

Poly(lactic acid)/Organoclay Nanocomposite Fibers: Preparation, Characterization and Curcumin Natural Dyeing

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The aims of the present study were to use organoclay to improve the property of poly(lactic acid) (PLA) fiber in the dyeing process. Chitosans were used to modify montmorillonite (MMT) to produce organoclay. Poly(lactic acid) was melt-mixed with organoclay using a twin-screw extruder to achieve a PLA/organoclay nanocomposite. The nanocomposite fiber was then prepared using single-screw extruder. The effects of organoclay on the structure, thermal and dyeing properties of the nanocomposite were also investigated. The results of dyeing show that the nanocomposite fiber was dyeable with natural dye extracted from curcumin. The colour strength was found to be dependent on the amounts of chitosan in the organoclay. The fastness properties such as wash fastness and light fastness were found to be similar to that in traditional fibers. Other properties such as thermal stability were also reported. This study demonstrates that poly(lactic acid) can exhibit natural dyeability through its preparation in nanocomposite form.

Keywords: Poly(lactic acid), Nanocomposite, Fiber, Dyeable, Natural dye.

INTRODUCTION

Nowadays, synthetic dyes are widely used in the textile industry because of their various ranges of colours, better colour fastness properties, low price and greater reproducibility [1]. However, synthetic dyes are ruled out by many producers because of their toxicity and carcinogenic effects, in addition to not being biodegradable [2]. Recently, the textile finishing industry has tended to restrict the use of such synthetic dyes for human health and environmental reasons. As a result, the use of natural dye has increased due to its biodegradability, non-toxicity, its sources not posing risk to human health or waste water as contaminant [3-5]. Curcumin is the most popular of the bright yellow-orange natural dyes. Curcumin is an active ingredient in turmeric (*Curcuma longa* L.) which has important medicinal and cultural uses.

Polymers from renewable resources are now considered as promising alternatives to petroleum-based polymers as they meet current environmental concerns in terms of environmental pollution, greenhouse gas emissions and the depletion of fossil fuel resources [6-8]. Poly(lactic acid) (PLA) is aliphatic polyester derived from the fermentation of renewable agricultural crops, such as, corn, potato, rice, sugar beet and other agriculture products [9,10]. Poly(lactic acid) is a highly versatile biopolymer and is highlighted due to its attractive mechanical properties,

renewability, biodegradability and relatively low cost [11]. Apart from its application in the packaging industry it is commonly used in the textile industry. The major commercial applications of PLA fibers are in apparel, home furnishing and hygiene products [12]. However, PLA fiber 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 [13-17].

However, traditional approaches to achieve dyeability of PLA fiber, such as UV/ozone irradiation [18], blending [19-22] and specially designed dyes [23] considerably increase the overall cost of fiber manufacturing and the dyeing procedure.

Nanotechnology has been used to improve the tensile strength, flexural modulus and thermal stability of polymeric materials. Nanoparticles, such as montmorillonite clay (MMT), normally reinforce the mechanical and thermal properties of nanocomposite fiber [24-30]. The dyeing of PLA fiber using nanoclay holds promise for the industry. The dye sites in nanocomposite PLA are expected to be the places where nanoclay particles are located.

In this study, MMT was modified with chitosan to provide organoclay. The dyeable PLA/organoclay nanocomposite fibers were prepared using a melt-spinning process. The resulting dyeing properties of PLA/modified MMT nanocomposite fibers dyed with natural dye curcumin were investigated.

EXPERIMENTAL

A fiber grade PLA (6100D), with melting point 165–180 °C and melt flow index (MFI) of 24 g/10 min was supplied by NatureWorks LLC (USA). Sodium montmorillonite with a cation exchange capacity (CEC) of 50 meq/100 g and a specific density of 2.3–2.4 and moisture content of 8–12 % was obtained from the Thai Nippon Chemical Industry Co., Ltd. Chitosan powder with an average molecular weight of 30 kDa and a deacetylation degree of 90 % was purchased from Seafresh Chitosan (Lab) Co., Ltd. (Thailand) and was used to modify MMT. Curcumin (*Curcuma longa* L.) powder was provided from Huai khwang market in Bangkok, Thailand.

Preparation of PLA/organoclay nanocomposite fibers:

The PLA and organoclay were dried in a vacuum oven for 24 h at 80 °C before melt-blending. PLA was melt-blended with the organoclay using a twin-screw extruder (CET-D20L800). The PLA/organoclay nanocomposite was then melt-spun into the fiber using of a single-screw extruder equipped with a spinneret (ThermoHaake). The extruder was set to five different temperature zones at, 200, 210, 220, 230 and 230 °C, respectively, at the feed, metering, die and spinneret sections. A drawing apparatus was also employed to perform hot drawing of the nanocomposite fibers. Details of the samples and codes are reported in Table-1.

TABLE-1
FIBER COMPOSITION AND CODES

Sample	PLA (wt %)	Chitosan (wt %)	MMT (wt %)
PLA	100	–	–
PLA/organoclay-1	100	–	3.00
PLA/organoclay-2	100	0.25	2.75
PLA/organoclay-3	100	0.50	2.50
PLA/organoclay-4	100	1.00	2.00

Characterization: Wide angle X-ray diffraction was used to study the morphological properties of the nanoclay composite. Data were obtained using an X-ray diffractometer (Bruker AXS Model D8 Discover) operated at a $\text{CuK}\alpha$ wavelength of 0.154 nm. The accelerating voltage and current were 40 kV and 40 mA, respectively. The diffraction curves were obtained from 3 to 40 ° at a scanning rate at 0.02 °/min.

The microstructure of PLA and PLA/organoclay nanocomposite fibers were obtained with scanning electron microscopy (SEM) using a JEOL JSM-6335F microscope. This can be used to evaluate the dispersion of the clay inside the polymeric materials. The surface of fiber was coated with a thin layer of Au, with a SEM-coating device and then tested using SEM with operating voltage of 15 kV and magnification of 300.

Thermogravimetric analysis was made with a thermogravimetric analyzer (209 F3 Tarsus). Sample of 8–10 mg were placed in a ceramic pan with cover and heated from 35 °C to 600 °C under a nitrogen atmosphere, at the heating rate of 10 °C/min. The thermal degradation properties taken into account were the T_{onset} (°C) and T_{max} (°C) as the temperatures for starting and maximum-rate of PLA degradation.

A differential scanning calorimeter (204 F1 Phoenix) was used to study the glass transition, cold crystallization and

melting behaviour. The samples were heated from 0 to 200 °C under a nitrogen atmosphere at the heating rate of 10 °C/min and kept at this temperature for 5 min before cooling down in order to assure that the materials melted uniformly and to eliminate the thermal history. The samples were then cooled down to room temperature at the cooling rate of 10 °C/min under a nitrogen atmosphere. The glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), cold crystallization enthalpy (ΔH_{cc}) and melting enthalpy (ΔH_m) were determined from the second heating curves. Crystallization and melting temperatures were taken at the maximum of the crystallization exotherm (T_{cc}) or of the melting endotherm (T_m). The degree of crystallization (χ_c) was obtained using the following equation:

$$\chi_c (\%) = \left[\frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0 \left(1 - \frac{\text{wt \% organoclay}}{100} \right)} \right] \times 100 \quad (1)$$

where ΔH_m and ΔH_{cc} are the melting enthalpy and the crystallization enthalpy respectively of the sample. ΔH_m^0 is the melting enthalpy of the 100 % PLA (93.0 J/g [31]) and % wt organoclay is the weight percentage of organoclay.

Dyeing procedure: The dyeing experiments with PLA/organoclay nanocomposite fibers were carried out with an exhaustion technique using an Infrared dyeing machine (RED/P, CUGOLINI). The samples were dyed in a dyeing bath containing 10 wt % of curcumin dye solution. The liquor ratio for all dyeing was 1:20. The pH of the bath was kept constant at 6. The dyeing temperature was raised from 40 to 100 °C at 1.5 °C/min, holding at 100 °C for 60 min and then cooled to 60 °C at a cooling rate of 3 °C/min. The dyed fibers were rinsed in distilled water for 5 min. The samples were then rinsed for 10 min with cold running water.

Colour measurement: The colourimetric 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^* refers to the yellow-blue coordinate (+ve = yellow, -ve = blue).

The reflectance of dyed samples was measured using an Ultra Scan VIS spectrophotometer at λ_{max} and colour strength (K/S values) of the coloured samples was determined using Kubelka-Munk equation [32]:

$$K/S = \frac{(1 - R_{\lambda_{\text{max}}})^2}{2R_{\lambda_{\text{max}}}} \quad (2)$$

where K is the absorption coefficient, S is the scattering coefficient and $R_{\lambda_{\text{max}}}$ is the reflectance value of the fibers at the wavelength of maximum absorbance.

The colour fastness to wash tests were evaluated using the AATCC test method 61-2003 test no 1A. To evaluate colour fastness to light, the dyed fibers were exposed to a Xenon-Arc lamp according to the AATCC test method 16-1998.

RESULTS AND DISCUSSION

X-ray diffraction: The XRD can offer valuable information on the intercalation and exfoliation processes in a bio-

polymer/clay nanocomposite. During the intercalation process, the chitosan chains enter the interspacing layer, forcing apart the layers, thus increasing the d-spacing value [33]. As can be seen from Fig. 1, the typical diffraction peak of neat MMT was 6.04° , corresponding to a d-spacing of 1.46 nm. After modification of MMT with different concentration of chitosan, the diffraction peak of the original MMT at $2\theta = 6.04^\circ$ disappeared and was substituted by a new diffraction peak around $2\theta = 5.93^\circ$, 5.27° and 4.72° , corresponding to a d-spacing of 1.49, 1.68 and 1.84 nm, for organoclay with 0.25, 0.5 and 1 wt % of chitosan, respectively.

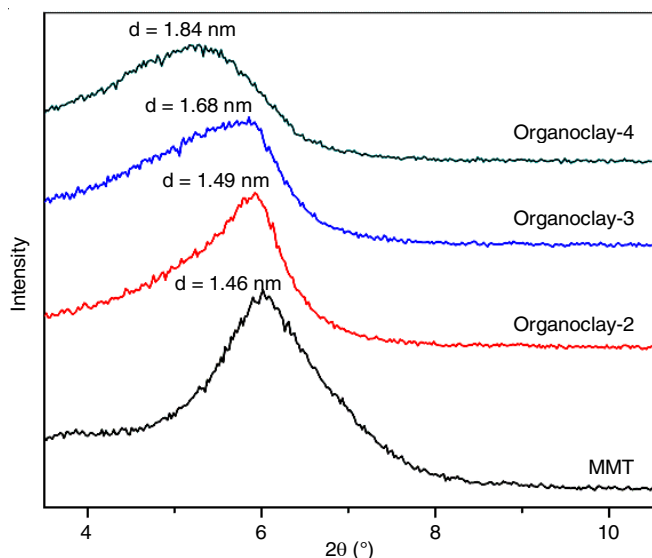


Fig. 1. XRD patterns of MMT and organoclay at various concentration of chitosan

The increase in d-spacing suggests that chitosan successfully enters the MMT inter layers. The diffraction peaks of

organoclay shift towards a lower angle compared with that of the original MMT, which demonstrates the intercalation of chitosan into MMT. Moreover, with increasing concentration of chitosan to MMT, the diffraction peak value of MMT gradually decreased, *i.e.*, the basal spacing gradually expanded. It can be inferred that an increased amount of chitosan brings about a stronger driving force for intercalation.

Scanning electron microscopy: Micrographs of the surface of PLA and PLA/organoclay nanocomposite fibers are shown in Fig. 2. The micrograph of neat PLA Fig. 2a) shows a smooth surface. In PLA/organoclay nanocomposite fibers a very uniform distribution of MMT can be observed in the polymer matrix (Fig. 2b-e).

Thermogravimetric analysis: TGA was used to evaluate the thermal stability of nanocomposite fibers. The results of TGA for PLA and PLA/organoclay nanocomposite fibers in a nitrogen environment are shown in Fig. 3 and Table-2. The solid residue ranges from 0.3 wt % for neat PLA to 2.9 wt % for the nanocomposite fiber with 3 wt % MMT (PLA/organoclay-1), which are close to the respective amounts of added MMT with the consideration of the loss of chitosan in the MMT. Moreover, the added MMT improves the thermal stability of PLA/organoclay nanocomposite fibers, as MMT particles block reactive chemical groups and suppress the weight loss of PLA/organoclay nanocomposite fibers [34,35]. However, the T_{onset} and T_{max} of PLA/organoclay-4 was lower than that of neat PLA which means that PLA/organoclay-4 started and completed decomposition earlier than neat PLA. This may be attributed to the addition of the chitosan, as modifier of MMT, which promotes the extent of thermal degradation of PLA.

Differential scanning calorimetry: Thermal properties of PLA and PLA/organoclay nanocomposite fibers from DSC were recorded as shown in Fig. 4, in which the glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting

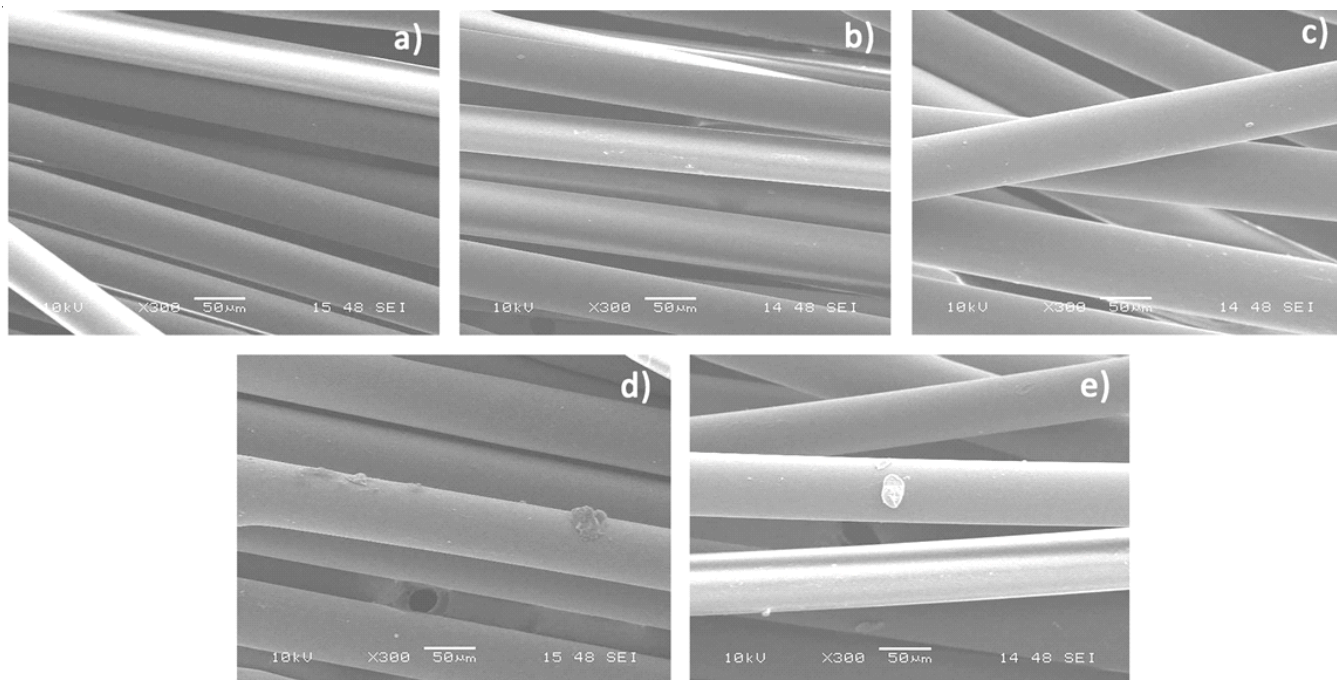


Fig. 2. SEM micrographs of a) PLA, b) PLA/organoclay-1, c) PLA/organoclay-2, d) PLA/organoclay-3 and e) PLA/organoclay-4 nanocomposite fibers

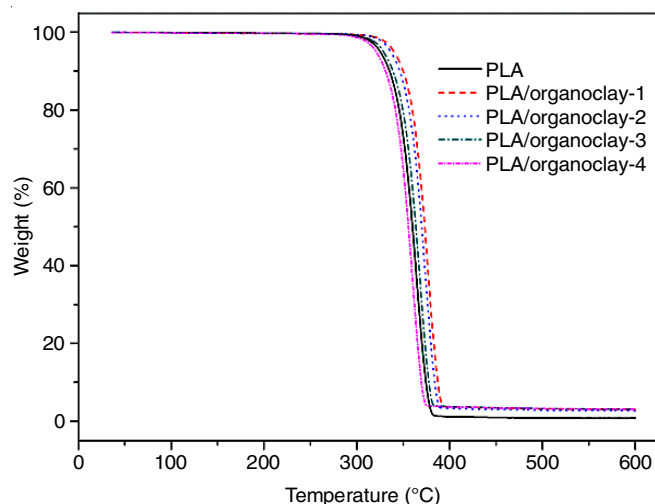


Fig. 3. TGA curves of the PLA and PLA/organoclay at various temperatures. The heating rate was 10 °C/min and the atmosphere was nitrogen

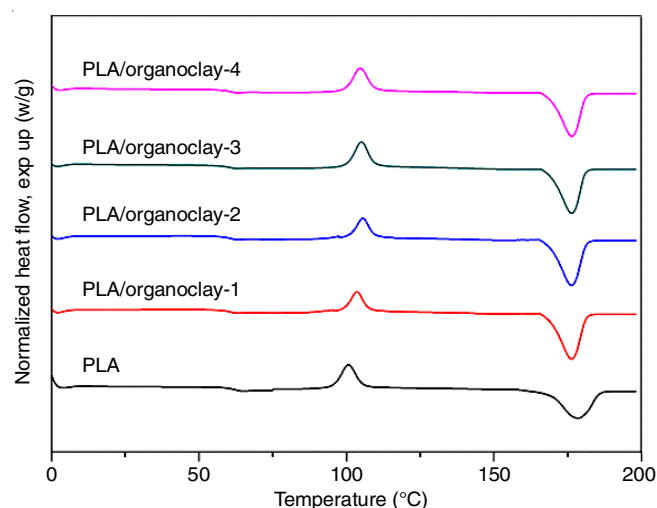


Fig. 4. DSC thermograms of the PLA and PLA/organoclay nanocomposite fibers. The heating rate was 10 °C/min and the atmosphere was nitrogen

TABLE-2
ONSET DEGRADATION TEMPERATURE (T_{onset}),
MAXIMUM-RATE DEGRADATION TEMPERATURE (T_{max})
AND SOLID RESIDUE AT 600 °C OF THE PLA AND
PLA/ORGANOCLAY NANOCOMPOSITE FIBERS

Sample	T_{onset} (°C)	T_{max} (°C)	Solid residue (%)
PLA	343.3	364.9	0.3
PLA/organoclay-1	358.7	378.7	2.9
PLA/organoclay-2	354.1	374.7	2.6
PLA/organoclay-3	347.2	370.5	2.5
PLA/organoclay-4	338.2	360.4	1.8

temperature (T_m) and degree of crystallization (χ_c) were all determined. The results are summarized in Table-3. It is known that the addition of the clay promotes the extent of crystallization of PLA during heating indicating that it acts as nucleating agents [31,36]. However, comparing the degree of crystallization (χ_c) of the PLA/organoclay-1 with the degree of crystallization (χ_c) of PLA/organoclay-2, PLA/organoclay-3 and PLA/organoclay-4 showed a progressive decrease with increasing chitosan contents. This decrease can be attributed to the heterogeneity and aggregate formation observed in this sample (Fig. 4). The

melting temperature (T_m) and glass transition temperature (T_g) of the nanocomposite fibers do not present significant variations with respect to neat PLA fiber.

Dyeing: The K/S values for dyeing PLA and PLA/organoclay nanocomposite fibers with natural dye extracted from curcumin are given in Table-4. The results indicate that the K/S dyeing values of PLA/organoclay nanocomposite fibers are higher than those of neat PLA fiber. This result confirms that chitosan in organoclay increases the amount of dye uptake in the PLA/organoclay nanocomposite fibers. This enhancement in K/S values of PLA/organoclay nanocomposite fibers is associated with the introduction of chitosan primary amino groups into the fiber structure [37].

The colourimetric parameters such as L^* , a^* and b^* of dyed nanocomposite fibers are shown in Table-4. The lightness value of the PLA/organoclay nanocomposite fibers was lower than that of PLA fiber. This is attributed to the higher value of colour strength. Furthermore, the colour depth of all dyed fabrics was rather yellowish and reddish as indicated by the values of a^* and b^* . These results showed that a^* and b^*

TABLE-3
THERMAL TRANSITION PROPERTIES OF THE PLA AND PLA/ORGANOCLAY
NANOCOMPOSITE FIBERS DETERMINED FROM DSC CURVES

Sample	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	χ_c (%)	T_g (°C)
PLA	97.2	27.6	178.4	48.4	23.1	61.1
PLA/organoclay-1	99.0	28.2	177.3	56.5	31.4	60.4
PLA/organoclay-2	102.1	27.9	177.3	53.6	28.5	60.3
PLA/organoclay-3	101.8	28.8	177.4	52.8	26.6	60.5
PLA/organoclay-4	101.7	30.6	177.4	52.2	24.0	60.6

TABLE-4
COLOUR CHARACTERISTICS OF PLA AND PLA/ORGANOCLAY NANOCOMPOSITE FIBERS DYED WITH CURCUMIN

Sample	Colour values				Colour obtained
	K/S	L^*	a^*	b^*	
PLA	1.45	83.42	-14.89	55.65	Light yellow
PLA/organoclay-1	1.83	78.36	-7.39	58.42	Yellow
PLA/organoclay-2	2.04	76.21	-6.46	58.44	Yellow
PLA/organoclay-3	3.16	74.30	-4.98	55.37	Yellow
PLA/organoclay-4	3.78	74.02	-5.73	56.34	Yellow

increased as the chitosan concentration in organoclay was increased.

Table-5 shows the colour fastness results of dyed PLA and PLA/organoclay nanocomposite fibers. All samples showed low (2) colour fastness to light. Organoclay has no effect on colour fastness to light properties of PLA fiber. Colour fastness to washing ratings for staining of adjacent fabrics in case of curcumin are good to very good (4-5) and those for change in colour are also good to very good (4-5). It should be noted that the improvement in rate of change in colour is observed at higher chitosan concentration in organoclay. This indicates the existence of strong bonds between the dye molecules and the PLA/organoclay nanocomposite fibers which can be explained on the basis that natural dyes contain ionizable groups (auxochromes) such as -OH. In aqueous solution at appropriate pH values, ionizable groups became soluble due to their conversion into anionic forms [38]. The introduction of chitosan primary amino groups thus has the ability to create a reaction with dye molecule.

TABLE-5
COLOUR FASTNESS OF PLA AND PLA/ORGANOCLAY
NANOCOMPOSITE FIBERS DYED WITH CURCUMIN

Sample	Washing fastness			Light fastness
	Assessment of change in colour	Assessment of staining		
		With cotton	With wool	
PLA	2	4	4-5	2
PLA/organoclay-1	2	4	4-5	2
PLA/organoclay-2	2-3	4-5	4-5	2
PLA/organoclay-3	3-4	4-5	4-5	2
PLA/organoclay-4	3-4	4-5	4-5	2

Conclusion

Poly(lactic acid) fibers based on nanocomposites prepared by adding chitosan modified montmorillonite were obtained by melt-blending. XRD and SEM analysis showed a good dispersion of organoclay into the PLA matrix. The introduction of organoclay induces a higher crystallization temperature and a lower melting point. The thermal stability of the PLA/organoclay nanocomposite fibers is higher than that of neat PLA fiber. The introduction of the organoclay improves the accessibility of the fiber and this favours the dyeing of the PLA/organoclay nanocomposite fibers with natural dye.

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REFERENCES

- L.G. Angelini, A. Bertoli, S. Rolandelli and L. Pistelli, *Ind. Crops Prod.*, **17**, 199 (2003); [https://doi.org/10.1016/S0926-6690\(02\)00099-7](https://doi.org/10.1016/S0926-6690(02)00099-7).
- N.A. Ibrahim, A.R. El-Gamal, M. Gouda and F. Mahrous, *Carbohydr. Polym.*, **82**, 1205 (2010); <https://doi.org/10.1016/j.carbpol.2010.06.054>.
- T. Bechtold, A. Mahmudali and R. Mussak, *Dyes Pigm.*, **75**, 287 (2007); <https://doi.org/10.1016/j.dyepig.2006.06.004>.
- N. Barka, A. Assabbane, A. Nounah, L. Laanab and Y.A. Ichou, *Desalination*, **235**, 264 (2009); <https://doi.org/10.1016/j.desal.2008.01.015>.
- S. Baliarsingh, A.K. Panda, J. Jena, T. Das and N.B. Das, *J. Clean. Prod.*, **37**, 257 (2012); <https://doi.org/10.1016/j.jclepro.2012.07.022>.
- J.F. Jenck, F. Agterberg and M.J. Driescher, *Green Chem.*, **6**, 544 (2004); <https://doi.org/10.1039/b406854h>.
- D.L. Kaplan, *Biopolymers from Renewable Resources*, Springer Berlin Heidelberg, Berlin, Heidelberg (1998).
- K. Kummerer, *Green Chem.*, **9**, 899 (2007); <https://doi.org/10.1039/b618298b>.
- L. Zaidi, M. Kaci, A. Bruzard, A. Bourmaud and Y. Grohens, *Polym. Degrad. Stab.*, **95**, 1751 (2010); <https://doi.org/10.1016/j.polymdegradstab.2010.05.014>.
- M. Gardette, S. Th  rias, J. Gardette, M. Murariu and P. Dubois, *Polym. Degrad. Stab.*, **96**, 616 (2011); <https://doi.org/10.1016/j.polymdegradstab.2010.12.023>.
- R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, **4**, 835 (2004); <https://doi.org/10.1002/mabi.200400043>.
- J. Lunt and J. Bone, *AATCC Rev.*, **1**, 20 (2001).
- D. Phillips, J. Suesat, M. Wilding, D. Farrington, S. Sandukas, J. Bone and S. Dervan, *Color. Technol.*, **119**, 128 (2003); <https://doi.org/10.1111/j.1478-4408.2003.tb00162.x>.
- Y. Yang and S. Huda, *J. Appl. Polym. Sci.*, **90**, 3285 (2003); <https://doi.org/10.1002/app.13062>.
- D. Karst, D. Nama and Y. Yang, *J. Colloid Interface Sci.*, **310**, 106 (2007); <https://doi.org/10.1016/j.jcis.2007.01.037>.
- S.M. Burkinshaw and D.S. Jeong, *Dyes Pigm.*, **92**, 1025 (2012); <https://doi.org/10.1016/j.dyepig.2011.06.020>.
- S.M. Burkinshaw, D.S. Jeong and T.I. Chun, *Dyes Pigm.*, **97**, 361 (2013); <https://doi.org/10.1016/j.dyepig.2011.12.007>.
- F. Fattahi, H. Izadan and A. Khodami, *Prog. Color Colorants Coat.*, **5**, 15 (2012).
- S. Jantip, S.B. Porntip and S. Potjanart, *Adv. Mater. Res.*, **486**, 253 (2012); <https://doi.org/10.4028/www.scientific.net/AMR.486.253>.
- P. Hansakulwat, P. Sae-Bae, J. Setthayanond and I.N. Phatthalung, *Appl. Mech. Mater.*, **535**, 641 (2014); <https://doi.org/10.4028/www.scientific.net/AMM.535.641>.
- H.F. Huang, Y.Y. Qu, Z.J. Fu and Y.F. Sun, *Adv. Mater. Res.*, **627**, 233 (2012); <https://doi.org/10.4028/www.scientific.net/AMR.627.233>.
- K.Q. Liu, Y.L. Rui and G.Q. Chen, *Adv. Mater. Res.*, **239-242**, 1739 (2011); <https://doi.org/10.4028/www.scientific.net/AMR.239-242.1739>.
- L. He, F. Zhang, B.T. Tang, L.L. Wang and J.Z. Yang, *Chinese Chem. Lett.*, **18**, 1151 (2007); <https://doi.org/10.1016/j.cclet.2007.07.031>.
- L. Razafimahefa, S. Chlebicki, I. Vroman and E. Devaux, *Dyes. Pigm.*, **66**, 55 (2005); <https://doi.org/10.1016/j.dyepig.2004.08.012>.
- D.W. Litchfield and D.G. Baird, *Polymer*, **49**, 5027 (2008); <https://doi.org/10.1016/j.polymer.2008.08.064>.
- A.R. Horrocks, B.K. Kandola, G. Smart, S. Zhang and T.R. Hull, *J. Appl. Polym. Sci.*, **106**, 1707 (2007); <https://doi.org/10.1002/app.26864>.
- M.P. Gashti and S. Moradian, *J. Appl. Polym. Sci.*, **125**, 4109 (2012); <https://doi.org/10.1002/app.35493>.
- D.W. Litchfield, D.G. Baird, P.B. Rim and C. Chen, *Polym. Eng. Sci.*, **50**, 2205 (2010); <https://doi.org/10.1002/pen.21758>.
- G.-H. Guan, C.C. Li and D. Zhang, *J. Appl. Polym. Sci.*, **95**, 1443 (2005); <https://doi.org/10.1002/app.21387>.
- A. Bigdeli, H. Nazockdast, A. Rashidi and M.E. Yazdanshenas, *J. Polym. Res.*, **19**, 9990 (2012); <https://doi.org/10.1007/s10965-012-9990-6>.
- K. Fukushima, D. Tabuani, M. Dottori, I. Armentano, J.M. Kenny and G. Camino, *Polym. Degrad. Stab.*, **96**, 2120 (2011); <https://doi.org/10.1016/j.polymdegradstab.2011.09.018>.
- R. McDonald, *J. Soc. Dyers Colour.*, **96**, 486 (1980); <https://doi.org/10.1111/j.1478-4408.1980.tb03544.x>.
- S.A. McGlashan and P.J. Halley, *Polym. Int.*, **52**, 1767 (2003); <https://doi.org/10.1002/pi.1287>.

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34. S. Qin, Q. Li, M. He, H. Shao, J. Yu, J. Guo, K. Zhang and W. Yan, *Polym. Eng. Sci.*, **54**, 2911 (2014);
<https://doi.org/10.1002/pen.23848>.
35. S.K. Sahoo, S. Mohanty and S.K. Nayak, *Prog. Org. Coat.*, **88**, 263 (2015);
<https://doi.org/10.1016/j.porgcoat.2015.07.012>.
36. A. Araújo, G. Botelho, M. Oliveira and A.V. Machado, *Appl. Clay Sci.*, **88-89**, 144 (2014);
<https://doi.org/10.1016/j.clay.2013.12.005>.
37. V.R.G. Dev, J. Venugopal, S. Sudha, G. Deepika and S. Ramakrishna, *Carbohydr. Polym.*, **75**, 646 (2009);
<https://doi.org/10.1016/j.carbpol.2008.09.003>.
38. M. Yusuf, M. Shahid, M.I. Khan, S.A. Khan, M.A. Khan and F. Mohammad, *J. Saudi Chem. Soc.*, **19**, 64 (2015);
<https://doi.org/10.1016/j.jscs.2011.12.020>.