

Developing Chromic Dyeable PET Nanocomposites: The Dye Absorption and Complex Formation Mechanisms

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ABSTRACT: This research aimed to investigate the possibility of enhancement of polyethylene terephthalate (PET) dyeability using nanotechnology. Different kinds of disperse, acidic, and chromic dyes were used for dyeing of produced PET/silver nanocomposite fine multifilament yarns produced at the take up speeds of 3000 m min⁻¹ and their prepared fabrics. Dyeability improved by using acidic dyes. However, the more promotion effect was achieved by chromic dyes. No effect on absorption of disperse dyes revealed that no physical effect can be considered for dye absorption. The electrostatic interaction between silver and acidic dye molecules and forming the coordinative bonds with chromic dye molecules on nanocomposite yarns and fabrics were concluded and thoroughly discussed. Applying chromic dye with the more potential of creating coordinative bonds intensified the improvement of dyeability. Optimized silver ratio for the

dyeability enhancement was affected by the mechanisms of dye absorptions discussed and proven by investigating dye concentrations in the effluent baths after the dyeing processes. It has been found that the steric hindrance is the key factor for absorption of chromic dyes; however, it is different in the case of acidic dyes, well discussed according to the dye absorptions mechanisms. The results can be also considered as evidence to prove forming the coordinative bonds with chromic dye molecules. This has also been confirmed by appearing a bathochromic shift in the absorption peaks by increasing dyeability using chromic dye. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: boosting PET dyeability; chromic dye; nanocomposite multifilament yarns; melt-mixing; coordinative bond

INTRODUCTION

Regarding unique properties of polymeric nanocomposites and their wide application potentiality in textile modifications,^{1–9} enhancement of textile dyeability using nanotechnology can be presented as a remarkable subject of interest.

Polyethylene terephthalate (PET) is widely applied polymer in the textile industries, because of its appropriate chemical, mechanical, and heat resistance, good resiliency and biocompatibility, in garments, high tech products, and even medical and sport applications.^{10–13} However, some characteristics of this polymeric substrate such as the high crystallinity, compact and rigid structure, inaccessible polymeric chain blocked in the crystalline structure and lack of reactant groups,¹⁴ limit dyeing of PET fabrics to special dyes and methods. Overcoming this problem is necessary for its further developing uses. Novel nanocomposites can be considered to improve dyeability

of textiles. Toshniwal et al. developed PP/clay nanocomposite to produce dyeable polypropylene yarns.¹⁵ The present article targets to promote dyeability of PET fabrics using silver nanoparticles. Silver nanoparticles and their polymeric nanocomposites have been received remarkable attention because of their excellent antibacterial activity.⁴ We have widely investigated antibacterial and mechanical properties of polymeric silver nanocomposites in our previous researches.^{7–9,12,16–19} Polymeric nanocomposites, with various concentrations of nanoparticles, were produced on a pilot plant melt spinning machine with a remarkable potentiality for mass production.^{16–19} Melt mixing of nanoparticles via three different mixing methods (single and twin screw extruder as well as masterbatch preparation) and their mechanical, thermal, morphological properties etc. have been investigated, compared and thoroughly discussed step by step via producing as-spun, drawn with different draw ratios and textured yarns. Finally, a three-ply textured yarn made of the three textured bobbin yarns of each sample was weft knitted. Then the antibacterial activity of produced fabrics has been evaluated.^{16–19} However, a new approach to investigating and introducing novel features of silver nanocomposites to develop multifunctional products

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would be a high topic of interest. The aim of this research is investigating the chemical interactions on the basis of coordinative bonds between dye molecules and Ag nanoparticles and electrostatic interaction between their oppositely charged groups. For this purpose, fine continuous multifilament nanocomposite yarns with various blending ratios of nanocomposite based on silver nanoparticles were prepared on a pilot plant spinning machine at the take up speeds of 3000 m min⁻¹. The yarn and their prepared fabrics have been examined in the term of dyeability with various concentrations of the three different classes of dyes. Since, producing nanocomposite multifilament yarns via a pilot plant or industrial process is required for preparing the fabrics, dyeability of this kind of nanocomposite fabrics has not been reported before. In addition, this article has presented a novel aim to investigate dyeability of melt mixed silver nanocomposite yarns and fabrics especially those based on their chemical interactions on acidic and chromic dyes. Moreover, comparing dyeability based on different dye molecular structures and comparing dyeability of nanocomposite yarns and fabrics has been presented and thoroughly discussed in this article as a novel research.

EXPERIMENTAL

Materials

Polyethylene terephthalate (PET) chips was supplied by Tondgooyan Petrochemical, Iran and PET masterbatch based on silver nanoparticles was produced by Nanoine, Korea.

Methods

Melt spinning

Pure PET fiber and the composite fibers containing 1, 5, 8, 12 wt % of silver/PET masterbatch were prepared from mixing of virgin PET chips and concentrated masterbatch during melt spinning by an Automatik pilot plant melt spinning machine (Germany). This machine has an extruder using two spinning nozzles. Two 36 holes spinnerets of 0.25 mm hole diameter were used for spinning multifilament yarns at the spinning temperature of 285°C and the take up speeds of 3000 m min⁻¹.¹⁷

Drawing and texturing

A Scragg-Shirley minibulk false-twist texturing machine (England) was employed with the heater temperature of 190°C, draw ratio of 1.6, texturing speed of 100 m min⁻¹. A three-ply textured yarn of each sample was weft knitted to prepare each kind of fabrics. Produced nanocomposite yarns and their

fabrics were termed according to their silver masterbatch contents as 1%, 5%, 8%, and 12% for nanocomposite yarns and fabrics containing 1, 5, 8, and 12 wt % silver masterbatch, respectively. The pure yarn and fabric without silver was termed as “pure” in the tables and figures.

Characterizations

A SDL International Textile Testing Solutions high temperature dyeing machine used for dyeing the prepared nanocomposite and pure PET yarns as well as their fabrics at different depths of shades. Dyeing, rinsing, and reduction clearing were performed following Toshniwal et al.¹⁵ but without leveling agent in dyeing bathes. Disperse dye (Foron Red S-FL), acidic dye (BEST acid Red FRILL), and chromic dyes (Fast Dark Blue RRL and Fast Blue BL 01) have been used for investigating dyeability of produced nanocomposites. Reflectance data were recorded using a Color Eye 7000A Spectrophotometer under illuminant D65, using a 2° standard observer. The K/S values were calculated according to the Kubelka–Munk equation using normalized reflectance data between 0 and 1.

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

Absorbance of dye bath effluents after the end of the dyeing time has been measured using a transmittance Milton Roy Spectronic 21D Spectrophotometer at the wavelength associated with the maximum absorbance peak. The dye concentrations, in dye bath effluents, have been measured using the absorbance data according to the calibration series prepared for each dye. The percentage of decreased dye concentrations in the dyeing baths of nanocomposite samples as compared to pure samples after the end of the each dyeing process have been calculated as follows:

$$R\% = \frac{(C_P - C_{NC})}{C_P} \times 100 \quad (2)$$

where C_P and C_{NC} refers to the dye concentrations in the dyeing baths of pure samples and nanocomposite samples after the end of the dyeing process, respectively. Absorbance data has been measured at the wavelength associated with the maximum absorbance peak for three diluted samples of each dyeing bath effluent and the related dye concentration has been obtained according to the calibration series prepared for each dye. Finally, the dye concentration of each bath has been calculated considering the used dilution factor.

The significance of discussed changes has been statistically checked by triplicate tests in each experiment and the average values have been reported.

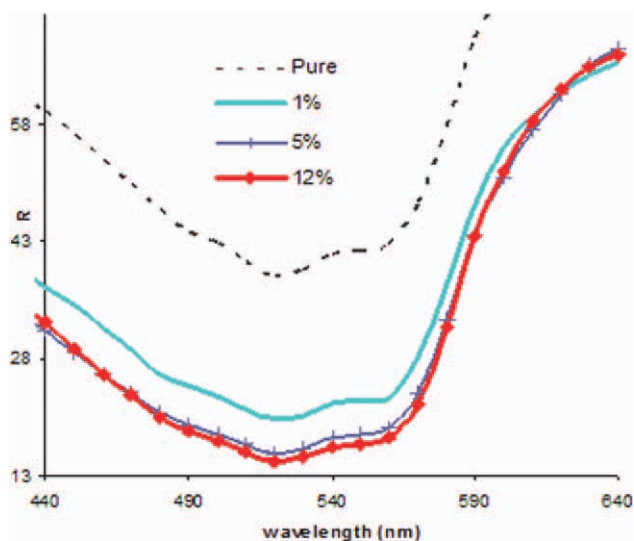


Figure 1 Reflectance curves of nanocomposite and pure yarns dyed by 4% (owf) the chromic dye (Fast Dark Blue RRL), nanocomposites termed according to their silver masterbatch contents (wt %) as 1%, 5%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Figure 1 shows reflectance curves of pure and nanocomposite yarns dyed by the chromic dye. As can be clearly concluded, the dyeability increased more than 5 times (400%) by increasing silver content of yarns (Table I). However, applying disperse dyes does not have any significant difference (Fig. 2). Dyeability of nanocomposite yarns increased as compared to pure yarns by using acidic dyes (Fig. 3). However, the more promotion effect was resulted by chromic dyes when compared to acidic dyes (Table I). No effect on absorption of disperse dyes means that no physical effect can be considered for dye absorption. Toshniwal et al.¹⁵ aimed successfully to improve dyeability of clay/PP nanocomposite yarns with disperse dyes. Improvement of dyeability of the clay/PP nanocomposite by disperse dyes can be justified by the physical blocking of the dye molecules between the clay nanolayers. However, in

TABLE I
The Percentage of Increasing Dyeability (K/S) as Compared to Pure Yarn

Samples	Chromic dye		Acidic dyes	
	K/S	Enhanced dyeability (%)	K/S	Enhanced dyeability (%)
0	0.487	0	0.443	0
1	1.577	223.8	–	–
5	2.228	357.4	1.493	236.8
12	2.456	404.3	2.204	397.1

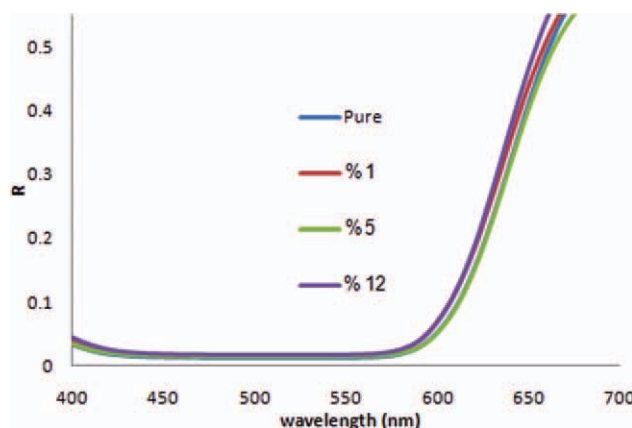


Figure 2 Reflectance curves of nanocomposite and pure yarns dyed by 4% (owf) the disperse dye, nanocomposites termed according to their silver masterbatch contents (wt %) as 1%, 5%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this research, silver nanoparticles cannot provide this nanolayered structure to physically trap dye molecules.

It is found that the electrostatic interaction between negative charged group of acidic dye molecules and positive charged silver nanoparticles can create the improvement of the dyeability with acidic dyes. Enhanced dyeability of nanocomposite samples dyed by chromic dyes as compared to acidic dyes implied forming coordinative bonds between

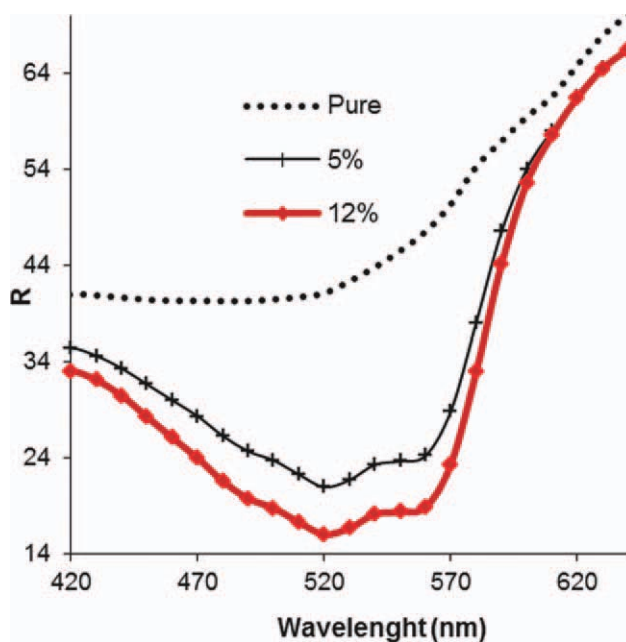


Figure 3 Reflectance curves of nanocomposite and pure yarns dyed by 4% (owf) the acidic dye nanocomposites termed according to their silver masterbatch contents (wt %) as 5% and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

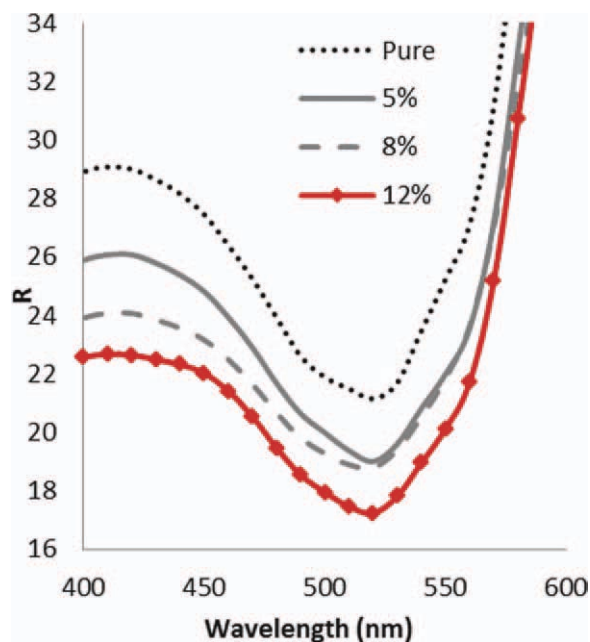


Figure 4 Reflectance curves of pure and nanocomposite fabrics dyed by 4% (owf) the acidic dye, nanocomposites termed according to their silver masterbatch contents (wt %) as 5%, 8%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dye molecules and Ag nanoparticles. As such, the chromic dye molecules can adsorb on the nanocomposite yarns on the basis of their electrostatic interaction and then, the coordinative bonds can be formed.

The prepared fabrics from nanocomposite yarns have been also examined in the term of dyeability.

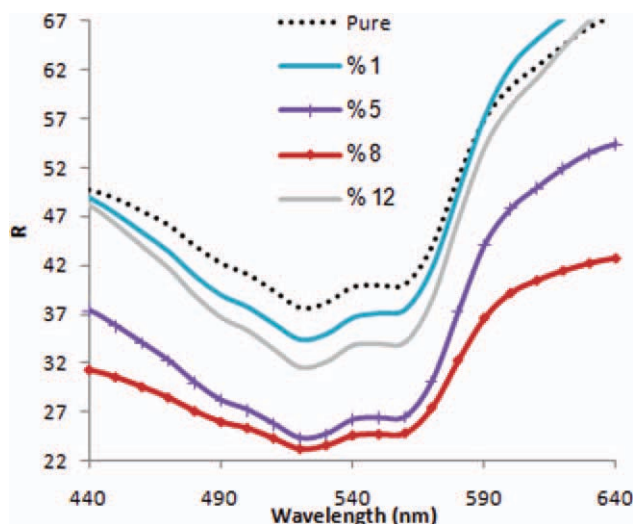


Figure 5 Reflectance curves of pure and nanocomposite fabrics dyed by 4% (owf) the chromic dye (Fast Dark Blue RRL), nanocomposites termed according to their silver masterbatch contents (wt %) as 1%, 5%, 8%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results confirmed the more enhanced dyeability for chromic dyes as compared to acidic dyes (cf. Figs. 4 and 5). Silver content does not have any considerable effect on dyeability with disperse dyes (Fig. 6). Comparing enhanced dyeability of yarns and fabrics disclosed more silver promotion effect on yarn samples. Fabrics were prepared after simultaneous drawing and texturing on the as-spun multifilament yarns produced at the take up speeds of 3000 m min^{-1} . Drawing can reduce the improved dyeability of fabrics. With respect to the decreased crystallinity of as-spun nanocomposite yarns when compared to pure yarns,¹⁶ enhanced dyeability in the case of yarns is more than fabrics, because only the amorphous polymeric regions have the ability to provide the dyeable sites.²⁰ However, drawing can compensate for these differences of crystallinity between pure and modified yarns.²¹ This is a physical reason for more enhanced dyeability of nanocomposite yarns as compared to fabrics, which can also include some chemical resulted phenomena by blocking particles into the crystalline structures. In fact, some silver particles act as the nuclei for crystallization during drawing.¹⁸ Consequently, bundling of particles inside the crystal structures limits their activity as the active chemical sites providing the electrostatic interactions and/or possibility of forming the coordinative bonds. Therefore, both the physical reasons are intensified by the chemical one and these physicochemical effects can reduce the promotion effect of silver nanoparticles on the fabrics as compared to the yarns. However, the positive effect of silver was also noticeably significant on the fabrics. As concluded in Table II, dyeability of nanocomposite fabrics containing 8% silver-based masterbatch increased about five times (375%) as compared to pure PET using Fast Blue BL 01. As discussed before, this effect implied forming the coordinative bonds between the dye molecules and silver

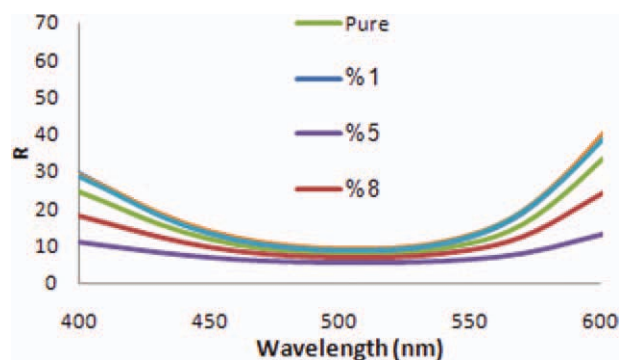


Figure 6 Reflectance curves of pure and nanocomposite fabrics dyed by 4% (owf) disperse dye, nanocomposites termed according to their silver masterbatch contents (wt %) as 1%, 5%, 8%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
The Percentage of Increasing Dyeability (K/S)
Compared to Pure Sample

Dye	Masterbatch (%)	R at the maximum absorbance	K/S	Enhanced dyeability (%)
Fast Blue BL 01	0	37.744	0.51	0
	8	14.86	2.44	375.44
	12	36.679	0.55	7.80
Fast Dark Blue RRL	0	37.7	0.51	0
	8	23.183	1.27	147.25
	12	31.52	0.74	44.52

nanoparticles. To investigate this effect, we selected two chromic dyes with the same structure but different potential of forming coordinative bonds. The structure of dye molecules is demonstrated in Figure 7. Fast Blue BL 01 has more potential of creating complex basis on the coordinative bonds, regarding two OH groups in ortho situations. Comparing Figures 5 and 8 revealed more enhanced dyeability by using the dye with the more potentiality of creating coordinative bonds.

Pure and nanocomposite yarns were dyed by three different concentrations of the acidic dyes. The sample containing 12 wt % masterbatch showed the maximum dyeability on all three concentrations of acidic dyes (Figs. 4 and 9). On the other hand, investigating dyeability with chromic dyes resulted in achieving maximum dyeability for the sample containing 8 wt % masterbatch using both different

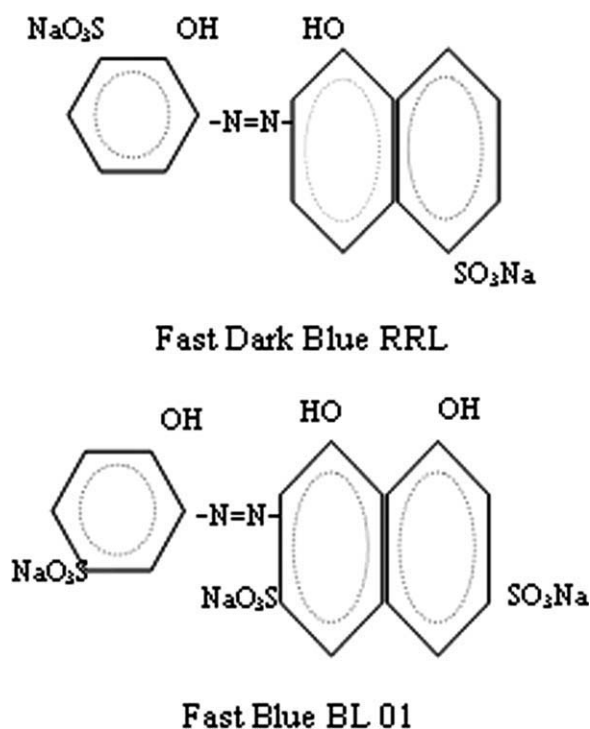


Figure 7 Molecular structure of applied chromic dyes.

kinds of chromic dyes (Figs. 5 and 8). The question is why the optimized ratio is different using acidic and chromic dyes. This can be interestingly answered regarding the mechanism of dye absorptions. In fact, by increasing the ratio of nanoparticles, the possibility of their agglomerations increases.²⁰ Absorption of acidic dyes occurs on the basis of the electrostatic interaction between negatively charged groups of acidic dye molecules. In this case, even agglomerated particles can provide suitable sites for dye absorptions. Agglomeration of particles can even intensify the electrostatic interactions. Although, rapid adsorption of chromic dyes takes place on the basis of the electrostatic interactions, the forming coordinative bonds can be limited by steric hindrance of agglomerated particles. In fact, steric hindrance is the key factor for absorption of chromic dyes because the dye molecules should be able to create a bond with one atom of silver nanoparticles and for this, dye molecules should have close contact with them. Investigating the dyeing effluent has also proven this hypothesis. Table III shows the percentage of decreased dye concentrations in the dyeing baths as compared to pure samples after the end of the dyeing process. Results showed that the sample containing 12 wt % could adsorb more dyes but they removed from the fabrics after rinsing and reduction clearing process. SEM micrographs (Fig. 10) have also verified the agglomeration effect by increasing silver content confirming this hypothesis.

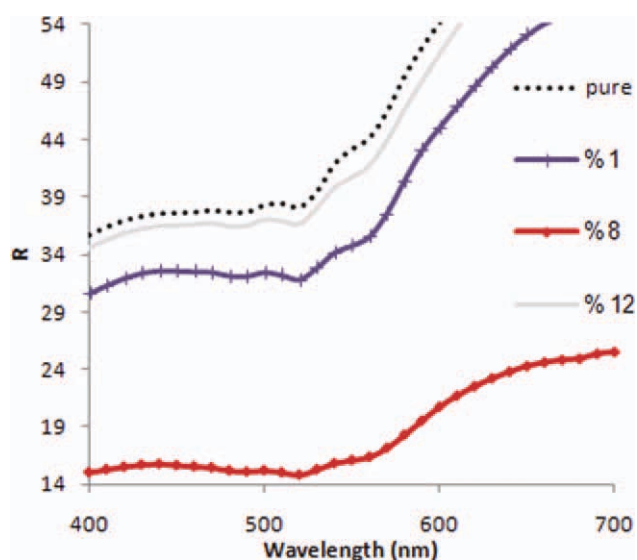


Figure 8 Reflectance curves of pure and nanocomposite fabrics dyed by 4% (owf) the chromic dye with more potentiality of creating complex (Fast Blue BL 01), nanocomposites termed according to their silver masterbatch contents (wt%) as 1%, 8%, and 12%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

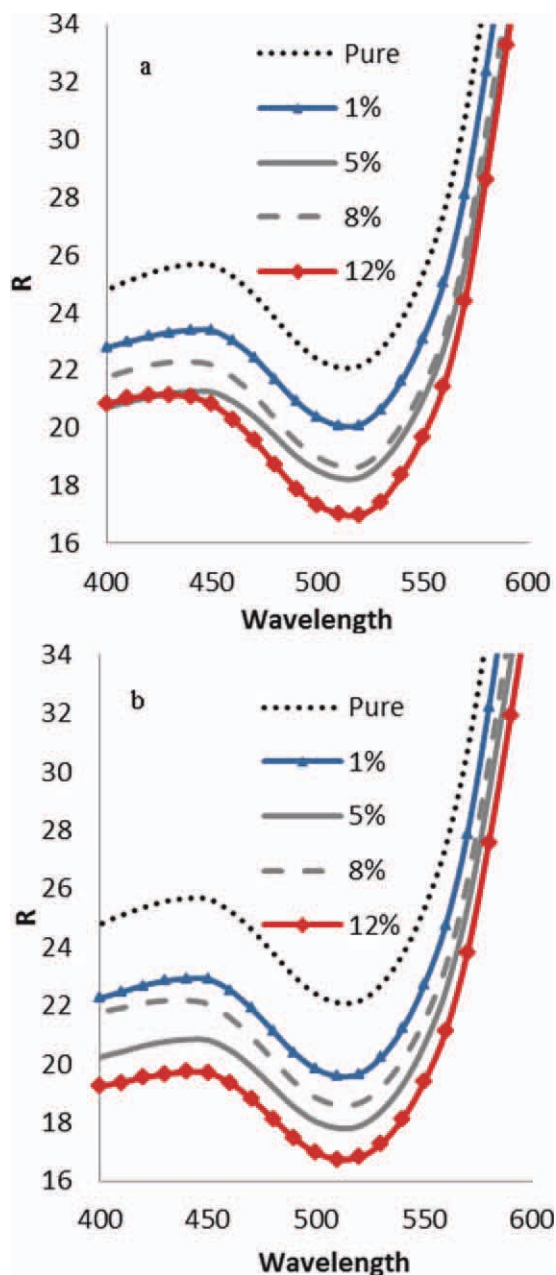


Figure 9 Reflectance curves of pure and nanocomposite fabrics dyed by (a) 8% and (b) 10% (owf) the acidic dye, nanocomposites termed according to their silver masterbatch contents (wt %) as 1%, 5%, 8%, and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III

The Percentage of Decreased Dye Concentrations ($R\%$) in the Dyeing Baths as Compared to Pure Samples After the End of the Dyeing Process

Dye	Masterbatch (%)	$R\%$
Fast Blue BL 01	8	31.65
	12	163.32
Fast Dark Blue RRL	8	18.03
	12	87.10

Figure 11 shows the compared dyeability of samples containing 5 and 12 wt % silver masterbatch dyed with 10% (owf) Fast Dark Blue RRL. As expected by increasing the dye concentration in the bath, the steric hindrance effect is more efficient. Agglomerated particles limited the forming of coordinative bonds on the sample containing 12 wt % silver masterbatch. Forming of coordinative bonds on the sample containing 5 wt % was proven by observing a bathochromic shift in absorption peak. Formation of these bonds can intensify the resonance of the chromophore groups by electron injection to the dye chromophore system, which can provide possible electron excitation even by absorbing longer wavelength and cause this bathochromic shift.⁷

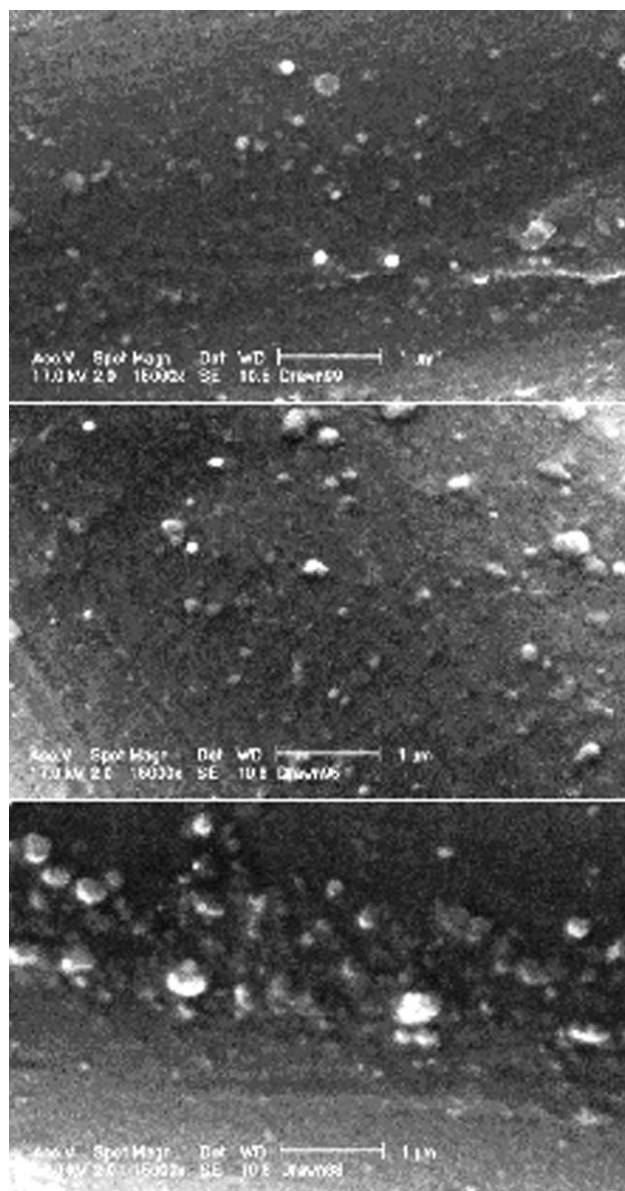


Figure 10 SEM micrograph of the produced samples containing (a) 1% silver-based masterbatch, (b) 5% silver-based masterbatch, (c) 12% silver-based masterbatch.¹⁷

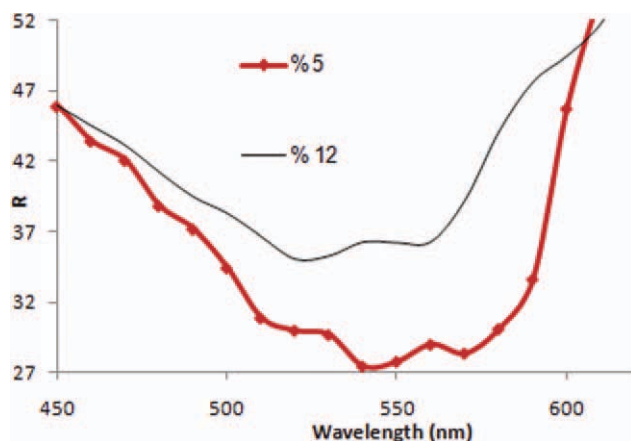


Figure 11 Bathochromic shift by the chromic dye (10% owf Fast Dark Blue RRL) nanocomposites termed according to their silver masterbatch contents (wt %) as 5% and 12%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is remarkable that produced fabrics with these silver content masterbatches demonstrate also excellent antibacterial and good mechanical properties.¹⁷ Consequently, these polymeric nanocomposite fine multifilament yarns produced via a pilot plant process present promising properties to develop multifunctional textiles for manufacturing scale-up.

CONCLUSIONS

Pure PET fiber and the composite fibers containing different ratios of silver nanoparticles were prepared from mixing of virgin PET chips and concentrated silver-based masterbatch during melt spinning by a pilot plant spinning machine at the spinning temperature of 285°C and the take up speeds of 3000 m min⁻¹. As-spun yarns were drawn-textured and finally weft knitted. Dyeability of as-spun yarns and their prepared fabrics have been examined. No effect on absorption of disperse dyes revealed that no physical effect can be considered for dye absorption. However, dyeing with acidic dyes resulted in enhanced dyeability. This can be related to electrostatic interaction between negatively charged groups of acidic dye molecules and positively charged silver nanoparticles. Interestingly, application of chromic dyes demonstrated more enhanced dyeability as compared to both disperse and acidic dyes. It can be concluded that the formation of a coordinative bond between dye molecules and Ag nanoparticles creates this phenomenon. To investigate this effect, we used two kinds of chromic dyes with different potentialities of forming coordinative bonds with metals. Applying dye with the more potential of creating coordinative bonds intensified the improvement of dyeability. In addition, a bathochromic shift in

absorption peak was observed by increasing dyeability with these chromic dyes. This can also confirm aforementioned hypothesis in the case of forming the coordinative bonds. Optimized silver content for dyeability with chromic dyes is affected by steric hindrance of agglomerated particles as the key factor while most silver content makes most dyeability promotion with acidic dyes. This has been discussed considering the mechanism of dye absorptions which was also proven by investigating dye concentrations in the effluent baths after dyeing processes. This can also be considered as the proving evidence for forming the complex with chromic dye molecules. Differences between yarns and fabrics have been discussed with respect to some physicochemical phenomena caused by morphological effect of nanoparticles.

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