Indian Journal of Fibre & Textile Research
Vol 43, September 2018, pp. 369-374

Coloration of PLA/modified montmorillonite nanocomposite fibres with acid and basic dyes

Walaikorn Nitayaphat[1,a] & Piyaporn Kampeerapappun[2]

[1]Department of Home Economics, Faculty of Science, Srinakharinwirot University, Bangkok, Thailand

[2]Division of Textile Chemical Engineering, Faculty of Textile Industries, Rajamangala University of Technology, Krungthep, Bangkok, Thailand

Received 18 November 2016; revised received and accepted 21 February 2017

The dyeable poly (lactic acid) (PLA) has been prepared based on the fundamental of nanotechnology. PLA is melt-mixed with montmorillonite (MMT) and quaternary ammonium compound using twin-screw extruder to achieve PLA/modified MMT nanocomposite. The nanocomposite fibre is then prepared using single-screw extruder for further investigations including dyeability, structural analysis, and thermal properties. The results show that the nanocomposite fibre is dyeable with both acid dyes (anionic dyes) and basic dyes (cationic dyes) due to the presence of dye sites, quaternary ammonium cation and anionic charge of MMT particles respectively. The color strength is found to be dependent on the amounts of quaternary ammonium compound as well as MMT applied. The fastness properties such as wash fastness and light fastness show similar trend as found in the traditional fibres. It is observed that the thermal stability of the nanocomposite fibre is lower than that of neat PLA fibre. This study demonstrates that PLA can exhibit the dyeability in the form of nanocomposite.

Keywords: Acid dyes, Basic dyes, Montmorillonite, Nanocomposite, Poly (lactic acid) fibre

1 Introduction

Poly (lactic acid) (PLA) is aliphatic polyester being considered as a green material. Lactic acid can be produced from renewable resource, such as corn, potato, sugar beet and other agriculture products[1,2]. Apart from its application in packaging industry it is used in textile industry. The major end uses of PLA fibres are apparel, home furnishing, and hygiene products[3]. PLA fibre is most commonly dyed with disperse dyes. One major concern with PLA is that only a limited number of disperse dyes have been found to have good sorption on PLA at the appropriate dyeing temperature[4-8].

Polymer nanocomposite is a class of composite material that consists of dispersion of nanometer size particles in a polymeric matrix. The matrix may be a single or multi component that is combination of two miscible and compatible polymer systems derived from nanoparticles with at least one dimension in nanometer range[9]. Nanocomposites have been divided into three categories defined in terms of the number of dimensions of their nanometer size, viz. three dimensions (nearly spherical particles), two dimensions (nanotubes or whiskers), and one dimension (platelets). Layered nanoparticles can be exfoliated into a dispersion of individual platelets[10].

One of the most commonly used layered silicates nanocomposites is montmorillonite (MMT).The crystals of MMT consist of three layers, viz. a silicon tetrahedron, an aluminium octahedron and another silicon tetrahedron. The unit structure is a very thin platelet (about 1 nm) thick and a lateral dimension of 100-200 nm with the stacks of clay platelets being held tightly together by electrostatic forces. Under the appropriate conditions, the gallery spaces can be filled with monomers, oligomers or polymers. Its advantages of a high surface area, large aspect ratio and a platelet thickness of 1 nm make it suitable for reinforcement purposes[11]. Polymer/MMT-layered silicate nano-composites have received significant research attention because they often exhibit remarkable improvement of mechanical, thermal, flame retardant, gas barrier, and optical properties, at low clay content[12]. PLA/MMT-layered silicate nanocomposites have already been prepared by melt intercalation method[13-16] and *in situ* polymerization method[17,18]. They found a good level of clay dispersion in the PLA matrix as well as a considerable improvement in the thermal, mechanical and gas barrier properties.

The dye sites in nanocomposite PLA are expected to be the places where nanoparticles are located.

[a]Corresponding author.
E-mail: walaikorn@g.swu.ac.th

Nanoclay attracts the dye molecules through Van der Waals forces and possibly ionic bonding. Since the clay is normally purified and properly surface modified after mixing, it is possible in the modification process to introduce some chemical group onto the surface of nanoclay. This also provides the desired dye affinity towards the nanocomposite PLA. In practice, cationic surfactants are used to modify the nanoclay. The cations thus introduced are expected to attract negatively charged dyes such as acid dyes. Nanoclay modified with quaternary ammonium salt was used to make PLA nanocomposite. The acid dyeability with PLA nanocomposite is due to anionic attraction between the negatively charged acid dyes and positively charged quaternary ammonium salt in nanoclay. For the dyeing with basic dye, it is proposed that there is attraction between the cationic dyes and the negatively charged suface of the nanoclay.

In this study, dyeable PLA/modified MMT nanocomposite fibres have been prepared by melt spinning process. The effects of nanoclay on acid and basic dyeability properties of PLA/modified MMT nanocomposite fibres are investigated.

2 Materials and Methods

2.1 Materials

The fibre grade PLA (6100D) with melt flow index (MFI) of 24 g/10 min and density of 1.24 g/cm^3 was supplied by NatureWorks LLC (USA). Sodium montmorillonite with a cation exchange capacity (CEC) of 50 meq/100 g, a specific density of 2.3-2.4 and moisture content of 8-12% was obtained from the Thai Nippon Chemical Industry Co., Ltd. Sodium dialkylmethyl sulfate (SDS), purchased from Star Tech Chemical Industry Co. Ltd., was used to modify MMT. Four acid dyes, C.I. Acid Blue 56, C.I. Acid Blue 350, C.I. Acid Red 336, and C.I. Acid Yellow 17 were purchased from Clariant (Thailand) Co. Ltd. Nonionic detergent was purchased from Clariant (Thailand) Co. Ltd. Four basic dyes, C.I. Basic Blue 3, C.I. Basic Blue 80, C.I. Basic Orange 22, and C.I. Basic Yellow 29 were purchased from Dystar Thai Co. Ltd.

2.2 Preparation of PLA/modified MMT Nanocomposite Fibres

2.2.1 PLA/modified MMT Nanocomposite

Polymer melt-direct intercalation is an approach to make polymer layered silicate nanocomposites by using a conventional polymer extrusion process. PLA was melt-mixed with the MMT (1, 2, and 3 wt%) and DMS (2, 4, and 6 wt%) using a twin-screw extruder (CET-D20L800). The rotational speed was 40 rpm in order to have high shear stress, and the temperatures of the five heating zones were 185 °C. The extrudate was then pelletized.

2.2.2 PLA/modified MMT Nanocomposite Monofilament Fibres

Monofilament fibres were produced out by melt spinning machine. The solid polymeric pellets were introduced in the spinning apparatus consisting of a single-screw extruder (ThermoHaake). The heating of the screw is regulated between 230 °C and 240 °C. A volumetric pump ensures the injection of molten polymer into the die with a flow of 100 cm^3/min. The molten filaments were air cooled and then wound.

2.3 Dyeing Procedure

All dyeing experiments were carried out according to exhaustion technique using an Infrared dyeing machine (RED/P, CUGOLINI) with a material-to-liquor ratio (M:L) of 1:20. The amount of acid dye used was 5 %owf at constant temperature (100 °C) for 1 h. The washing-off was then carried out by exhaustion method followed by (cold rinse → warm rinse → soaping-off → warm rinse → cold rinse). The soaping-off was carried out for 15 min at boil, the M:L ratio was 1:50, and the soaping bath contained 2 g/L nonionic detergent.

The treated PLA/modified MMT nanocomposite monofilament fibre was dyed with basic dyes. The samples were dyed in aqueous solution composed of 5 %(owf) basic dyes, 1:20 M:L ratio at 100 °C for 1 h. The washing-off was then carried out by exhaustion method. The soaping-off was carried out for 15 min at boil; the M:L ratio was 1:50, the soaping bath contained 2 g/L nonionic detergent.

2.4 Characterization

Wide angle X-ray diffraction was used to study the morphological properties of the nanoclay composite. Data were obtained using a X-ray diffractometer (Bruker AXS Model D8 Discover) operated at CuKα wavelength of 0.154 nm. The accelerating voltage and current were 40 kV and 40 mA respectively. Diffraction spectra were obtained over a 2θ range of 1-30° (in step of 0.02°) for PLA, MMT, and nanocomposite.

A scanning electron microscope (SEM JEOL JSM-6335F) was used to observe the microstructure of the nanocomposites. This can be used to evaluate the dispersion of the clay inside the polymeric materials. The surface of monofilament fibre was coated with thin layer of Au, with a SEM-coating device and then experimental using SEM with operating voltage of 15 kV and magnification of x700.

TGA measurement was made with a thermogravimetric analyzer (Netzch TG 2093F). Sample of 8-10 mg was placed in ceramic pan with cover and heated from 30 °C to 800 °C at the rate of 10°C/min. The thermal degradation properties considered were the T_o (°C) and T_f (°C), as the temperatures for starting and finishing PLA degradation.

2.5 Color Measurement and Related Parameters

The colorimetric parameters (L^*, a^*, b^*) of dyed samples were measured using illuminant D65, with a 10° standard observer. L^* corresponds to the brightness, a^* refers to the red-green coordinate (+ve = red, -ve = green), and b^* is related to the yellow-blue coordinate (+ve = yellow, -ve = blue).

The reflectance of dyed samples was measured using UV-Vis spectrophotometer at λ_{max} and color strength (K/S values) of the colored fabrics was determined using Kubelka-Munk equation[19].

2.6 Color Fastness Test

The color fastness properties of dyed samples were performed for acid and basic dyes. Color fastness to washing was evaluated according to AATCC test method 61-2003 test no 1A. To evaluate color fastness to light, the dyed monofilament fibres were exposed to Xenon-Arc lamp according to the AATCC test method 16-1998.

3 Results and Discussion

3.1 Morphology Characterization

Morphology of PLA/modified MMT nanocomposite was studied by XRD and SEM. To aid with the dispersion of the clay layers within the polymer matrix, the hydrophilic character of the interlayer space of smectite, due to the presence of hydrated cations (Na^+, Ca^+, etc) is usually modified. This is done by the exchange of interlayer cations with organic ammonium, sulfonium or phosphonium cations which possess at least one long alkyl chain[20]. After modification of the clay by such compounds, the expansion of the interlayer space can permit the diffusion of other molecules into it[21]. XRD was also used to evaluate the nanocomposite structure. The position, shape, and intensity of different peaks are used to evaluate the dispersion of clay layers within the polymer matrix[1,22]. Figure 1 presents XRD patterns of MMT, PLA, and PLA/modified MMT nanocomposite. The typical diffraction peaks of MMT and PLA are 5.95° and 15.71°, corresponding to a basal spacing of 14.83 A° and 5.64 A° respectively. After modification of MMT with SDS and melt spinning process, the diffraction peak of original MMT at 2θ = 5.95° disappears and is substituted by a new diffraction peak at around 2θ = 1.25°, corresponding to a basal spacing of 70.41 A°. The movement of the typical diffraction peak of MMT to lower angle indicates the expansion of basal spacing and intercalation within the layer space[10]. Moreover, the intensity of the peak decreases and even disappears, indicating the formation of an intercalated-exfoliated structure in PLA/modified MMT nanocomposite.

Micrographs of the surface of PLA and PLA/modified MMT nanocomposite monofilament fibres are shown in Fig. 2. The micrograph of neat PLA [Fig. 2(a)] shows a smooth surface. Contrarily, the PLA/modified MMT nanocomposite with 3 wt% of MMT and 6 wt% of DMS exhibits some clay aggregates dispersed in poly matrix [Fig. 2(b)].

The results of TGA for PLA and PLA/modified MMT36 nanocomposite in nitrogen environment are shown in Fig. 3. The degradation for PLA and PLA/modified MMT36 nanocomposite are similar but the residues left behind after decomposition are different. Neat PLA decomposes without formation of solid residue while PLA/modified MMT36 nanocomposite produces around 3% solid residue. MMT particle blocks reactive chemical groups and suppresses the weight loss of PLA/modified MMT36

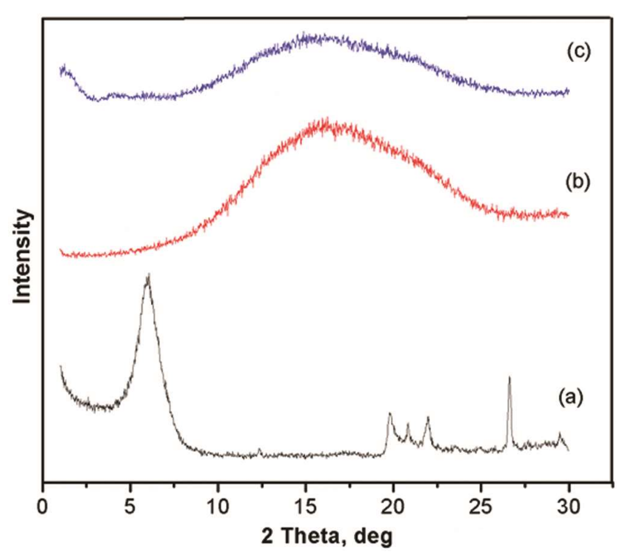

Fig. 1 — XRD patterns of (a) MMT, (b) PLA, and (c) PLA/modified MMT nanocomposite

nanocomposite. The T_o and T_f of PLA are 339.4 °C and 374.4 °C respectively. The T_o and T_f of PLA/modified MMT36 nanocomposite are lower than that of neat PLA, which means that PLA/modified MMT nanocomposite starts and complete decomposition earlier than neat PLA. It is well established in the literature that clay/polymer nanocomposites display improved thermal properties[23-26]. However, this indicates that PLA has greater thermal stability than the PLA/modified MMT36 nanocomposite. This is due to the addition of the SDS as modifier of MMT, where promotes the extent of thermal degradation of PLA.

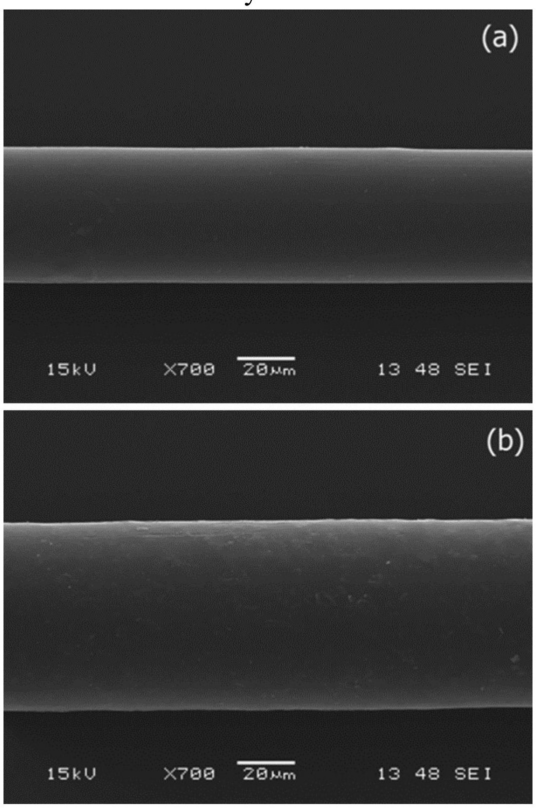

Fig. 2 — SEM micrographs of (a) PLA and (b) PLA/modified MMT nanocomposite fibre

3.2 Dyeability of PLA/modified MMT Nanocomposite Fibre

The dyeability of PLA/modified MMT nanocomposite fibre with acid and basic dyes is presented in Table 1. The results show that the nanocomposite fibre is dyeable with both acid dyes (anionic dyes) and basic dyes (cationic dyes) due to the presence of dye sites, quaternary ammonium cation and anionic charge of MMT particle respectively. The color strength is found to be dependent on the amounts of quaternary ammonium compound as well as MMT applied. The color strength of acid dyed nanocomposite fibre increases with increasing the amount of quaternary ammonium compound. In addition, the color strength of basic dyed nanocomposite fibre increases with increasing the amount of MMT.

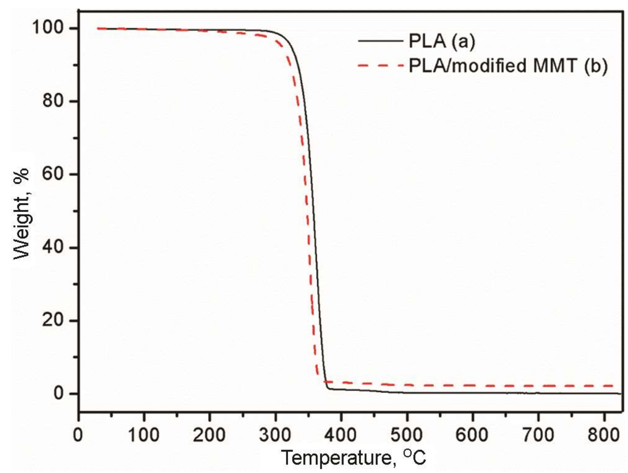

Fig. 3 — TGA of (a) PLA and (b) PLA/modified MMT nanocomposite

Table 1 — *K/S* values of dyed PLA/modified MMT nanocomposite fibres

MMT wt%	SDS wt%	Acid dye				Basic dye			
		C.I. Acid Yellow 17	C.I. Acid Red 336	C.I. Acid Blue 56	C.I. Acid Blue 350	C.I. Basic Yellow 29	C.I. Basic Orange 22	C.I. Basic Blue 80	C.I. Basic Blue 3
1	2	0.12	0.13	0.14	0.20	1.28	1.69	0.71	0.90
	4	0.14	0.15	0.16	0.21	1.69	2.10	0.83	0.91
	6	0.22	0.16	0.21	0.21	2.01	2.25	0.90	1.02
	2	0.28	0.16	0.21	0.23	2.51	3.39	0.95	1.40
2	4	0.29	0.17	0.22	0.29	2.55	3.48	1.11	1.60
	6	0.31	0.18	0.26	0.31	2.69	4.04	1.17	1.81
	2	0.31	0.19	0.35	0.39	2.78	4.18	1.40	1.86
3	4	0.34	0.30	0.40	0.51	2.82	4.70	1.51	2.23
	6	0.38	0.36	0.78	2.55	3.18	5.56	1.71	9.41

Table 2 — Fastness of dyed PLA/modified MMT nanocomposite fibres

MMT	SDS	Acid dye				Basic dye			
wt%	wt%	C.I. Acid Yellow 17	C.I. Acid Red 336	C.I. Acid Blue 56	C.I. Acid Blue 350	C.I. Basic Yellow 29	C.I. Basic Orange 22	C.I. Basic Blue 80	C.I. Basic Blue 3
						Wash fastness			
1	2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	4	3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
	6	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
		3-4	3-4	3-4	3-4	3-4	3-4	3-4	3-4
	2								
2	4	4	4	4	4	4	4	4	4
	6	4	4	4	4	4	4	4	4
	2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
3	4	4	4	4	4	4	4	4	4
	6	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
						Light fastness			
1	2	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5
	4	4-5	4-5	4	4-5	3-4	4-5	4	4-5
	6	4-5	4	4-5	4-5	3-4	4-5	4-5	4
	2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
2	4	4-5	4-5	4-5	4-5	3-4	4-5	4-5	4-5
	6	4-5	4-5	4-5	4-5	3	4-5	4-5	3-4
	2	4-5	4-5	4-5	4-5	4	4-5	4-5	4
3	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4
	6	4-5	4-5	4-5	4-5	4	4-5	4-5	4-5

3.3 Color Fastness

The wash and light fastness of PLA/modified MMT nanocomposite fibre with acid and basic dyes are presented in Table 2. All samples have shown fair (3) to good wash fastness and good to very good (4-5) light fastness. The fastness properties of nanocomposite such as wash fastness and light fastness show similar trend as found in the traditional fibres

4 Conclusion

The results of dyeing properties show that the nanocomposite fibres are dyeable with both acid dyes (anionic dyes) and basic dyes (cationic dyes) due to the presence of dye sites, quaternary ammonium cation and anionic charge of MMT particle respectively. The color strength is found to be dependent on the amounts of quaternary ammonium compound as well as MMT applied. The fastness properties such as wash fastness and light fastness are found to show similar trend as found in the traditional fibres. Thermal stability is also reported. The end uses of dyed PLA nanocomposite fibres are desired to be compostable, like diapers, active wears, and apparels.

Acknowledgement

The authors are grateful for the funding support by Srinakharinwirot University, Bangkok, Thailand

References

1 Zaidi L, Kaci M, Bruzaud A, Bourmaud A & Grohens Y, *Polym Degrad Stab,* 95 (2010) 1751.
2 Gardette M, Thérias S, Gardette J, Murariu M & Dubois P, *Polym Degrad Stab,* 96 (2011) 616.
3 Lunt J & Bone J, *AATCC Rev*, 1 (2001) 20.
4 4 Phillips D, Suesat J, Wilding M, Farrington D, Sandukas S, Bone J & Dervan S, *Color Technol*, 119 (2003) 128.
5 Yang Y & Huda S, *J Appl Polym Sci*, 90 (2003) 3285.
6 Karst D, Nama D & Yang Y, *J Colloid Interface Sci*, 310 (2007) 106.
7 Burkinshaw S M & Jeong D S, *Dyes Pigm,* 93 (2012) 1025.
8 Burkinshaw S M, Jeong D S & Chun T I, *Dyes Pigm,* 97 (2013) 361.
9 Lei S G, Hoa S V & Ton-That M T. *Compos Sci Technol*, 66 (2005) 1274.
10 Alexandre M & Dubois P, *Mat Sci Eng R*, 28 (2000) 1.
11 López-Manchado M A, Arroyo M, Herrero B & Biagiotti J, *J Appl Polym Sci*, 89 (2003) 1.
12 Shibata M, Someya Y, Orihara M & Miyoshi M, *J Appl Polym Sci*, 99 (2006) 2594.
13 Fukushima K, Tabuani D & Camino G, *Material Sci Eng C*, 29 (2009) 1433.
14 Picard E, Espuche E & Fulchiron R, *Appl Clay Sci*, 53 (2011) 58.

15 Najafi N, Heuzey M C & Carreau P J, *Compos Sci Technol*, 72 (2012) 608.

16 Stępień M & Figiel L, *Polym Test.,* 42 (2015) 79.

17 Briesenick D & Bremser W, *Prog Org Coat*, 82 (2015) 26.

18 Ortenzi M A, Basilissi L, Farina H, Silvestro G D, Piergiovanni L & Mascheroni E, *Eur Polym J*, 66 (2015) 478.

19 McDonald R, *J Soc Dyers Colour*, 96 (1980) 486.

20 Raquez J, Habibi Y, Maruriu M & Dubois P, *Prog Polym Sci*, 38 (2013) 1504.

21 Wang X, Tao F, Xue G, Zhu J, Chen T, Sun P, Winter H H & Shi A-C, *Macromol Mater Eng*, 294 (2009) 190.

22 Ray S S & Okamoto M, *Prog Polym Sci*, 28 (2003) 1539.

23 Cai Y, Huang F, Wei Q, Song L, Hu Y, Ye Y, Xu Y & Gao W, *Polym, Degrad, Stab,* 93 (2008) 2180.

24 Carvalho H W P, Santilli C V, Briois V & Pulcinelli S H, *RSC Adv*, 3 (2013) 22830.

25 Qin S, Li Q, He M, Shao H, Yu J, Guo J, Zhang K & Yan W, *Polym Eng Sci*, 54 (2014) 2911.

26 Sahoo S K, Mohanty S & Nayak S K, *Prog Org Coat*, 88 (2015) 263.