (Eq. (1)) their reflectance (R) in visible spectrum (400–700 nm) using Datacolor spectrophotometer:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \tag{1}$$

Physical properties (tensile, elongation and work at break) of samples were measured by Instron (CRE) 5566.

The following fastness properties of the dyed samples were evaluated according to ISO procedures: light fastness (Xenotest, ISO 105-B02:



(a) (b)

Fig. 3. SEM micrograph of (a) untreated PP sample and (b) oxidized PP sample (1000×).

Table 1
Physical properties of treated (oxidized) PP samples

	Tensile strength	Breaking strain	Work of rupture
Oxidized PP	23.40 ± 0.2061 (cN/tex)	0.712 ± 0.1316 (mm/mm)	2.61 ± 0.5357 (J)
Decrease	−9.66%	−35.39%	−44.89%

1994), washing fastness (ISO 105-C01: 1989), rubbing fastness (ISO 105-X12: 1993).

3. Results and discussion

FTIR spectrum of oxidized PP (Fig. 2) confirms the presence of polar groups mainly −OH at 3430 cm^{-1}, and =C=O at 1653 cm^{-1}.

SEM study of untreated (Fig. 3a) and treated (Fig. 3b) PP samples shows mainly physical changes by etching the surface and creating microcracks which result in an increase of surface friction.

Mechanical properties of treated samples are also investigated. Results show decrease of tensile strength, breaking strain and work of rupture (Table 1). Decrease of tensile strength is not so large (about 10%) but breaking strain and work of rupture decrease considerably. Creating polar groups such as carbonyl and chain breaks or cracks on the surface can explain decreasing tensile strength.

The oxidized PP samples were dyed with different classes of dyes (C.I. Acid Yellow 59, C.I. Disperse Red 60, C.I. Basic Blue 41) and $(K/S)_{\lambda=400-700\ \mathrm{nm}}$ (absorption to scattering coefficient) values of dyed samples have been calculated for comparison (Figs. 4–6). Results show considerable dyeability improvement of oxidized PP samples specially for C.I. Acid Yellow 59 (Fig. 4) and C.I. Basic Blue 41 (Fig. 5), while untreated PP samples couldn't be dyed with them. Improvement of dyeability can be attributed to the presence of polar groups and physical changes on the surface.

Light fastness (Table 2), washing fastness (Table 3), and rubbing fastness (Table 4) of oxidized PP samples were evaluated. In these tables, other fibers' fastness properties have been also included for comparison. Light fastness properties of dyes on oxidized PP are poor to moderate although these dyes have very good light fastness properties on the other fibers. Washing and rubbing fastness properties are moderate to good and are the same as fastness properties on other fibers.

4. Conclusions

In this work, drawn continuous filament (CF) of PP (knitted fabric form) is oxidized in $KClO_3 + H_2SO_4$ mixture. IR spectrum of treated sample confirms the presence of polar groups such

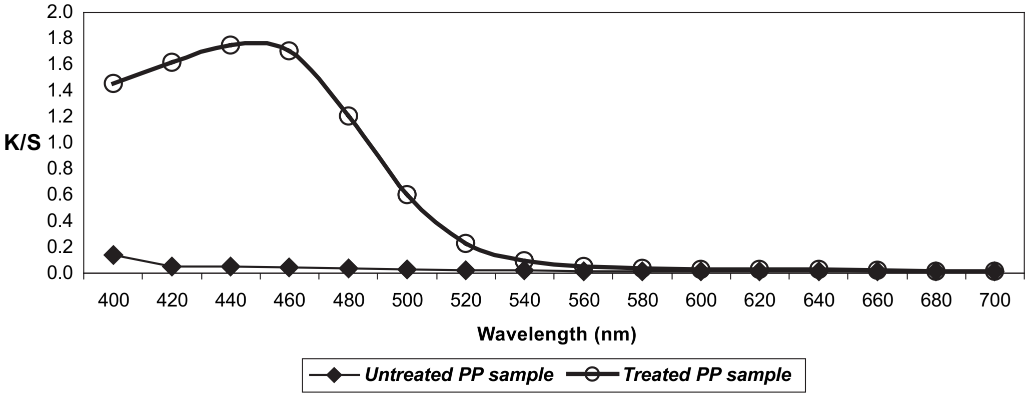


Fig. 4. Comparison (K/S) values of treated (oxidized) and untreated PP samples dyed with C.I. Acid Yellow 59 (depth 2%).

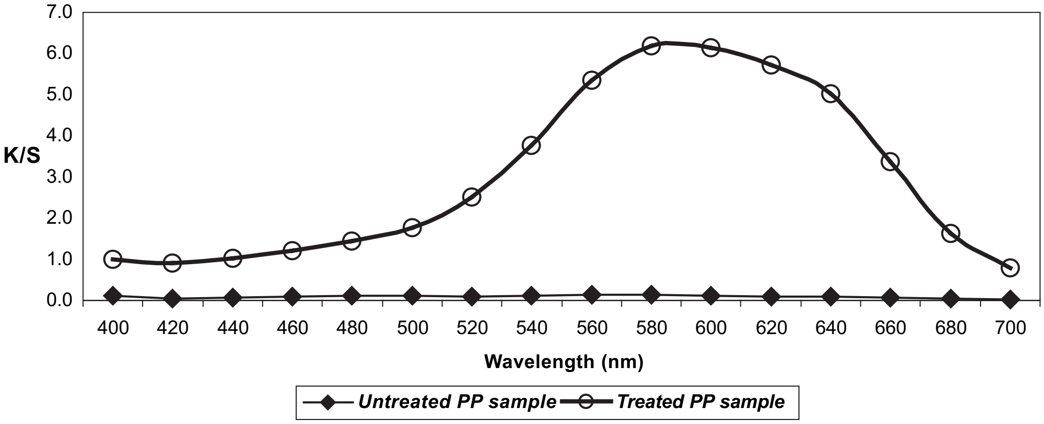


Fig. 5. Comparison (*K*/*S*) values of treated (oxidized) and untreated PP samples dyed with C.I. Basic Blue 41 (depth 2%).

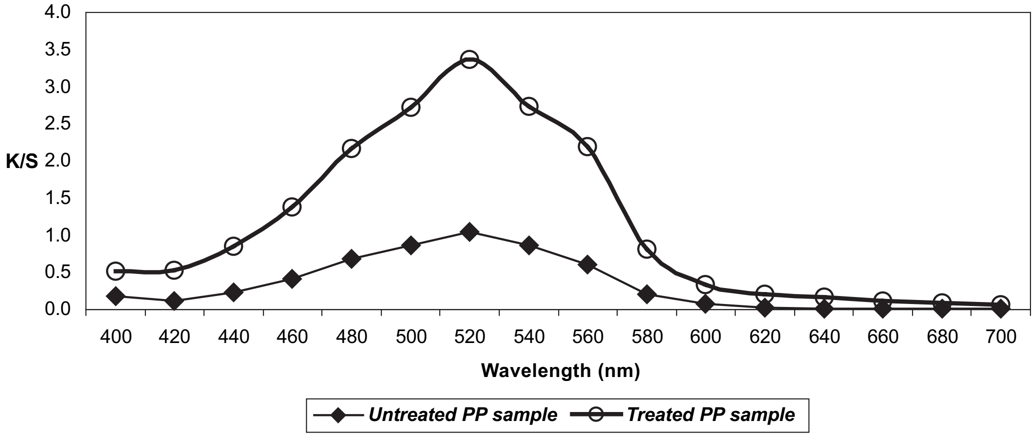


Fig. 6. Comparison (*K*/*S*) values of treated (oxidized) and untreated PP samples dyed with C.I. Disperse Red 60 (depth 2%).

as hydroxyl and carbonyl. SEM of oxidized PP shows some physical changes on the surface in comparison with untreated ones. Tensile strength, breaking strain and work of rupture decrease by oxidation.

Dyeability of oxidized samples by using dyes increase considerably. Light fastness properties of used dyes on treated polypropylene (PP) are poor to moderate, but washing and rubbing fastness properties are moderate to good.

Table 2
Light fastness of oxidized PP samples dyed with different dyes

Dyes (depth = 2%)	Light fastness oxidized PP	Light fastness (other fiber)
C.I. Acid Yellow 59	5	6–7 (nylon)
C.I. Basic Blue 41	3	6–7 (acrylic)
C.I. Disperse Red 60	1–2	6–7 (polyester)

Table 3
Washing fastness of oxidized PP samples dyed with different dyes

Dyes (depth = 2%)	Washing fastness oxidized PP	Staining on cotton	Washing fastness (other fiber)
C.I. Acid Yellow 59	4	4	4–5 (nylon)
C.I. Basic Blue 41	3–4	4	4–5 (acrylic)
C.I. Disperse Red 60	3–4	4–5	4–5 (polyester)

Table 4
Dry rubbing fastness of oxidized PP samples dyed with different dyes

Dyes (depth = 2%)	Rubbing fastness oxidized PP	Staining on cotton	Rubbing fastness (other fiber)
C.I. Acid Yellow 59	4–5	3–4	4–5 (nylon)
C.I. Basic Blue 41	4	2–3	4 (acrylic)
C.I. Disperse Red 60	4	2–3	4 (polyester)

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