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Investigation of UV Protection, Self-Cleaning and Dyeing Properties of Nano TiO_2-Treated Poly(lactic acid) Fabric

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Investigation of nano TiO_2 treatment on poly(lactic acid) (PLA) fabric was conducted in this study. The treatment conditions were found to be optimal at 130 °C with 20 g/L acrylic binder. Nano TiO_2 exhibited a positive influence on UV protection and self-cleaning properties of PLA fabric. The degree of UV protection expressed as ultraviolet protection factor values of PLA fabric increased with nano TiO_2 concentration. Moreover, self-cleaning property was also imparted to PLA fabric. The photodegradation of methylene blue stains was observed on the treated fabric. The stain fading percentage increased with nano TiO_2 concentration. Nano TiO_2 was also found to enhance the dyeability of PLA fiber when dyed with C.I. Disperse Red 60 and Violet 33 dyes. Higher colour strength was obtained on the nano TiO_2-treated PLA fabric. Dyeing the nano TiO_2-treated PLA at the boiling temperature was also compared with the untreated and dyed PLA under typical dyeing conditions.

Keywords: Poly(lactic acid), Nano titanium dioxide, TiO_2, Dyeing, Self-cleaning property, UV protection.

INTRODUCTION

Titanium dioxide (TiO_2) is a semiconductive material with an excellent photocatalytic property. With a powerful oxidizing effect, TiO_2 can be used for eliminating undesirable organic and inorganic substances to create a self-cleaning surface on particular materials. Among the three crystal structures (anatase, rutile and brookite), anatase is the one with the highest photoactivity. Titanium dioxide nanoparticles (nano TiO_2) have been brought to textiles as a finishing agent rendering self-cleaning properties for easy-care textile products. Nano TiO_2-finishing was studied on several textile substrates *e.g.* cotton, regenerated cellulose, wool, polyester and fiber blends [1-7]. Apart from self-cleaning, nano TiO_2 also promotes the ultraviolet (UV) protection and antimicrobial properties of textiles [5,8,9]. In addition, its influence on dyeing properties was also reported [10,11]. Nazari *et al.* [10] studied the effect of nano TiO_2 on acid dyeing of wool by treating wool fiber with nano TiO_2 and 1,2,3,4-butanetetracarboxylic acid (BTCA) prior to acid dyeing in the absence of acid auxiliary. It is reported that the acid dyeing of wool fiber as well as their resultant colour fastness properties were improved with the optimized nano TiO_2 treatment. The carrier-free disperse dyeing process for polyester was developed by Harifi and Montazer [11]. Nano TiO_2 treatment on polyester fabric advanced the disperse dye absorption to the level that is nearly equal to the carrier-dyed fabric. In addition, there was not any adverse effect on the colour fastness properties of the dyed polyester fabric.

Poly(lactic acid) (PLA) is a polymer of which its monomer (lactic acid) is obtained from plant materials *via* fermentation. Owing to its eco-friendliness, PLA has been researched for its use in various fields. At the early stage when mass production was still underdeveloped, PLA was only used in the medical field due to its small scale production and high price. Now-a-days, with the industrial scale production, applications of PLA materials have been widened into other areas, for example packaging and textiles. Although it is majorly exploited in the packaging industry, its uses in the textiles field are also intriguing. As global environmental awareness has driven the textile industry towards greener or cleaner production, PLA fiber has become one of the promising materials to serve the eco-friendly strategy of textile production. Poly(lactic acid) is considered as a green polyester fiber. It can be manufactured into wovens, knits and nonwovens. Owing to its hydrophobic nature, PLA is coloured by dyeing with disperse dyes in a similar way as the conventional polyester, poly(ethylene terephthalate) (PET).

Development of PLA dyeing process has been studied *via* proper selection of dyestuffs and by assisting techniques *e.g.* ultrasound [12]. Poly(lactic acid) is typically dyed at 110 °C for 30 min at pH 5. Several studies shows that PLA is dyed well with disperse dyes having azo chromophoric structure [13-15]. Dyeing and fastness properties of disperse-dyed PLA fiber are normally found slightly lower than those of PET fiber [16,17].

In this research, the influence of nano TiO_2 treatment on the PLA fabric was investigated in the aspect of UV protection, self-cleaning and dyeing properties. Nano TiO_2 was treated on the fabric *via* padding method in the presence of acrylic binder. The optimized treatment condition was investigated. The UV-protection and self-cleaning properties of nano TiO_2-treated PLA fabrics was evaluated. The effect of nano TiO_2 treatment on the dyeing properties of PLA was studied with two different types of disperse dyes, *viz.* C.I. Disperse Red 60 and C.I. Disperse Violet 33. The build-up characteristics of both dyes on nano TiO_2-treated and untreated PLA fabric were also compared. In addition, the lower-temperature dyeing, at boiling temperature, was also conducted in order to gain an insight into an energy-saving dyeing process for PLA.

EXPERIMENTAL

The 90 % anatase and 90 % rutile TiO_2 nanoparticles with average size of 30 nm were purchased from US nano, USA. The 40 Ne PLA yarn purchased from Hebei Tianlun Textiles Co., Ltd., China, was pique knitted by Far East knitting & Spinning Co., Ltd., Thailand. The disperse dyes, *i.e.* Dianix Red E-FB (C.I. Disperse Red 60, an anthraquinone disperse dye) and Dianix Rubine SE-B (C.I. Disperse Violet 33, a monoazo disperse dye) were supplied by DyStar, Thailand. Dypidol 101B, an nonionic/anionic wetting agent, was obtained from Brenntag, Co. Acrylic binder was provided by Thai Mitsui Specialty Chemicals Co., Ltd. and methylene blue for self-cleaning test was purchased from Ajax Finechem.

Pretreatment of poly(lactic acid) fabric: The PLA fabric was scoured before use with 1 g/L sodium carbonate and 1 g/L wetting agent, with 30:1 liquor ratio for 15 min at 70 °C. The scoured fabrics were treated in 5 g/L KOH solution at 80 °C for 30 min and then rinsed with water and air dried.

Nano TiO_2 treatment conditions: The nano TiO_2 mixture (80:20 anatase:rutile) was prepared into a colloidal suspension in water at a concentration of 1 % w/v with 0.25 % w/v ethylene glycol as a dispersing aid. The TiO_2 colloids were homogenized at 15,000 rpm for 15 min. The freshly prepared nano TiO_2 colloids were applied onto PLA fabric *via* padding process. The fabrics were impregnated in the nano TiO_2 colloids for 5 min and squeezed through a pad mangle at 110 % wet pick-up and then dried at 120 °C for 3 min. Acrylic binder was subsequently applied to the fabrics by padding at various concentrations *i.e.* 20, 50 and 100 g/L. The treated fabrics were air dried followed by curing at different temperatures *viz.* 130 and 140 °C. The obtained fabrics were washed in 1 g/L wetting agent solution at 60 °C for 15 min to remove the loosely bound TiO_2 on the fiber surface, followed by rinsing and air drying. The amount of titanium on the fabric was analyzed by Perkin Elmer inductively coupled plasma optical emission spectrophotometer (ICP-OES) and the surface characteristics of the fabrics were monitored by JEOL scanning electron microscope.

Self-cleaning measurement: The nano TiO_2-treated PLA fabrics (0.05, 0.1, 0.5, 1 and 2 % w/v TiO_2) were tested for their self-cleaning properties with 0.01 %w/v methylene blue. The fabrics were immersed in the stain solution until being wetted out thoroughly and left to dry at room temperature. Initial colour strength (K/S) value of stained PLA fabric was measured with a Macbeth ColorEye 7000 spectrophotometer. After that, the stained fabrics were UV irradiated at the wavelength of 365 nm for 0, 3, 6, 12, 24, 48 and 60 h. After each time period, the K/S values of the UV-irradiated fabrics were determined. The stain fading percentage (%) was calculated from eqn. 1:

$$\text{Stain fading (\%)} = \frac{(K/S_0 - K/S_t)}{K/S_0} \times 100 \qquad (1)$$

where K/S_0 is the initial colour strength of the stained fabric and K/S_t is the colour strength of the stained fabric after each UV-irradiation time.

UV protection analysis: The treated fabrics were analyzed for their ultraviolet protection properties by following AATCC 183 standard. The UV protection ability of the fabrics is expressed with ultraviolet protection factor (UPF). The test was also performed on the untreated PLA fabric for comparison.

Disperse dyeing study: The PLA fabrics treated with nano TiO_2 at different concentrations were UV irradiated for 2 h and then were directly taken to dye with two disperse dyes *viz.* C.I. Disperse Red 60 and C.I. Disperse Violet 33 at 110 °C at pH 5 for 30 min. After dyeing, the reduction clearing of the dyed fabrics was carried out in the solution containing 2 g/L sodium dithionite and 2 g/L sodium carbonate for 15 min at 60 °C. The reduction-cleared fabrics were then dried at room temperature. The K/S value of the nano TiO_2-treated, dyed fabrics was measured with a MacBeth ColorEye 7000 spectrophotometer in comparison with the untreated and dyed counterparts.

Lower-temperature dyeing for PLA was conducted at boiling temperature (100 °C), in order to examine whether there is a possibility to develop a more energy-saving dyeing process for PLA fiber.

RESULTS AND DISCUSSION

Characterization of nano TiO_2 treatment on poly(lactic acid) fabric: The effect of acrylic binder concentration to help fixing nano TiO_2 on PLA fabric is shown in Table-1. It is known that synthetic fibers are generally semi-translucent and that is the reason why delustrants, such as TiO_2 are usually added to the synthetic fiber spinning dope in order to deluster and whiten the resultant fibers. Therefore as expected, untreated PLA fiber itself originally had titanium as a delustrant which was previously applied during the fiber spinning process, thus some trace of titanium was observed on the untreated fabric. By curing at 130 °C, the amount of titanium detected for those of 20 and 50 g/L acrylic binder was not much different and the highest titanium content was obtained when 100 g/L of the binder was applied. Higher binder concentration was found to lessen the fabric hand properties. Harsher and stiffer fabric handle was prominently observed for that treated with 100 g/L acrylic binder. Thus, the binder concentration chosen for this study was 20 g/L. By raising the curing temperature to 140 °C, the

TABLE-1
ANALYSIS OF TITANIUM CONTENT ON THE PLA FABRIC TREATED WITH 1 % NANO TiO_2 AT VARIOUS BINDER CONCENTRATIONS AND CURING TEMPERATURES

Treatment condition		Titanium content (ppm)
Curing temperature (°C)	Acrylic binder (g/L)	
Untreated	0	56.0 ± 0.2
130	20	271.7 ± 4.1
	50	250.7 ± 2.7
	100	302.2 ± 3.0
140	20	238.7 ± 0.6

binding capacity of TiO_2 on PLA fabric does not seem to have any improvement. Therefore, it can be said that the appropriate binder concentration for nano TiO_2 treatment on PLA was 20 g/L at the curing temperature of 130 °C.

The visual evidence for nano TiO_2 presence on PLA fiber surface is demonstrated in Fig. 1. The fiber surface of PLA fabric treated with nano TiO_2 was compared against the untreated counterpart. Poly(lactic acid) fiber has a smooth surface. After it passed through nano TiO_2 treatment, the particles of nano TiO_2 bound along the fiber surface could clearly be seen in Fig. 1.

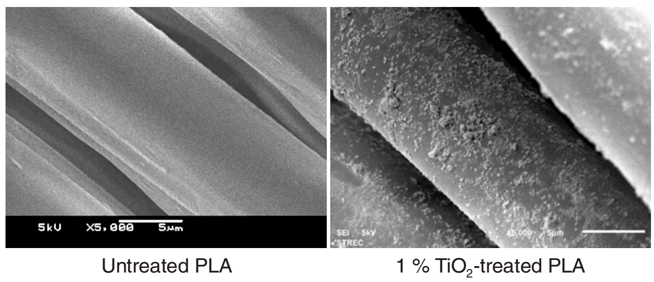

Fig. 1. SEM photographs of the untreated and 1 % TiO_2-treated PLA fabrics

Self-cleaning study: The self-cleaning property of nano TiO_2-treated PLA fabrics was studied by staining with methylene blue. After irradiating the stained fabrics for a designated time, the K/S values of the stains were collected. The K/S values represent the colour strength of the stains. The lower K/S values indicate higher stain fading degree leading to better self-cleaning effect. The stain was more rapidly faded (with lower K/S values measured) with increasing the nano TiO_2 content (Fig. 2). The % stain fading increased drastically for the first 12 h of UV irradiation (Fig. 3). With 1-2 % nano TiO_2 treatment, about 90 % stain fading could be achieved after 60 h UV irradiation.

UV protection properties: Poly(lactic acid) is known for its more UV transmitting behaviour as compared with the conventional polyester fiber (PET) owing to its chemical structure. Therefore, UV protection properties of textiles made from PLA fiber are generally worse than those of PET. In this study, the UV protection properties of PLA fabrics were assessed using ultraviolet protection factor values. Before nano TiO_2 treatment, the ultraviolet protection factor value of PLA was 16, being in a good protection category (Table-2). It is clear that nano TiO_2 application on the PLA fabric enhanced the UV blocking performance of PLA. The ultraviolet protection factor values of the treated fabrics were increased with nano TiO_2 concentration. The fabric treated with 0.1 and

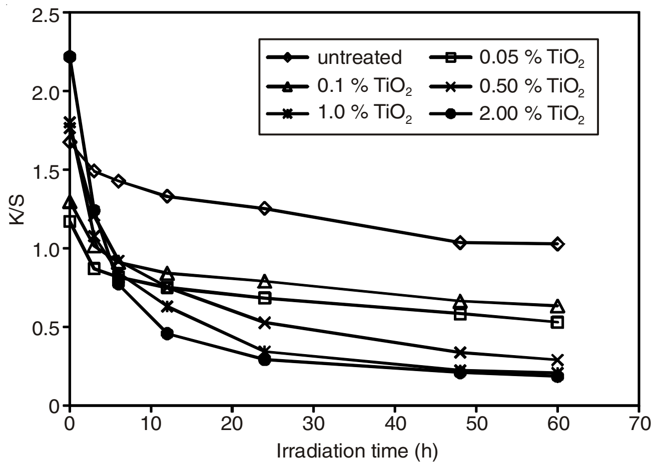

Fig. 2. Colour strength (K/S) of methylene blue stain on the nano TiO_2-treated PLA fabric at different UV irradiation times

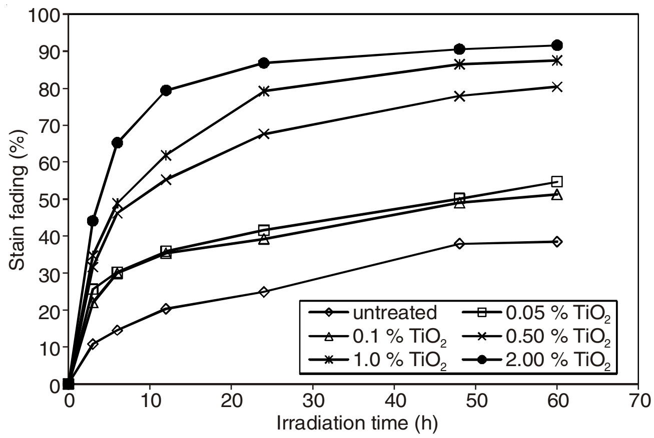

Fig. 3. % Fading of methylene blue stain on the nano TiO_2-treated PLA fabric after UV irradiation

TABLE-2
UV PROTECTION PROPERTIES OF PLA FABRIC TREATED WITH NANO TiO_2 AT VARIOUS CONCENTRATIONS

TiO_2 (%)	Ultraviolet protection factor value
0	16.0
0.05	23.2
0.10	26.6
0.50	33.9
1.00	50+
2.00	50+

0.5 % nano TiO_2 exhibited good UV protection (ultraviolet protection factor range: 25-39) [18] and the excellent UV protection was observed on 1 % and 2 % nano TiO_2-treated PLA fabric. Therefore, the poor UV protection properties of PLA can be improved by the application of nano TiO_2 and the level of protection can be increased with the amount of applied nano TiO_2.

Dyeing properties: The effect of % nano TiO_2 on the dyeing properties of PLA is shown in Fig. 4. Both disperse dyes (C.I. Disperse Red 60 and C.I. Disperse Violet 33) displayed the similar dyeing trend. The K/S values of PLA fabrics dyed with Violet 33 (medium-energy azo dye) were superior to those of dyed with Red 60 (anthraquinone dye) which is actually in line with the previous studies. It was earlier reported that anthraquinone disperse dyes generally exhibit

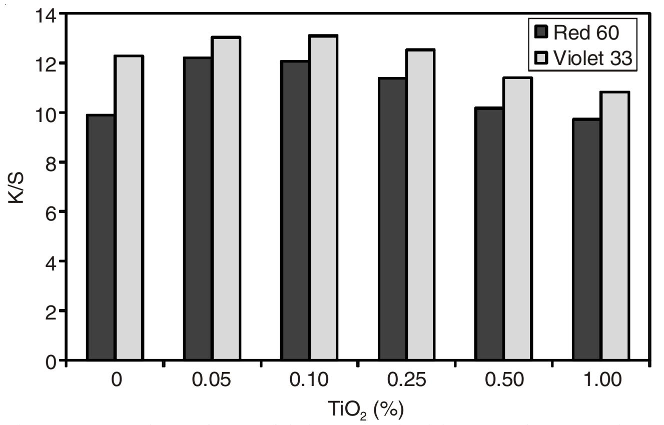

Fig. 4. K/S values of PLA fabrics treated with nano TiO_2 at various concentrations and dyed with C.I. Disperse Red 60 and C.I. Disperse Violet 33 at 2 % owf

poorer dyeing performance on PLA fiber and medium-energy azo disperse dyes can be recommended for PLA dyeing [13,19-21]. Nano TiO_2 application as a pretreatment affected the disperse dyeing performance of PLA fiber. The measured colour strength values of dyed PLA fabric after low concentration nano TiO_2 pretreatment applications were higher than the untreated but dyed PLA fabric. Indeed, at low % nano TiO_2 application (0.05, 0.1 %), the colour strength (K/S) of the dyed fabric was increased but beyond 0.1 % TiO_2, the colour strength gradually declined. The reason for higher dye uptake caused by nano TiO_2 may be explained that nano TiO_2 makes PLA fiber more hydrophilic. A more hydrophilic surface would improve fibers' wettability and hence facilitate better dye diffusion and the dye uptake into the fiber is increased. Oppositely, when the amount of nano TiO_2 becomes too high, a layer of nano TiO_2 particles would restrict the dye diffusion into the fiber, thereby lowering the colour strength on PLA.

This result infers that nano TiO_2 could enhance the disperse dyeing ability of PLA when applied in low concentrations. More nano TiO_2 pretreatment application prior to dyeing may have a negative effect on the dyeing performance of PLA fiber.

The build-up curves of Red 60 and Violet 33 dyes on PLA treated with 0.05 and 0.1 % nano TiO_2 are shown in Fig. 5. With low nano TiO_2 applied levels, the dyeing properties of both disperse dyes were improved. The build-up curves of the disperse dyes on the treated (with nano TiO_2) PLA were compared with those of the untreated ones (Fig. 5). It was apparent that nano TiO_2 enhanced the dye uptake into PLA; the colour strengths of the nano TiO_2-treated fabrics were higher than their untreated counterparts, in particular at higher % of applied dye concentrations. A more hydrophilic surface generated by nano TiO_2 is expected to facilitate the dye diffusion into the fiber. Therefore, under typical dyeing condition for PLA (110 °C), nano TiO_2 could act as a dyeing auxiliary to promote dye uptake into PLA fibers. A noticeable increase in K/S values suggests that, with nano TiO_2, lower temperature dyeing of PLA might be practically feasible.

Therefore, dyeing PLA fiber under a lower temperature was also conducted to evaluate whether dyeing PLA at the boiling temperature under atmospheric pressure could be a viable option with the help of nano TiO_2. Fig. 6 shows that the build-up performance of Red 60 and Violet 33 disperse dyes on 0.1 % nano TiO_2-treated PLA dyed at 100 °C is in between those of the untreated ones dyed at 100 and 110 °C. By lowering the dyeing temperature to 100 °C, the K/S values were decreased as a result of lower accessibility of the fiber structure for dyes to get in. It is known that the tight physical structure of the polyester fiber loosens up more by thermal agitation at higher dyeing temperatures leading to reduction in the intermolecular bonding and rise in the penetration of the disperse dyes leading to higher colour strength [22]. Since, as higher dyeing temperature enhances the free volume of polyester fiber, the dyeing rate escalates [23]. Therefore, less dye can diffuse into PLA fiber at lower dyeing temperature (100 °C *versus* 110 °C) thereby lowering the colour strength of the dyed fabric. Nano TiO_2 (0.1 %) could enhance the dye uptake into PLA fiber (nano TiO_2 treated and dyed at 100 °C) as seen from the better build-up characteristic of both dyes as compared with the untreated fabric dyed at 100 °C (Fig. 6). Nevertheless, the positive effect of nano TiO_2 could not adequately overcome the influence of structural changes of PLA when the dyeing temperature was reduced to 100 °C. The dyeability of both C.I. Disperse Red 60 and Violet 33 on the 0.1 % nano TiO_2-treated PLA dyed at 100 °C was enhanced

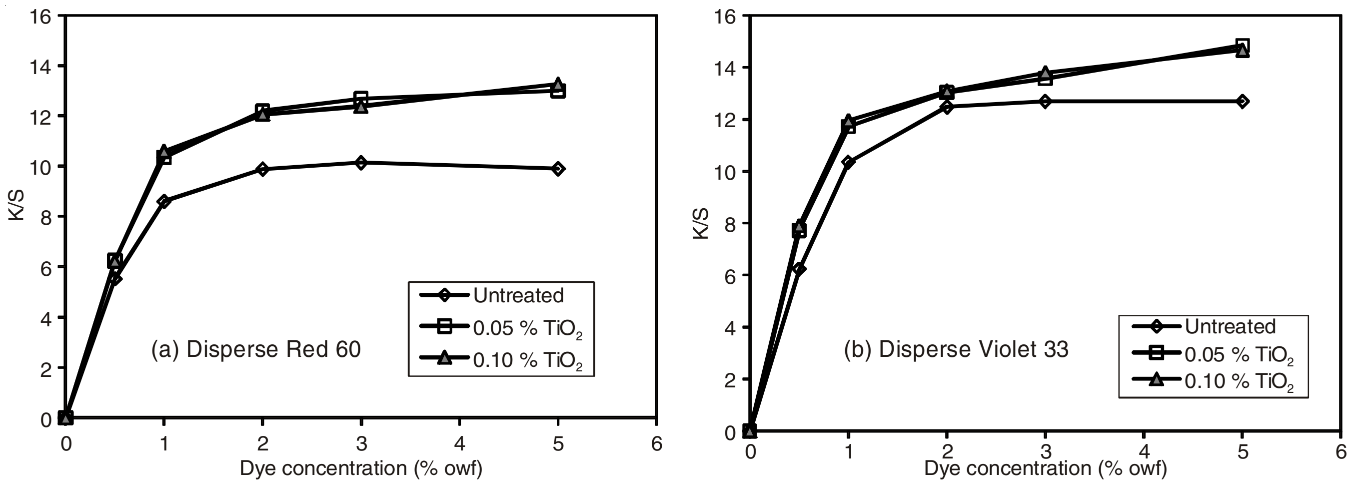

Fig. 5. Build-up curves of the disperse dyes on PLA fabrics treated with 0.05 and 0.1 % nano TiO_2 and then dyed at 110 °C compared with the untreated PLA fabric dyed at 110 °C

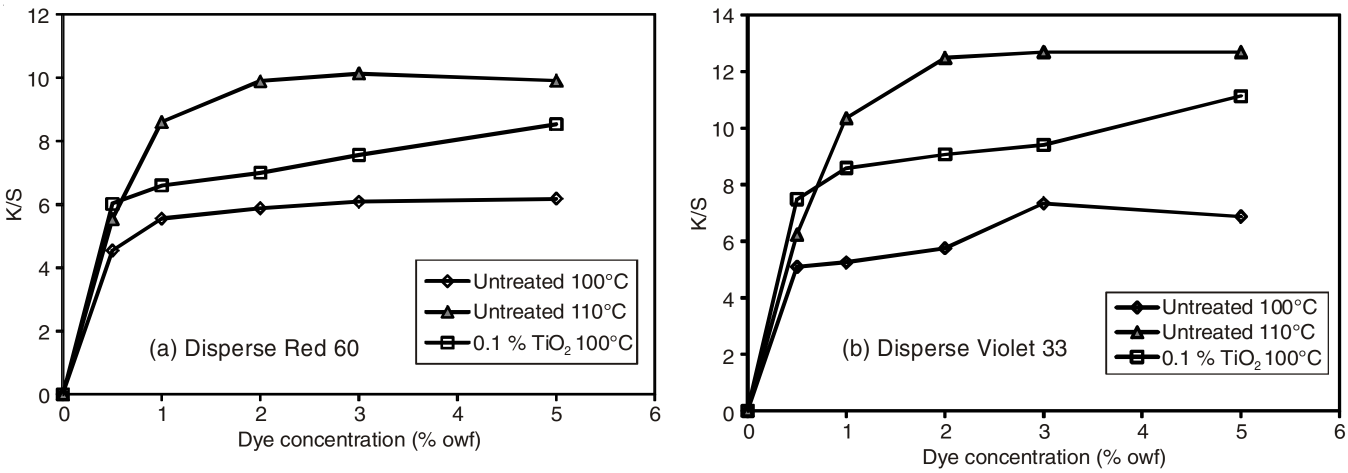

Fig. 6. Build-up curves of the disperse dyes on PLA fabrics treated with 0.1 % nano TiO_2 and then dyed at 100 °C in comparison with the untreated PLA fabrics dyed at 100 and 110 °C

but could not reach the typical-dyeing level obtained at 110 °C. This study indicates that nano TiO_2 pretreatment prior to disperse dyeing could improve the dyeing properties of C.I. Disperse Red 60 and Violet 33 on PLA fabric.

Conclusion

Multifunctional properties could be developed on PLA fabric by nano TiO_2 treatment. By optimally treating PLA with nano TiO_2 and 20 g/L acrylic binder at 130 °C, the UV protection properties of PLA was considerably improved and self-cleaning properties were developed. The hydrophilic surface of PLA caused by nano TiO_2 applied at low concentration (≤ 0.1 %) was expected to ease the dye accessibility into the fiber and, hence, increased the dye uptake of C.I. Disperse Red 60 and Violet 33 dyes on PLA. Too much nano TiO_2 caused adverse effects on dyeability of PLA. A study on dyeing PLA at the boiling temperature shows an improvement in dye uptake after nano TiO_2 treatment compared with the untreated PLA fabric. However, the obtained colour strength of PLA fabrics (nano TiO_2 treated and dyed at 100 °C) could not yet reach the normal dyeing level (untreated and dyed at 110 °C).

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