

## **Properties and Performances of Fabrics made from Bio-based and Degradable PLA/PHBV Filament Yarns**

Huang X. X.<sup>1</sup>, Tao X.M.\*<sup>1</sup>, Zhang Z.H.<sup>1</sup>, Chen P.<sup>2</sup>

1. Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong
2. Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Materials Technology and Engineering (NIMTE), CAS, Ningbo 315201, China

### **Abstract**

This paper reports a comparative experimental study of single jersey knitted fabrics made from a novel bio-based and degradable polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) multi-filament yarn, together with polylactide acid, Cupro, polyethylene terephthalate (PET) and polyamide 6 (PA 6) multi-filament yarns. Their structures, mechanical, thermal and surface properties and performances as well as anti-bacterial behavior are measured and compared. It has been found that the polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) filament yarn has adequate thermal and mechanical properties for normal textile and coloration/finishing processes. The Young's modulus of polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) multi-filament yarn is the lowest among all the candidates investigated except for polyamide 6 (PA 6). The dyed polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) fabric has the highest softness rating among all the fabrics.

Single jersey knitted fabrics from the polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) filament yarn have a bursting strength, extension and recovery that satisfy the industrial requirement. In addition, after fully relaxation, the dyed polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) knitted fabrics exhibit an outstanding pilling resistance, favorable snagging property, as well as good air permeability,  $Q_{\max}$  and smoother surface. Finally, this study has led to a discovery of excellent anti-bacterial performance of 100% polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV) fabrics against *staphylococcus aureus*, *klebsiella pneumoniae*, *candida albicans* according to AATCC100-2012.

**Key words:**

anti-bacterial performance, bio-based, degradable, fabric properties, filament yarns, polylactide acid/poly (hydroxybutyrate-co-hydroxyvalerate) (PLA/PHBV), softness

**Introduction**

As a part of the fight against rapid global warming and reduction of natural resources, the high carbon emission in the production processes and life cycle of petroleum-based synthetic fibers, numerous studies have been conducted and efforts made to improve the degradability of the synthetic fibers,<sup>1-5</sup> as well as to develop novel bio-based materials from renewable resources.<sup>6-8</sup> In particular, the bio-based and degradable polymers and blends have attracted considerable interests for textile academics and industries. They can be classified into three types according to the sources: natural polymers such as cellulose, protein and starch; synthetic polymers from natural monomers, for example, polylactide acid (PLA);<sup>9-14</sup> and polymers from bacterial fermentation, including polyhydroxybutyrate (PHB).<sup>15-18</sup> They exhibit great potentials in both conventional durable goods and disposable goods. However, the use of the bio-based products is still far below that of the petroleum-based counterparts, because most textile goods made from these bio-based polymers or blends possess unsatisfactory thermal and mechanical properties. PLA/ PHBV blends with various ratios were investigated in order to improve the processibility and properties of PLA-based polymers.<sup>19-23</sup> Researchers<sup>24</sup> have developed PLA/PHBV blend fibers by means of conventional melt-spinning and hot-drawing process and also optimized the spinning parameters. The developed blend fibers exhibited favorable physical and mechanical properties such as good softness, acceptable tensile properties for textile applications. Furthermore, the low-energy disperse exhaustion dyeing processes of 100% PLA/PHBV fabrics have been investigated and optimized. The fabrics exhibit excellent dyeing effect, acceptable bursting strength and favorable color fastness.<sup>25</sup> Nevertheless, only one more study<sup>26</sup> has reported the development of PLA/PHBV knitting fabric for socks, but did not conduct any measurement or assessment on the fabric properties and performance.

In this work, we make a comparative study on the properties and performance of five types of synthetic multi-filament yarns and their corresponding knitted fabrics, including three bio-based types (PLA/PHBV, PLA, Cupro) and two petroleum-based types (PET, PA6).

**Experimental****Materials**

PLA/PHBV multi-filament yarns were obtained from Ningbo Hesu Fibers Co. Ltd. Other commercial multi-filament yarns with similar specifications were used for

comparison, including PET and PA6 (Qingdao Innovative Fiber Development Ltd, China), and Cupro (Asahikasei Fibers International (Shanghai) Co., Ltd., China). PLA mulit-filament yarns were produced by Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science. The PLA chips (Ingeo™ 2003D, Nature Works LLC, USA) were the same as those used in producing PLA/ PHBV filament yarns. The cross-sections of these filaments were all circular, and all of the adopted filament yarns were fully drawn filament yarns (FDY). The specifications of the proposed filament yarns are presented in Table 1. In particular, the volume density, boiling water shrinkage, moisture regain of PLA/PHBV filaments were 1.294 g/cm<sup>3</sup>, 10.7±0.7% and 0.4, respectively. Additionally, Chitosan staple yarn was also selected in anti-bacterial tests together with the PLA/ PHBV and others. Chitosan staple fibers of 1.5D in diameter and 35 mm in length were obtained from Tian Jin Zhong Shen Bioengineering Co. Ltd, and has been processed as 20 Ne ring yarns in the laboratory of the Hong Kong Polytechnic University.

Table 1 Specifications of filament yarns

Materials	Yarn count (dtex)	No. of filaments in yarn cross-section (f)	Fineness of single filament (dtex)	Yarn code
PLA/PHBV	82.8	48	1.73	PLA/PHBV-75D/48f
PLA	88.9	48	1.85	PLA-80D/48f
PET	83.2	48	1.73	PET-75D/48f
PA6	78.7	48	1.64	PA6-70D/48f
Cupro	80.6	45	1.79	Cupro-73D/45f

### Fabric preparation

BAINLONG circular knitting machine with the gauge of 28 needles per inch was adopted for producing single jersey knitted fabrics made of the five kinds of multifilament yarns, respectively. Two filament yarns of each kind were fed side by side. The pretension used was 2~3 cN. The knitting process was conducted in WUXI ERVA Knitted Fashion Co. Ltd. The fabrics made were used for most of assessment tests.

The exhaustion dyeing of the PLA/PHBV fabrics was carried out in the laboratory at Hong Kong Polytechnic University using the AHIBA IR dyeing machine (Datacolor, Switzerland). The dyestuff was C.I. Disperse Red 74 with a dosage of 1% o.m.f. and a liquid ratio of 30:1; the dyeing process lasted for 30min with a maximum temperature

of 100°C; and the pH value maintained around 5.0, which was based on our previous study of PLA/PHBV dyeing condition.<sup>25</sup>

For the anti-bacterial tests, owing to the limit quantity of 20 Ne chitosan yarns, the chitosan fabric sample was prepared on TRICOLAB Cylinder Hosiery machine in the laboratory of the Hong Kong Polytechnic University. The machine gauge, knitting tension and speed were 25G, 2 gf and 40r/min, respectively.

## Testing

### Yarn measurement

By using Instron 5944, the tenacity, elongation and Young's modulus of PLA/PHBV, PLA, PET, PA6 and Cupro filament yarns were examined, respectively. According to Standard ISO 2062-2009, the gauge length was adjusted to 250 mm, and the drawing speed was 250 mm/min. Twenty samples of each yarn were prepared for measuring yarn tensile properties. All the specimens were examined under a pretension of  $0.5 \pm 0.1$  cN/tex. Before measurement, all yarn samples were conditioned for 24 h at  $20 \pm 2$  °C and  $65 \pm 2$  % RH.

### Fabric measurement and assessment

After 24h conditioning in the standard environment of  $20 \pm 2$  °C and  $65 \pm 2$  % RH, the structure parameters including loop length (10 samples for each test), fabric weight (three samples for each test) and thickness (five samples for each test) of various prepared fabrics were first measured according to the standards of BS EN14970:2006, ASTM D3776:2013 and BS EN ISO5084:1997, respectively. The tightness factor (TF) in SI units of each fabric sample could be calculated from equation (1) as follows

$$TF = \frac{\sqrt{tex}}{l} \text{ in SI units} \quad (1)$$

where  $L$  is the loop length (mm) and  $tex$  is the yarn count.

Additionally, the mechanical properties and performances of the six types of knitted fabrics were tested and compared. The testing standard and apparatus are listed in Table 2. In particular, the softness of each fabric was evaluated by five experienced evaluators. In every evaluation, each fabric was reckoned as a benchmark in turn. When the softness of a specimen was better than that of the benchmark, the softness of the specimen was record as 1; if worse, it was record as -1; and if similar, it was record as 0. After all fabrics were evaluated by one evaluator, the total score of each specimen

was the softness rating the evaluator provided. The resultant softness rating was the mean value of five evaluators' assessment for each kind of fabric.

Table 2 Testing standards and apparatus of fabric properties and performance

Properties /Performances	Standards	Apparatus	No. of samples for each fabric
Bursting strength	ISO 13938-2 (1999)	TRUBURST Bursting Strength Tester	5
Elasticity	EN 14704	Instron 5566	6
Tensile and shear	----	KES FB1-AU-A Automatic Tensile & Shear Tester	4
Bending	----	KES FB2 Pure bending	4
Compression	----	KES FB3-AUTO-A Automatic Compression Tester	4
Surface property	----	KES FB4-AUTO-A Automatic Surface Tester	4
Softness rating	----	----	6
Pilling property	TM 152	ICI Pilling Tester (M227)	4
Abrasion resistance	ISO 12947- 2:1998	SDL M295 Martindale	4
Snagging	ASTM D3939	SDL M078 MACE Snag Tester	4
Air permeability	----	KES-F8-AP1 tester	5
Thermal property	----	KES-F7 THERMO LABO II	5
Anti-bacterial performance	AATCC100 -2012	----	*

\*: The number of specimens used for each test of anti-bacterial performance was determined when the amount of absorbed inoculum reached  $1.0 \pm 0.1$  mL.

AATCC100-2012 was followed to conduct anti-bacterial tests, which were carried on at Guangzhou Fiber Product Testing and Research Institute. The adopted bacterial included *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Candida albicans*. For each kind of washed test fabric, several circular swatches with the diameter of  $4.8 \pm 0.1$  cm were prepared. The measured specimens were incubated over 18 h at  $37 \pm 2$  °C. The

reduction percentage of bacterial on one specific sample was obtained from the following equation,

$$R = 100\% \times (B - A)/B \quad (2)$$

where  $A$  represents the quantity of living bacterial on the inoculated treated samples after the demanded contact period;  $B$  is the quantity of living bacterial on the inoculated treated samples once being inoculation, that is, at 0 contact time.

Before the tests of anti-bacterial performance, all the prepared knitted fabrics were washed in water for 30min at the  $40 \pm 2$  °C by using non-ionic detergent Diadavin EWN, 200 %, 2 g/L with a liquor ratio of 60:1, and then balanced for 24 h in the standard condition of 22 °C, 65 % RH.

## **Results and discussion**

### **Mechanical properties of filament yarns**

As presented in Table 3, the mean and minimum tenacity of 75D/48f PLA/PHBV filament yarns are 3.23 cN/tex and 2.84 cN/tex, respectively, higher than Cupro, but lower than the other three including PLA, PET and PA6. The measured mean tenacity of PLA is similar to that of PET. Besides, the elongation of PLA/PHBV yarns is 27.71 %, similar to PET, but smaller than PA6 and PLA. In particular, Cupro exhibits significantly lower elongation, 8.82 %.

Fiber stiffness is related to its rigidity, a product of modulus and moment of inertia (a pure geometry defined term). Thus, for fibers of the same cross-section and size, a high modulus results in higher stiffness, and vice versa.<sup>26</sup> The multi-filament yarns used are twistless thus the yarn stiffness is directly related to fiber stiffness as the sum of rigidity of all fibers. The filaments used are of similar cross section and the variation of their diameter is small. Hence PLA/PHBV yarns with a relatively lower modulus (44.02 cN/tex) manifests that the fabrics made of PLA/PHBV yarns have a good softness and pleasant handle. The mean modulus of PA 6 yarn (20.80 cN/tex) is much smaller than that of PLA/PHBV yarn. Furthermore, 73D/45f Cupro presents a modulus of 115.88 cN/tex, quite higher than that of PLA/PHBV, although Cupro fabrics were reckoned to possess rather smooth and soft hand feel, which were even smoother and softer than 100% silk Dupion, 100% cotton, etc.<sup>27</sup>

Table 3 Tensile properties of multi-filament yarns of PLA/PHBV and others

Yarn code	Tenacity (cN/tex)		Elongation (%)		Young's modulus (cN/tex)	
	Mean	Min	Mean	Min	Mean	Min
	[CV%]		[CV%]		[CV%]	
PLA/PHBV-75D/48f	3.23 [4.58]	2.85	27.71 [2.56]	25.81	44.02 [2.71]	41.61
PLA-80D/48f	3.84 [8.25]	3.23	33.72 [3.18]	31.14	53.50 [3.10]	52.68
PET-75D/48f	3.85 [3.48]	3.53	28.02 [9.13]	22.81	77.17 [2.72]	70.40
PA6-70D/48f	4.65 [2.72]	4.41	41.99 [5.43]	35.98	20.80 [3.54]	19.43
Cupro-73D/45f	2.93 [3.06]	1.93	8.82 [11.00]	6.56	115.88 [2.78]	109.53

### Structures, properties and performance of fabrics

#### Fabric structural parameters

The measured structural parameters of single jersey knitted fabrics made of the five kinds of filament yarns as well as the dyed PLA/PHBV fabric are listed in Table 4, including loop length, tightness factor, fabric weight and thickness. Generally, the six types of fabrics have quite similar structures attributing to the use of the same knitting conditions and the yarns with a similar yarn count. However, Cupro shows markedly higher fabric weight than the other five kinds of fabrics, which may arise from the higher density of Cupro fiber (i.e. 1.50~1.52 g/cm<sup>3</sup>) comparing with the other four kinds of fibers. Additionally, the tightness factor of PLA/PHBV fabric increased from 1.55 to 1.67 after dyeing, because the high boiling shrinkage (10.7%) of PLA/PHBV fibers<sup>24</sup> may lead to the shrinkage of the fabric during exhaustion dyeing process.

Table 4 Structure parameters of single jersey knitted fabrics

Fabric name	Fabric composition	Fabric type	Loop length (mm) [CV%]	Tightness factor ( $\sqrt{\text{tex}}$ /mm)	Fabric Weight (g/m <sup>2</sup> ) [CV%]	Thickness (mm) [CV%]
PLA/PHBV	PLA/PHBV	Greige	2.62 [0.58]	1.55	105.17 [1.43]	0.324 [2.76]

PLA	PLA	Greige	2.64	1.60	99.10	0.328
		e	[0.32]		[2.40]	[3.34]
PET	PET	Greige	2.62	1.56	107.59	0.308
		e	[0.51]		[1.78]	[3.56]
PA 6	PA 6	Greige	2.63	1.51	105.95	0.328
		e	[1.02]		[1.21]	[3.34]
Cupro	Cupro	Greige	2.51	1.60	145.07	0.384
		e	[0.36]		[1.15]	[2.33]
PLA/PHB	PLA/	Dyed	2.44	1.67	137.00	0.298
V(D)	PHBV		[1.16]		[1.38]	[1.89]

Note: PLA/PHBV (D) represents the dyed knitted fabrics made of PLA/PHBV filament yarns.

#### Bursting strength

As shown in Table 5, the bursting strength of PLA/PHBV knitted fabric (i.e. 375.8kPa) meets the requirement of textile industrial products, which is higher than that of degradable PLA fabric, but lower than PET, PA 6 and Cupro. Cupro knitted fabric exhibits a high bursting strength, ranking the second place among all the fabrics, even though the Cupro filament yarn has the lowest tenacity. It is presumably because of the markedly higher fabric weight and thickness of Cupro fabrics. Nevertheless, the PET fabric sample was not broken by the bursting ball in the test, which indicates that the PET fabric possesses a high bursting strength, which exceeds the measurement range of TRUBURST Bursting Strength Tester. It was reported <sup>25</sup> that the dyed PLA/PHBV knitted fabric had an enhanced bursting strength when compared with the greige fabric, thus the last column includes the data for comparison.

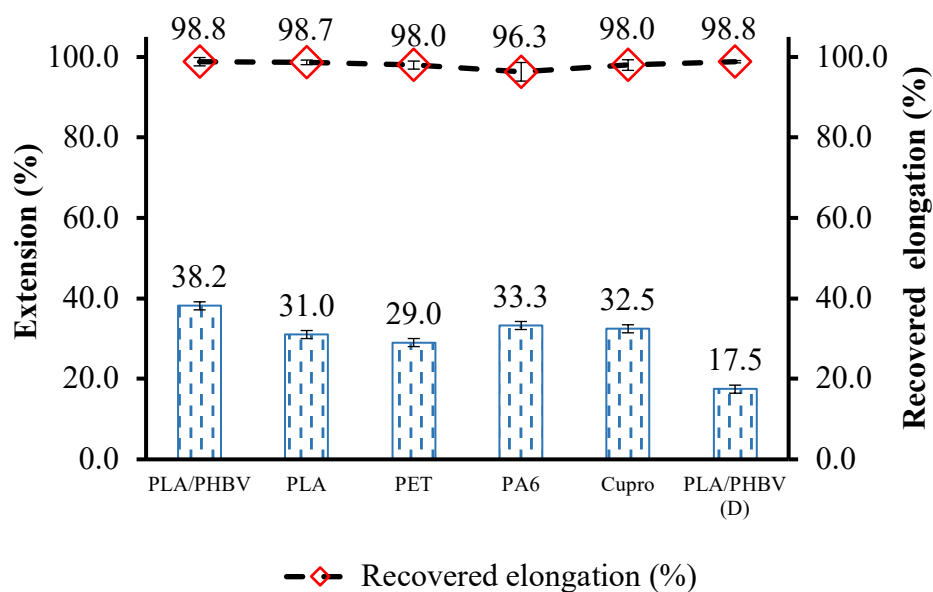
Table 5 Comparison on bursting strength of SJ-PLA/PHBV fabrics with others

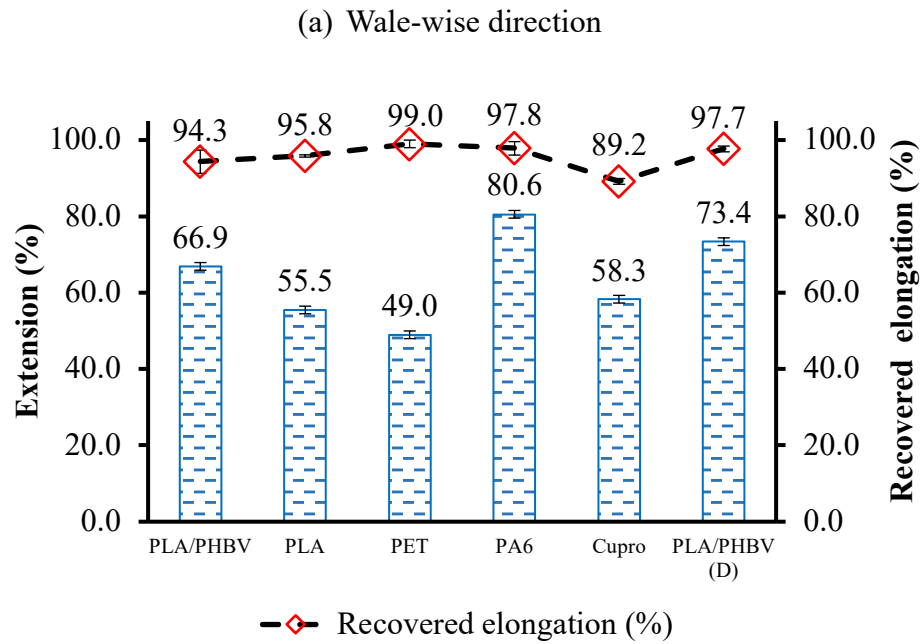
Fabric code	PLA/PHBV	PLA	PET	PA 6	Cupro	PLA/PHBV(D) <sup>25</sup>
Bursting strength (kPa)	375.8	340.0	>827.3	504.8	547.9	397.1
[CV%]	[0.53]	[3.43]	[/]	[2.23]	[5.21]	[0.34]
Bursting height (mm)	12.0	11.5	Not	10.2	11.3	13.5
[CV%]	[0.82]	[3.60]	broken	[0.82]	[2.76]	[1.75]

## Elasticity

According to standard EN14704, with the maximum load of 35N and the extension rate of 500 mm/min, the extension and recovered elongation of the prepared fabric samples were examined, respectively. As shown in Figure 1, all the fabric samples extend apparently more in the course-wise than in the wale-wise direction, which is possibly rooted in the intrinsic characteristic of single jersey fabrics. The extensions of PLA/PHBV fabric in wale-wise and course-wise are 38.2% and 66.9%, respectively, which are generally higher than the other samples. In addition, the PLA/PHBV fabric exhibits the lowest extensibility in the wale-wise direction after dyeing, and the extension of the fabric samples decreases more than half comparing with the value of the greige fabric. This is perhaps because the shrinkage of the PLA/PHBV fabric samples during dyeing brings about an increment in fabric compactness in the wale-wise direction, e.g. the increase of tightness factor. The extension of PLA/PHBV fabrics in the course-wise direction is raised from 66.9% to 73.4%, which may be attributed to the reduction of the fabric elongation in the walewise direction.

Most fabric samples recover over 95.0% of their initial length in both wale-wise and course-wise directions after being stretched under the load of 35N, except for Cupro fabric (89.2%) and PLA/PHBV greige fabric (94.3%) in the course-wise direction. However, the recovered elongations of PLA/PHBV greige fabric and dyed fabric in the wale-wise direction (98.8%) are both the highest among all samples. Moreover, the dyed PLA/PHBV fabric can recover about 3.4% more than the corresponding greige fabric in the course-wise direction, implying that the dyeing process results in molecular structure rearrangement owing to stress relaxation in PLA/PHBV fibers.





(b) Course-wise direction

Figure 1 Elasticity of PLA/PHBV fabrics and other kinds of fabrics. (a) Wale-wise direction. (b) Course-wise direction. PLA: polylactide acid; PHBV: poly (hydroxybutyrate-cohydroxyvalerate).

#### Low-stress tensile properties

The tensile properties including extension rate (EMT), tensile resilience (RT), linearity of extension curve (LT) and tensile energy (WT), were obtained by using KES FB1. As exhibited in Table 6, PLA/PHBV knitted fabrics have a relatively higher extension rate and the highest resilience comparing with the other fabric samples. After dyeing, the extension rate of PLA/PHBV knitted fabrics apparently decrease from 26.85% to 14.23%, almost by half, which is similar to the measured results obtained from Instron 5566; and the tensile resilience (RT) is reduced from 53.52% to 44.96%, but still higher than those of the other kinds of fabrics. The Bio-based PLA fabric possesses an extensibility (19.67%), markedly lower than those of the greige fabrics made from filament yarns; whereas, it has a modest resilience (30.90%).

#### Low-stress shear properties

The shear properties of the knitted fabrics, including shear stiffness (G) and shear hysteresis (2HG), were measured by means of KES FB1. Shear stiffness (G), a property related to the ability for in-plane rotation of yarn in a fabric, contributes to fabric softness. As presented in Table 6, PLA/PHBV fabric has the lowest shear stiffness among the five kinds of greige fabrics, but close to that of PA6. It is demonstrated that

PLA/PHBV greige fabrics have the lowest resistance in in-plane shear deformation. However, the shear stiffness of the dyed PLA/PHBV fabrics increases to 0.66 g/cm·degree from 0.57 g/cm·degree of PLA/PHBV greige fabric.

Moreover, shear hysteresis (2HG) means the energy loss occurred in a shear deformation cycle, which in most cases, is used to overcome the frictions at the intersections of loops or between the warp yarn and the weft yarns as well as the friction between sliding fibers. Alternatively, it is related to the energy for plastic or viscoelastic deformation of the fibers. Therefore, shear hysteresis has a relationship with fabric structure as well as yarn rigidity and surface properties of fibers and yarns. Table 6 depicts no large differences in the shear hysteresis of the five kinds of greige fabrics. In particular, the PLA/ PHBV fabric sample has a moderate value of shear hysteresis of 2.91g/cm·degree, close to that of PA6; PET fabrics show the highest value of 3.48 g/cm·degree. After dyeing, the shear hysteresis of PLA/PHBV fabric decreases slightly, from 2.91g/cm to 2.58g/cm.

#### Bending properties

Bending rigidity (B) and bending hysteresis (2HB) measured by using KES FB2 are shown in Table 6. The bending rigidity (B) is related to the perceived out-plane deformation resistance of fabric. The lower the bending rigidity, the more easily the fabric is bent. The PLA/PHBV greige fabric has a moderate bending rigidity (0.037 g·cm<sup>2</sup>/cm), lower than most greige fabrics except Cupro fabric. The rigidity is reduced to 0.015 g·cm<sup>2</sup>/cm after dyeing process, which may be related to the reduction of inter-fiber friction owing to the stress relaxation during dyeing. Moreover, the Cupro fabric has the lowest bending rigidity of 0.010 g·cm<sup>2</sup>/cm among all the fabrics, dyed or not dyed. Relatively, PET fabrics have the highest bending rigidity of 0.091 g·cm<sup>2</sup>/cm.

Bending hysteresis (2HB) measures the inter-yarn and inter-fiber friction. The greige PLA/PHBV fabric exhibits a moderate bending hysteresis of 0.055 g·cm<sup>2</sup>/cm. After dyeing, it is significantly reduced to 0.012 g·cm<sup>2</sup>/cm. Similar to the cases of bending rigidity, the Cupro fabric and the PET fabric also possess the lowest bending hysteresis of 0.001 g·cm<sup>2</sup>/cm and the highest bending hysteresis of 0.144 g·cm<sup>2</sup>/cm, respectively.

#### Compression properties

Table 6 displays linearity of compression thickness curve (LC), compression energy (WC) and compressional resilience (RC) of the six knitted fabrics, which were obtained from KES FB3. The compression linearity of all fabric specimens is far from 1.0, which indicates that the six fabrics possess low linearity between compressional stress and

fabric strain.

In addition, the PLA/PHBV greige knitted fabric has a slightly higher compression energy of  $0.129 \text{ g}\cdot\text{cm}^2/\text{cm}$  and the relatively lowest compressional resilience of 33.46%. After dyeing, its compression energy is mildly reduced to  $0.108 \text{ g}\cdot\text{cm}^2/\text{cm}$ , and its compressional resilience is increased to 38.15%. It is implied that the dyed PLA/PHBV has an improved compressibility. Cupro fabric samples show the lowest compression energy ( $0.086 \text{ g}\cdot\text{cm}^2/\text{cm}$ ) and the highest compressional resilience (43.41%).

#### Surface properties (KES)

By using KES-F4, the fabric surface property was measured in terms of coefficient of friction (MIU), mean deviation of friction (MMD) and geometrical roughness. As shown in Table 6, there are no significant differences of friction coefficient among six types of knitted fabric specimens; and the mean friction deviation of all fabric samples is around 0.009, except that of Cupro fabric (0.040). Geometrical roughness is actually a measure of the variation of fabric thickness around the central point, which is located at the center of the lowest and highest places on the measured fabric surface, that is, the lower the value of geometrical roughness, the smoother the fabric surface<sup>28</sup>. As shown in Table 6, the geometrical roughness of PLA/PHBV greige fabrics ( $4.97\mu\text{m}$ ) was close to those of PA6 ( $5.10\mu\text{m}$ ) and Cupro greige fabrics ( $4.52\mu\text{m}$ ), and apparently higher than that of PLA, PET and PA6 fabrics. It is manifested that PLA/ PHBV knitted fabrics and-Cupro knitted fabrics possess favorably smoother surfaces. Furthermore, after dyeing, PLA/PHBV fabrics present even lower geometrical roughness ( $3.31\mu\text{m}$ ), namely, smoother surface.

#### Softness rating

Softness is a very important indicator of fabric performance, and the subjective evaluation can directly reflect the real soft feel for certain fabrics. From -8 to 8, the higher the evaluated value obtained, the softer the fabric specimen. As is shown in Figure 2, PLA/PHBV greige has the lowest softness rating (-4.2) among all the knitted fabrics. However, the dyed PLA/ PHBV fabric has the highest softness rating of 5.6. The large difference of the subjective softness rating between the PLA/PHBV greige fabric and the dyed fabric may attribute to the stress relaxation of fibers during dyeing process, which possibly results in the reduction of inter-fiber friction as well as the decrease of fabric rigidity.

Additionally, Cupro knitted fabrics also present a good softness, even though its rating of 3.8 is lower than the dyed PLA/PHBV fabric, which is consistent with previous

research finding<sup>27</sup>. The subjective ratings are also in consistence with the low-stress mechanical properties and surface properties measured by KESF system.

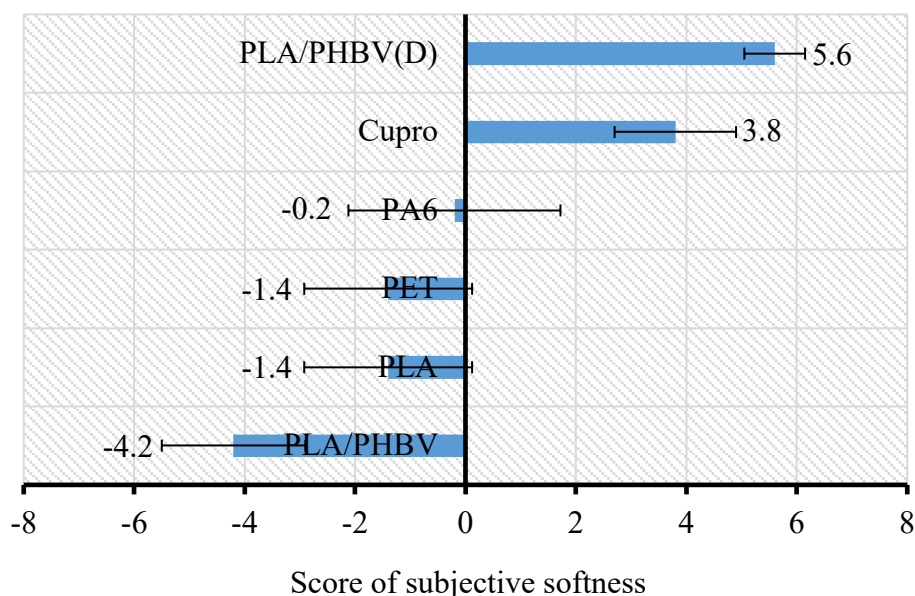


Figure 2 Softness rating of PLA/PHBV fabrics and other kinds of fabrics

### Pilling resistance

All the fabrics made from filament yarns have excellent pilling resistance of grade 5. After 14,400 revolutions of ICI pilling box, which took about 4 h, there were not or seldom pills produced on all the fabric samples.

### Abrasion resistance

Using Martindale Abrasion Tester, all the six types of knitted fabrics were rubbed with the regulated auxiliary specimen. Figure 3 depicts that PLA/PHBV knitted fabric is broken after 2250 rubs, the worst abrasion resistance comparing with other fabric samples, which may arise from the rough surface and low strength of PLA/PHBV filament yarns. However, the dyed PLA/PHBV fabric has an improved abrasion resistance probably because of stress relaxation during dyeing and smoother surface after dyeing.

PET fabrics possess the highest abrasion resistance (>50 000 rubs) at which there is still no sign of any broken yarns. The Cupro fabric has a high fabric weight and thickness

and smooth surface, which all contribute to its relatively high abrasion resistance.

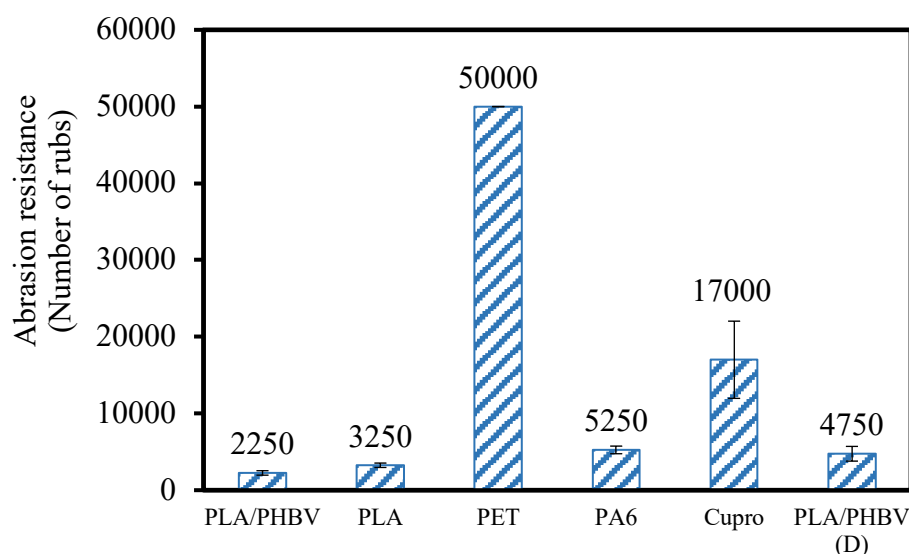


Figure 3 Abrasion resistances of PLA/PHBV fabrics and other kinds of fabrics

### Snagging

The fabric samples after the snagging test present protrusions (i.e. a visible bundle of fibers or a yarn protruding out of fabric surface), or distortions (i.e. some fibers, or a yarn displacing from their original positions on the examined fabric surface, or a yarn breaking off), or both. Based on the assessment by three experienced evaluators for each fabric sample in wale-wise and course-wise, Figure 4 shows that PLA/ PHBV fabrics have a similar snagging resistance to PLA, PET, and PA6 fabrics, and the snagging resistance of PLA/PHBV in wale-wise (4.2) is better than that in course-wise (3.6). The dyed PLA/PHBV fabrics present improved snagging resistance both in the walewise direction (4.5) and the course-wise direction (4.3), which is almost the same as that of PA6 greige fabrics (wales-wise: 4.4, course-wise: 4.3). Moreover, Cupro knitted fabrics show a brilliant snagging resistance, 5.0 for both wale-wise and course-wise directions.

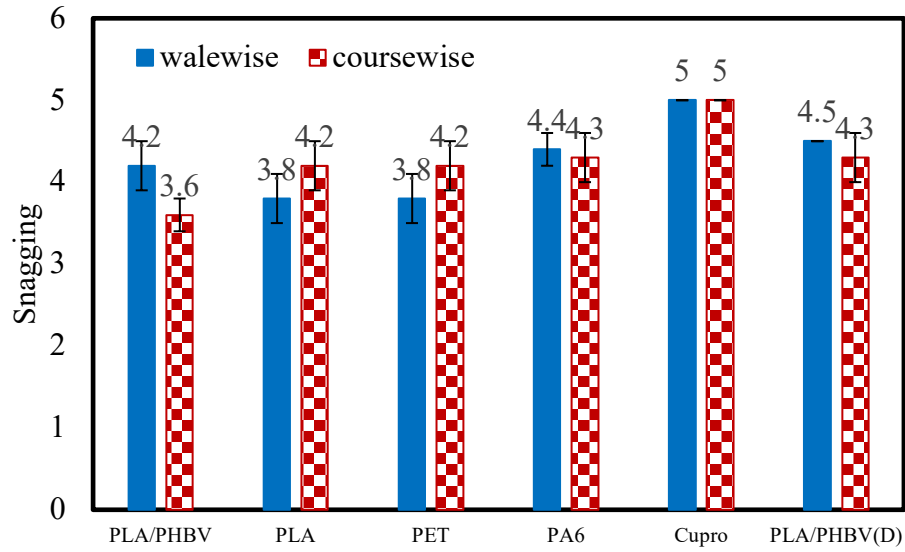


Figure 4 Snagging ratings of PLA/PHBV fabrics and other kinds of fabrics

#### Air permeability

Fabric air permeability relates to the pore size distribution within a fibrous structure like fabric. Fiber cross-sectional shape and dimension, yarn structure and fabric structure are all contributing factors. KES-F8-AP1 tester was used to provide the permeating resistance to air ( $R$ ) of the six knitted fabrics. The smaller the permeating resistance to air, the better the air permeability of the tested specimen. As is shown in Figure 5, the PLA/PHBV knitted fabric has a permeating resistance to air of  $0.0103 \text{ kPa}\cdot\text{S/m}$ , which is higher than PA6 knitted fabric ( $0.0079 \text{ kPa}\cdot\text{S/m}$ ), and similar to PLA ( $0.0109 \text{ kPa}\cdot\text{S/m}$ ) and PET ( $0.0096 \text{ kPa}\cdot\text{S/m}$ ) fabric samples. The PLA/PHBV greige fabric has a low air permeability. Additionally, the dyeing further increases the air resistance of PLA/ PHBV fabric ( $0.0145 \text{ kPa}\cdot\text{S/m}$ ), which may be attributed to the shrinkage of the fabric thus the increased fabric packing density (weight and tightness factor). Cupro fabric samples present the highest air permeating resistance to air, because of their relatively and apparently higher packing density as indicated by fabric weight and thickness.

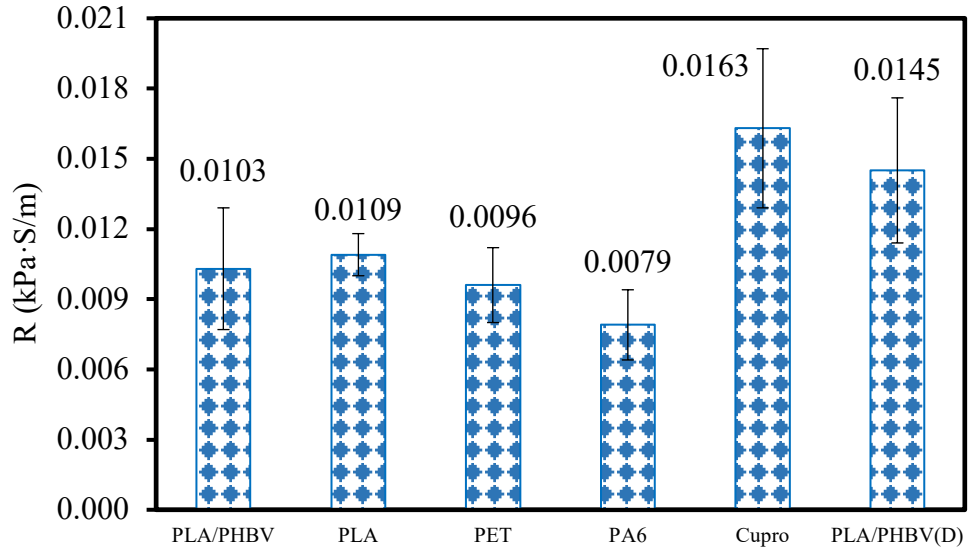


Figure 5 Air resistances of PLA/PHBV fabrics and other kinds of fabrics

#### Thermal properties

The thermal properties of the six types of knitted fabrics were examined on KES-F7 THERMO LABO II in terms of thermal conductivity (K) in the thickness direction and  $Q_{\max}$ . In particular,  $Q_{\max}$  represents the peak value of the heat flow which was measured immediately when the heated plate touched the fabric specimen surface.  $Q_{\max}$  indicates the bulk thermal conductivity which contributes to the cool or warm feel of a person while his finger or skin touches the fabric sample. The higher the  $Q_{\max}$ , the cooler the person can feel.

Figure 6 illustrates that the  $Q_{\max}$  of PLA/PHBV knitted fabrics, no matter greige or dyed, is only smaller than Cupro, and higher than the other fabrics made of PLA, PET and PA6 filament yarns, respectively, which implies that the PLA/PHBV fabric can provide people a pleasantly cooler feel in summer. Moreover, there seems to be no marked differences in the thermal conductivities of PLA/PHBV, PLA, PET and PA6 greige fabric, as well as the dyed PLA/PHBV fabric; whereas, the thermal conductivity of Cupro fabric is significantly higher than that of the other five types of fabrics.

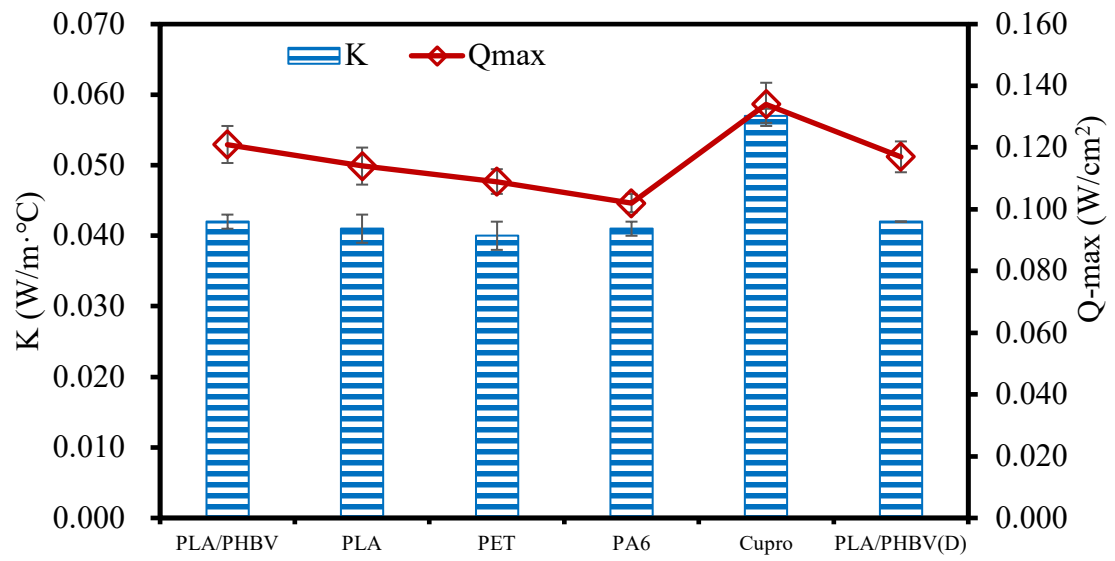


Figure 6 Thermal properties of PLA/PHBV fabrics with other kinds of fabrics

Table 6 Low-stress mechanical and surface properties of the fabrics evaluated by KESF system

Fabric name	Tensile				Shear		Bending		Compression			Surface		
	EMT (%)	LT	WT (g·cm/cm <sup>2</sup> )	RT (%)	G (g/cm·degree)	2HG (g/cm)	B (g·cm <sup>2</sup> /cm)	2HB (gf·cm <sup>2</sup> /cm)	LC	WC (g·cm/cm <sup>2</sup> )	RC (%)	MIU	MM D	SMD (μm)
PLA/PHBV	26.85	0.298	20.95	53.52	0.57	2.91	0.037	0.055	0.377	0.129	33.46	0.265	0.009	4.97
PLA	19.67	0.458	23.77	30.90	0.69	3.33	0.061	0.061	0.438	0.113	40.30	0.207	0.008	7.49
PET	27.07	0.461	33.45	21.04	0.75	3.48	0.091	0.144	0.397	0.132	39.44	0.237	0.010	7.62
PA6	27.05	0.401	29.97	27.44	0.59	2.89	0.074	0.109	0.550	0.111	37.86	0.258	0.014	5.10
Cupro	26.90	0.312	20.00	36.62	0.63	2.61	0.010	0.001	0.546	0.086	43.41	0.234	0.040	4.52
PLA/PHBV(D)	14.23	0.33	10.61	44.96	0.66	2.58	0.015	0.012	0.559	0.108	38.15	0.200	0.009	3.31

## Anti-bacterial performance

The anti-bacterial properties of the fabrics were examined according to the Standard AATCC100-2012. Table 7 presents the measured percentages of bacteria reductions of the fabrics by using three types of common bacterial, e.g. staphylococcus aureus, klebsiella pneumoniae, and candida albicans. PLA/PHBV fabric samples have the highest percentages of reduction after 18 h contact for all the three kinds of bacterial, that are 99.99%, 99.99% and 99.31%, respectively. The bacterial percentage reduction of PLA fabrics is 36.31% for staphylococcus aureus, 53.71% for klebsiella pneumoniae, and 41.08% for candida albicans. It implies that PHBV may also has anti-bacterial properties. Moreover, PA 6 fabrics show some anti-bacterial properties for staphylococcus aureus (32.22%) and candida albicans (37.24%), and have a moderate antibacterial performance for klebsiella pneumoniae (63.28%). PET fabrics do not possess any anti-bacterial properties at all for the three types of bacterial. The bacterial on chitosan fabric samples after 18 h contact time reduce 96.9% for staphylococcus aureus, 90.50% for klebsiella pneumoniae, and 97.62% for candida albicans, respectively; however, these values are slightly smaller than those of PLA/PHBV fabrics.

Table 7 Measured anti-bacterial behaviors of the knitted fabrics

Materials	Anti-bacterial performance	
	Bacterial	Percentage reduction (%)
PLA/PHBV	Staphylococcus aureus	99.99
	Klebsiella pneumoniae	99.99
	Candida albicans	99.31
PLA	Staphylococcus aureus	36.31
	Klebsiella pneumoniae	53.71
	Candida albicans	41.08
PET	Staphylococcus aureus	0
	Klebsiella pneumoniae	0
	Candida albicans	0
PA 6	Staphylococcus aureus	32.22
	Klebsiella pneumoniae	63.28
	Candida albicans	37.24
Chitosan	Staphylococcus aureus	96.90
	Klebsiella pneumoniae	90.50

Note: all fabric samples used for anti-bacterial assessment were greige fabrics.

Further tests on PLA/PHBV fabrics were carried out in two commercial laboratories (Intertek Testing Service Ltd. Shanghai Ningbo Branch and Bureau Veritas Hong Kong Ltd.), and confirmed the new finding of their anti-bacterial performance. On-going study is focusing on the mechanism of the anti-bacterial behavior and we will report its findings in near future. Figure 7 shows the numbers of living bacterial on the inoculated PLA/PHBV fabric samples at 0 h contact time and 18 h contact time, respectively. Apparently, the number of living bacterial is markedly decreased after 18 h contact with the PLA/PHBV fabric sample, which indicates that 100% PLA/PHBV fabric possesses a positive anti-bacterial performance.

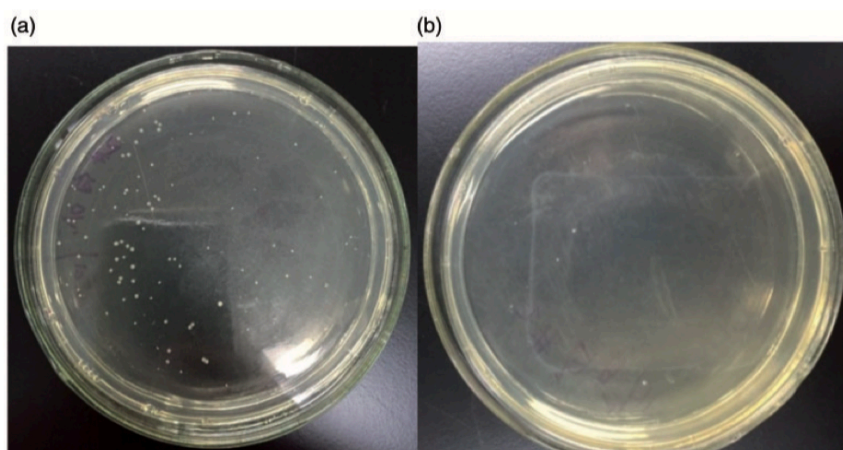


Figure 7 Living bacterial count on the inoculated PLA/PHBV fabric samples: (a) contact time of 0 h; (b) contact time of 18 h.

## Conclusion

This paper reports a comparative experimental study of single jersey knitted fabrics made from a novel biobased and degradable PLA/PHBV multi-filament yarn, with respect to mechanical, thermal and surface properties and performances as well as anti-bacterial behavior. Two types of bio-based (PLA, Cupro) and two types of petroleum-based (PET, PA6) filament yarns have been made into fabrics of the same structure with similar parameters.

It has been found that the PLA/PHBV filament yarn has adequate thermal and mechanical properties for normal textiles and coloration/finishing processes, as it possesses a lower tenacity than PLA, PET and PA 6, but higher than that of Cupro. The

Young's modulus of PLA/PHBV multi-filament yarns (44.02 cN/tex) is the lowest by comparing with those of PLA, PET, and Cupro yarns, except for PA6, indicating that PLA/PHBV yarns are quite soft among all the candidates investigated.

Single jersey knitted fabrics from the PLA/PHBV filament yarns have a bursting strength of 375.8 kPa, higher than that of PLA fabrics, similar to that of PA 6, and significantly lower than PET fabrics. The extension of PLA/PHBV fabric is generally higher than the other four kinds of fabrics. The PLA/PHBV fabric can recover 98.8% in wale-wise direction and 94.3% in course-wise direction, similar to other fabric samples. After exhaustion piece dyeing, the shear rigidity of PLA/PHBV fabric is increased, but the bending rigidity is markedly reduced. This may be due to the increased inter-fiber friction without significant changes in fiber stiffness. The dyed PLA/PHBV fabric has the highest softness rating among all the fabrics.

In addition, after fully relaxation, dyed PLA/PHBV knitted fabrics exhibit an outstanding pilling resistance (5.0), favorable snagging property (4.2 in wale-wise and 3.6 in course-wise), as well as pleasant air permeability, cooler feel and smoother surface. Finally, this study has led to the discovery of excellent anti-bacterial performance of 100% PLA/PHBV fabrics according to AATCC100-2012.

## **Acknowledgement**

The authors would like to acknowledge Hongshan Textile and Clothing Ltd and Qingdao Innovative Fiber Development Ltd for their technical support in fiber and fabric preparation, Guangzhou Fiber Product Testing and Research Institute for their support in testing anti-bacteria properties of fabrics, as well as Cui Ai hui, Wu Jia bao and Lau Hoi ching for their contributions to the yarn and fabric measurement in this study.

## **Declaration of conflicting interests**

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

## **Funding**

The authors disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was partially funded by the Hong Kong Research Institute of Textiles and Apparel Limited, Innovation and Technology Commission and the Government of the Hong Kong Special Administrative Region, Beijing DEWIN Co. Ltd., Linyi Domore Textile Technology

Co. Ltd., Ningbo Tian An Biologic Material Co. Ltd., and TAL Apparel Ltd (grant number ITP/050/13TP).

## References

1. Lam CC and Wu W. Development of low cost degradable polyester fibers. *Chemical Fibers International*. 2016; 66: 25-8.
2. Stanciu MC and Nichifor M. New degradable polyesters from deoxycholic acid and oligo(ethylene glycol)s. *Polymer International*. 2013; 62: 1236-42.
3. Grzebieniak K and Wesolowski J. Glycolysis of PET Waste and the Use of Glycolysis Products in the Synthesis of Degradable Co-polyesters. *Glikoliza odpadów PET oraz wykorzystanie produktów glikolizy do syntezy degradowalnych kopoliestrów*. 2004; 12: 21-4.
4. Matsui M, Ozeki E, Kondo Y, et al. Spontaneously degradable fibers and goods made thereof. Patent US 6322887 B1, USA, 2001.
5. Ikada Y and Tsuji H. Biodegradable polyesters for medical and ecological applications. *Macromolecular rapid communications*. 2000; 21: 117-32.
6. Yu L, Dean K and Li L. Polymer blends and composites from renewable resources. *Progress in polymer science*. 2006; 31: 576-602.
7. Mohanty A, Misra M and Drzal L. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. *Journal of Polymers and the Environment*. 2002; 10: 19-26.
8. Mohanty A, Misra M and Hinrichsen G. Biofibres, biodegradable polymers and biocomposites: an overview. *Macromolecular materials and engineering*. 2000; 276: 1-24.
9. Lim L-T, Auras R and Rubino M. Processing technologies for poly (lactic acid). *Progress in polymer science*. 2008; 33: 820-52.
10. Rasal RM, Janorkar AV and Hirt DE. Poly (lactic acid) modifications. *Progress in polymer science*. 2010; 35: 338-56.
11. Tsuji H and Fukui I. Enhanced thermal stability of poly (lactide) s in the melt by enantiomeric polymer blending. *Polymer*. 2003; 44: 2891-6.
12. Shinoda H, Asou Y, Kashima T, Kato T, Tseng Y and Yagi T. Amphiphilic biodegradable copolymer, poly (aspartic acid-co-lactide): acceleration of degradation rate and improvement of thermal stability for poly (lactic acid), poly (butylene succinate) and poly ( $\epsilon$ -caprolactone). *Polymer degradation and stability*. 2003; 80: 241-50.
13. Chen C-C, Chueh J-Y, Huang H-M and Lee S-Y. Preparation and characterization of biodegradable PLA polymeric blends. *Biomaterials*. 2003; 24: 1167-73.
14. Urayama H, Kanamori T and Kimura Y. Properties and Biodegradability of Polymer Blends of Poly (L-lactide) s with Different Optical Purity of the Lactate Units. *Macromolecular Materials and Engineering*. 2002; 287: 116-21.
15. Yang X, Zhao K and Chen G-Q. Effect of surface treatment on the biocompatibility

- of microbial polyhydroxyalkanoates. *Biomaterials*. 2002; 23: 1391-7.
16. Deng Y, Zhao K, Zhang X-f, Hu P and Chen G-Q. Study on the three-dimensional proliferation of rabbit articular cartilage-derived chondrocytes on polyhydroxyalkanoate scaffolds. *Biomaterials*. 2002; 23: 4049-56.
  17. Zhao K, Deng Y, Chen JC and Chen G-Q. Polyhydroxyalkanoate (PHA) scaffolds with good mechanical properties and biocompatibility. *Biomaterials*. 2003; 24: 1041-5.
  18. Chen G-Q and Wu Q. The application of polyhydroxyalkanoates as tissue engineering materials. *Biomaterials*. 2005; 26: 6565-78.
  19. Ohkoshi I, Abe H and Doi Y. Miscibility and solid-state structures for blends of poly [(S)-lactide] with atactic poly [(R, S)-3-hydroxybutyrate]. *Polymer*. 2000; 41: 5985-92.
  20. Zhao H, Cui Z, Sun X, Turng L-S and Peng X. Morphology and properties of injection molded solid and microcellular polylactic acid/polyhydroxybutyrate-valerate (PLA/PHBV) blends. *Industrial & Engineering Chemistry Research*. 2013; 52: 2569-81.
  21. Gérard T, Budtova T, Podshivalov A and Bronnikov S. Polylactide/poly (hydroxybutyrate-co-hydroxyvalerate) blends: Morphology and mechanical properties. *eXPRESS Polymer Letters*. 2014; 8: 609-17.
  22. Zembouai I, Kaci M, Bruzard S, Benhamida A, Corre Y-M and Grohens Y. A study of morphological, thermal, rheological and barrier properties of Poly (3-hydroxybutyrate-Co-3-Hydroxyvalerate)/polylactide blends prepared by melt mixing. *Polymer Testing*. 2013; 32: 842-51.
  23. Zembouai I, Bruzard S, Kaci M, et al. Poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/polylactide blends: thermal stability, flammability and thermo-mechanical behavior. *Journal of Polymers and the Environment*. 2014; 22: 131-9.
  24. Li L, Huang W, Wang B, Wei W, Gu Q and Chen P. Properties and structure of polylactide/poly (3-hydroxybutyrate-co-3-hydroxyvalerate)(PLA/PHBV) blend fibers. *Polymer*. 2015; 68: 183-94.
  25. Zhang Z.H., Xu Z.Q., Huang X.X. and Tao X.M., Dyeing Processes of 100% Bio-based and Degradable PLA/PHBV Textiles, *Textile Research Journal*, under revision. 2016.
  26. Pivsa-Art S, Srisawat N, Narongchai O, Pavasupree S and Pivsa-Art W. Preparation of knitting socks from Poly (Lactic Acid) and Poly [(R)-3-Hydroxybutyrate-co-(R)-3-Hydroxyvalerate](PHBV) blends for textile industrials. *Energy Procedia*. 2011; 9: 589-97.
  27. Griffiths P and KULKE T. Clothing movement–visual sensory evaluation and its correlation to fabric properties. *Journal of sensory studies*. 2002; 17: 229-55.
  28. Behera BK and Hari P. *Woven textile structure: Theory and applications*. Elsevier, 2010.