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Towards UV-curable inkjet printing of biodegradable poly (lactic acid) fabrics

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Abstract There has been growing interest in using poly (lactic acid) (PLA) fibres because of its natural-based origin and good biodegradability; however its adoption within the textile industry has been limited to lower temperature wet and dry processing, because of its relatively lower glass transition temperature (T_g) and melting point (T_m). Here we report for the first time inkjet printing of heat-sensitive PLA fabrics using ambient temperature UV curable inks as a way of overcoming the potential degradation at higher temperature. The UV-cured inkjet printed PLA fabrics exhibited good performance characteristics such as acceptable colour fastness, relatively high colour strength, K/S , and comparable colour difference, ΔE , after washing to the thermally-cured ink system, without affecting the physical and mechanical properties of the fabrics. In contrast thermally cured inkjet printed PLA fabrics exhibited significantly reduced bursting strength and stiffer handle attributed to the thermal degradation and lower fibre flexibility imparted at the higher temperature. Investigation of the radiation-cured printing approach indicates UV curable inkjet printing may be considered as an alternative to conventional thermally-cured pigment printing of heat sensitive biodegradable PLA-based fabrics.

Introduction

Although inkjet printing constitutes only about 2% of the total printed textile market, it is by far the fastest growing sub-segment in textile printing. It has been growing rapidly as the technology provides a number of advantages over traditional printing methods (e.g. screen printing, roller printing and transfer printing) such as versatility, quicker delivery, mass customisation in the production process, reduction in downtime and sampling cost, lower waste output and lower usage of water and chemicals [1-3]. UV curing of polymers has also found a number of applications in the printing and surface coatings industry, and is already well established in terms of traditional printing processes such as lithography, flexography and screen printing on papers and hard substrates.

Synthetic textile materials, such as polyester and nylon, have been used extensively over the past 50 years mainly because of their excellent performance properties and durability. However, increasing concerns over greenhouse gas emissions due to solid waste management processes such as incineration has led to focused attention on the development of biodegradable materials [4, 5]. Moreover, there has been growing interest to use biodegradable fibres because of the increasing environmental pressure due to fossil fuel consumption in PET production. Poly (lactic acid) (PLA) is an environmentally friendly biodegradable product, which is derived from the fermentation of glucose contained in corn starch. In addition to offering good biodegradability, it also has similar performances characteristics to Polyethylene Terephthalate (PET) fabrics with further added reported advantages such as unique handle and touch, drape, low flammability and smoke generation and excellent UV resistance [6]. In addition, the density and refractive index of PLA fibres are lower than those of PET imparting light weight and deep silky lustre without

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brightness [7]. As an alternative material to reduce greenhouse gas emissions, many manufacturers have put efforts, in collaboration with their customers, into developing market applications for PLA-based textile materials. It has already found a number of applications such as geotextiles, medical textiles, industrial fabrics, filters, towels and wipes, home furnishings, clothing and personal belongings [7]. However the processing of PLA fabrics is restricted to lower temperatures because of its relatively lower melting point, 130–170 °C [8, 9]. It has been recommended not to dye PLA fibres above 120 °C because of its susceptibility to hydrolysis at higher temperature and humidity, particularly under alkaline conditions [7]. In our previous study on the effect of thermal curing on the properties of pigment printed PLA, we also demonstrated possible degradation above 130 °C with dry heat [10]. Therefore, inkjet printing of PLA fabrics using UV-curable inks is of interest due to the “ambient” temperature curing of the surface inks, which can offer an opportunity to overcome this traditional processing limitation.

The use of UV curing technology in printing has increased significantly because of a number of advantages such as the low energy consumption, short start-up period, fast and reliable curing, low environmental pollution, curing at room temperature and space savings [11, 12]. The mechanism of UV curing of prints is based on the photo-polymerisation of the binder, where UV radiation of specific wavelength is absorbed by a photoinitiator and produces radicals to initiate the propagation and polymerisation reactions in the binder molecule. Thereafter, the cross-linking of the binder occurs in the form of a thin film that entraps the pigments onto the fibre. This radical-induced polymerisation is significantly faster than the thermal-induced polymerisation [13, 14]. In addition thermal curing consumes more energy and reduces the strength of certain fabrics due to higher temperature treatment [10]. Therefore, there has been growing interest to incorporate UV curing with inkjet printing so that the benefits of these two technologies could be exploited.

Herein we present for the first time a study focused on printing heat sensitive biodegradable PLA fabrics using UV-curable inkjet inks in order to overcome the potential problems of thermal degradation and rigid inter-fibre bonding occurring with thermal-curing at higher temperatures and extended time. Single jersey PLA knit fabrics were printed with UV and thermal pigment inks, where printed fabrics were UV-cured and thermally-cured subsequently to printing. The performance characteristics of UV-cured and thermally-cured printed fabrics were evaluated and compared in terms of thermal, physical and mechanical properties of inkjet printed fabrics.

Experimental

Materials

100% PLA single jersey knit piqué fabric, 268 g/m², purchased from Valuable Enterprise, Taiwan, was used in this investigation after scouring at 60 °C for 20 minutes in a solution containing 2 g/L soda ash and 0.5 g/L Kieralon Jet B Conc [8] and air dried. LH-100, LF-140 and LF-200 UV-curable inks of Cyan (C), Magenta (M), Yellow (Y) and Black (K) colours were kindly supplied by Hybrid Services Ltd, Crewe, UK, and printed on their Mimaki UJF - 3042 UV LED flatbed printer. ‘Mexar’ cyan, magenta, yellow and black coloured thermal-inks were supplied by Mexar inkjet solutions, Newcastle upon Tyne, UK.

Methods

Inkjet Printing of PLA

A Mimaki UJF-3042 UV LED flatbed printer was used to print UV curable LH-100, LF-140 and LF-200 CMYK inks onto PLA fabrics. A solid pattern of 20 cm × 20 cm area of each colour was printed for each sample and UV cured using the overhead UV curing LED device. The Mimaki UJF-3042 printer uses a UV light range UV-A (wavelength: 400 - 315 nm), almost identical to direct sunlight exposure, and the printer was operated at 350VA or lower power. A R-Jet 4 DTG inkjet printer was used to print ‘Mexar’ thermal inks onto PLA fabrics, and printed fabrics were dried at 90 °C for 5 minutes using a heat press machine and cured at 150 °C for 5 minutes using a Werner Mathis laboratory dryer.

Colour Measurement

Colour fastness to washing of printed fabrics was evaluated by rotating the fabrics in a solution containing 4 g/L ECE detergent (supplied by SDC Enterprises Ltd., Bradford, UK) with 1 g/L sodium perborate and 25 stainless steel balls, adjusted to pH 10.5, at 60 °C for 30 min. The fabrics were rinsed subsequently in running water at ambient temperature and air dried at room temperature prior to colour analysis. SDC multi-fibre fabrics were incorporated into the washing solution as adjacent fabrics in this test in order to assess cross-staining [15]. The colour fastness to rubbing of printed fabrics, both dry and wet rubbing, was measured according to the BS EN ISO 105-X12:2002 test method using a crock meter. The printed samples were exposed to simulated day-light condition in a James Heal Xenon Light fastness tester in order to measure the colour fastness to light. The tested samples were graded on 1-5

scale following the BS EN ISO 105-B01:1999 test method, where grade 5 indicates “Excellent–no colour change” and Grade 1 indicates “very poor–higher degree of colour change”.

A Datalcolor Spectraflash 600 was used to measure K/S and CIE $L^*a^*b^*$ values and the mean value was calculated from the average of four measurements. Colour measurements were taken before and after washing of printed samples and the colour difference values, ΔE , were also noted. The colour strength (K/S) was calculated from reflectance measurements using the Kubelka-Munk equation (Eq. 1):

$$(K/S)_\lambda = (1-R_\lambda)^2/2R_\lambda \quad (1)$$

where K is the absorption co-efficient, S is the scatter co-efficient and R is the reflectance expressed as a fractional value at wavelength λ_{\max} .

DSC Measurement of Thermal Properties

A Perkin Elmer Diamond DSC was used to characterise the thermal properties of printed and untreated PLA fabrics. About 5 mg samples were placed in a DSC pan and subjected to a heating rate of 10 °C/min under a flow of nitrogen. The samples were first scanned from -20 to 220 °C and then cooled to -20 °C and again heated up to 220 °C in a second scan. The glass transition temperature (T_g) and melting temperature (T_m) were determined from the data of the second scan. T_m was determined from the maximum region of endothermic melting peak and T_g was a inflection temperature from baseline at the second heating scan. The degree of crystallinity (X_c) of printed samples was calculated using the following equation (Eq. 2):

$$X_c = (\Delta H_f \times 100)/\Delta H_f^\circ \quad (2)$$

where, ΔH_f is the heat of fusion of the untreated and printed PLA, and ΔH_f° is the heat of fusion for 100% crystalline PLA ($\Delta H_{100} = 93.7$ J/g) [16].

Thermogravimetric analysis (TGA) was used to evaluate thermal decomposition of untreated and printed PLA using a TA instrument, TGA Q5000. The heating rate was 10 °C/min over the temperature range from 30 °C to 600 °C in a nitrogen environment.

Measurement of Bursting Strength

Following conditioning of the samples for 24 h at 20°C and 65% relative humidity, a TruBurst Pneumatic Bursting Strength Tester, supplied by James Heal, UK, was used to measure the bursting strength of untreated and printed samples according to BS EN ISO 13938-2:1999 method. The area of the samples to be tested was clamped over an elastic diaphragm and an increased air pressure was applied

to the underside of the diaphragm until the specimen burst. Bursting strength measurements were taken as the pressure required to rupture tested samples and the mean value was calculated from six measurements taken per sample.

Measurement of Flat Abrasion Resistance

The flat abrasion resistances of the untreated and printed samples were measured using a Martindale abrasion and pilling tester according to the BS EN ISO 12947-2:1999 procedure. The tested samples were conditioned for 24 h at 20°C and 65% relative humidity; four circular specimens were cut from each fabric, placed in the specimen holders and were rubbed against a standard abrasive fabric under a 12 kPa load. The number of cycles required to breakdown a single yarn in a specimen was taken as the abrasion resistance and the mean value was calculated from the four sample measurements.

Kawabata Evaluation System

The mechanical and surface properties of untreated and printed PLA fabrics were determined using the Kawabata Evaluation System for Fabrics (KES-F). The samples (20×20cm) were conditioned for 24 hours at 20°C and 65% relative humidity prior to analysis of the tensile, shear, bending, surface, and compression properties. Knit outerwear winter dress (KN-402-KT) mathematical transformation equation was used to characterize the fabrics.

Surface Topography

A Philips XL 30 field emission scanning electron microscope (SEM) was used to analyse the surface topography of untreated and printed PLA fabrics (before and after a Wascator 5A wash cycle). The samples were fixed horizontally onto stubs and gold coated in order to prevent accumulation of electric charging on the sample during analysis. The typical SEM parameters were: working voltage 6 kV; working distance 10mm; and magnification ×100-4000.

Results and discussion

The application of piezoelectric drop-on-demand (DOD) UV curable inkjet technology has experienced double digit growth on paper and hard substrates because of the advantages offered by the integration of the inkjet and UV curing technologies [11]. However, careful attention is required in order to effectively integrate these two technologies together for textiles application [17]. Moreover, the absorption spectrum of the photoinitiator, the

transmission spectrum of the pigment and the emission spectrum of the UV lamp need to be adjusted to deliver the appropriate level of cross-linking of the binder. A UV curable ink formulation typically contains reactive monomers, oligomers, photoinitiator, colorants and additives such as surfactants and inhibitors. It has been suggested that the optimal formulation is required to contain at least 0.3 wt% photoinitiator and 10% wt% binder [18, 19]. The cross-link density of the polymer films can be increased by increasing the functionality of the acrylates, resulting in less flexible, harder films that have higher resistance to solvents, abrasion, and scratches [20]. As per the material safety data sheet supplied, LH-100 contains acrylic ester (75-90 wt-%) or both di and tri-acrylates monomers such as hexamethylene diacrylate and pentaerythritol triacrylate (40-60 wt%) in their formulations, Fig. 1, whereas LF-140 contains both mono and di-acrylates such as hexamethylene diacrylate and 2-ethylhexyl acrylate (15-30 wt%). LF-200 contains mixtures of mono-acrylates, predominantly isobornyl acrylate (50-60 wt-%), and acrylate oligomers in its formulation.

Colour analysis

The colour fastness of textile materials is one of the most important performance parameters necessary to achieve customer acceptability; however the minimum fastness grade requirement varies depending on the end use of the garments and individual customer needs. One of the main challenges with inkjet pigment printing is poor colour fastness. In addition, binding of pigments with fibrous substrates still remains a challenge because of the number of stringent, sometimes contradictory, requirements for viscosity, surface tension, particle size, size distribution and substrate wettability [21]. In general, the colour fastness to washing of UV-cured inkjet printed PLA fabrics was found to be better or similar to that of thermally cured inkjet printed PLA fabrics, Table 1. The wash fastness of

LH-100 inks was found to be acceptable with a rating of 3-4 for cyan, magenta and yellow inks, which is better than that achieved by the LF-140, LF-200 and thermal inks. As LH-100 inks contain acrylates of higher functionalities in their formulations than that of LF-140 and LF-200, it is therefore likely that they would produce higher density of shorter cross-links, resulting in overall better entrapment of the pigments [20]. Similarly higher dry rubbing fastness grade was achieved with LH-100 and LF-140 inks than that with LF-200 and thermal inks. The wet rubbing fastness rating found to be poor for all the Cyan and Magenta inks but slightly increased with yellow and black. The light fastness of all UV-cured inkjet printed PLA fabrics was observed to be excellent, grade 5 with no change of colour. As the inks are pigment based and pigments exhibit very good resistance to light in general, it was therefore expected that excellent light fastness would be achieved for all the colours of inks of different types [22]; however the thermal inks surprisingly provided poorer colour fastness to light.

The colour performance observed with the black and yellow colourants appeared to be different to that of the Cyan and Magenta inks which may be due to the nature of the black and yellow colorants which are based on carbon black and nickel compounds, respectively, whereas, cyan and magenta inks are based on phthalocyanine and quinacridone compounds, respectively, (as per the composition described in Mimaki's UV inks safety data sheets). In particular, the colour fastness to wash and dry rubbing was found to be marginally lower for the black inks, which might be attributed to the relatively larger particle size of black pigments hence provided less binding between colour and the fibres.

The colour strength (K/S) of cyan and magenta UV inks was clearly higher than that of the comparable thermal inks, and vice versa for the yellow inks, Fig. 2. The LH-100 inks imparted higher colour strength than the other ink types with the reason at present being uncertain. However,

Fig. 1 Chemical structures:
a hexamethylene diacrylate,
b pentaerythritol triacrylate, **c** 2-ethylhexyl acrylate and
d isobornyl acrylate

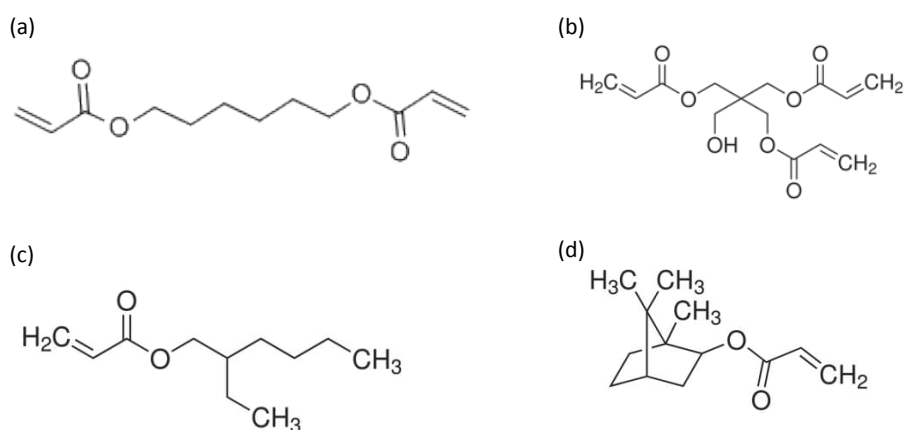
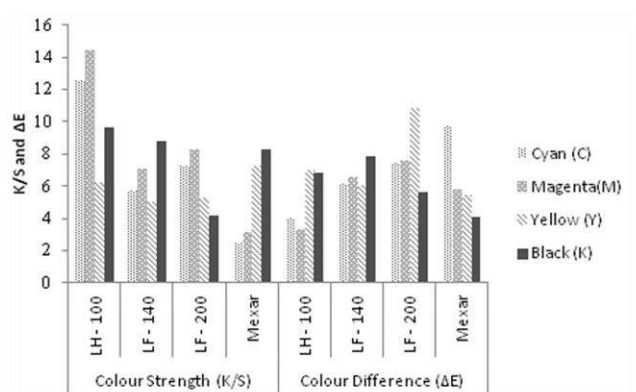


Table 1 Colour fastness properties of UV-cured and thermally-cured inkjet printed PLA fabrics

Inks			Wash Fastness	Dry Rubbing	Wet Rubbing	Light Fastness	
Cyan	UV	LH - 100	3	4	2-3	5	
		LF - 140	2-3	3-4	3	5	
		LF - 200	2	3	2-3	5	
Magenta	Thermal	Mexar	2	2-3	2-3	3-4	
		UV	LH - 100	3-4	4	2	5
			LF - 140	2-3	3-4	3	5
LF - 200	2-3		2-3	3	5		
Yellow	Thermal	Mexar	2-3	3-4	2-3	3-4	
		UV	LH - 100	3	4	3-4	5
			LF - 140	4	4	3-4	5
LF - 200	3		3-4	3	5		
Black	Thermal	Mexar	3-4	3	3	5	
		UV	LH - 100	2	3	3	5
			LF - 140	2	3	3-4	5
LF - 200	2-3		3-4	3-4	5		
	Thermal	Mexar	3	3-4	3	4	

**Fig. 2** Colour strength (K/S) of UV-cured and thermally-cured inkjet printed PLA fabrics and colour difference (ΔE) after washing

the colour strength for all inks reduced significantly after a single washing cycle, demonstrating the low wash stability of the prints. Although the colour difference between unwashed and washed printed samples was found to be high, the LH-100 inks provided lowest ΔE values compared with the other inks, which again is probably due to the higher cross-link densities produced by LH-100 inks with their higher level of acrylate functionalities.

Thermal properties

The DSC technique provides information regarding thermal properties including glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (ΔH_f). The results for untreated and printed PLA samples of cyan colours are summarised in Table 2. The T_g and peak T_m of untreated PLA fabrics were found to be about 61.4 °C and

164.4 °C, respectively. The UV-curable inkjet printed samples did not exhibit any significant difference in T_g and T_m ; however, the heat of fusion and degree of crystallinity of UV-cured printed samples decreased slightly, whereas a significant increase was observed for thermally cured printed samples. This increase in the degree of crystallinity of thermally-cured printed samples is likely a result of thermal nucleation where some chains or their segments become increasingly parallel as a result of heating.

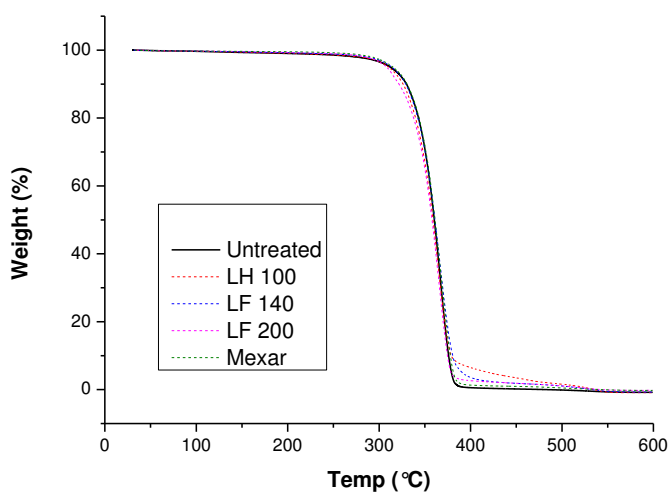
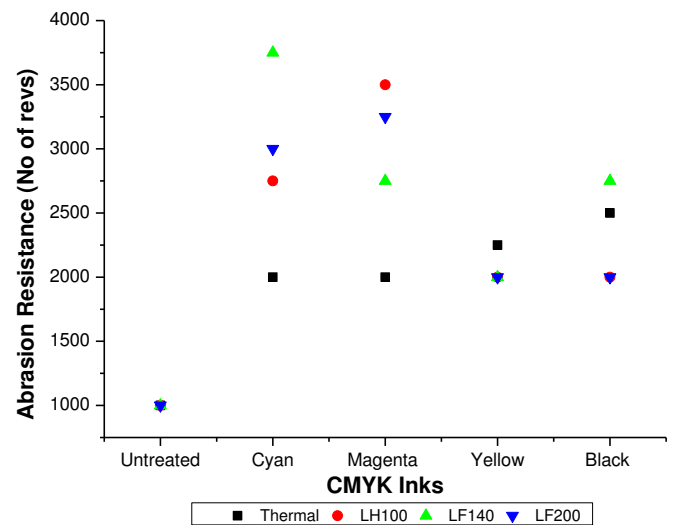
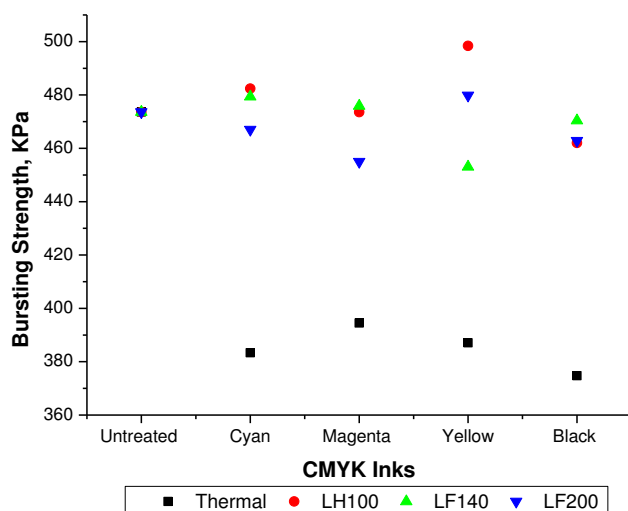
Figure 3 illustrates thermogravimetric analyses of untreated and printed PLA fabrics, where no significant difference in thermal characteristics of untreated and treated sample was observed. The TGA thermogram of PLA samples, both treated and printed, can be divided into three stages. The first stage (30-130°C) involves desorption of moisture in the fibres. The second transition (130-390°C) is mainly due to the random main-chain scissions to generate linear and cyclic oligomers and unzipping depolymerisation reactions because of thermal degradation [23]. In this stage only relatively slow degradation of PLA fabrics occurs up to about 260°C with more rapid degradation observed above that temperature. In the third stage (390-600°C), some non-PLA-based materials remains with an almost linear relationship between wt% loss and temperature observed up to 600°C.

Bursting strength

The bursting strength of PLA fabrics, Fig. 4, reduced significantly after thermal-curing of Mexar inks at 150 °C for 5 min. This was probably due to thermal degradation of PLA and the likely increase of brittleness of the three dimensionally linked fabric/binder structure at higher curing

Table 2 Thermal properties of untreated and printed PLA of cyan colour

Colour	Ink type	Glass transition temperature, T_g (°C)	Peak melting temperature T_m (°C)	Heat of fusion ΔH_f (J/g)	Degree of crystallinity X_c
Cyan	Untreated	61.4	164.4	41.6	44.4
	LH 100	61.4	161.5	37.3	39.9
	LF 140	61.7	165.8	36.2	38.6
	LF 200	60.6	164.4	38.1	40.7
	Mexar	59.7	159.9	51.2	54.6

**Fig. 3** Thermogravimetric curves of untreated and printed PLA fabrics with cyan colours**Fig. 5** Abrasion resistance of untreated and printed PLA fabrics**Fig. 4** Bursting strength of untreated and printed PLA fabrics

temperature. Our previous study on screen pigment printed PLA fabrics also suggested a reduction in bursting strength of printed fabrics with the increase of curing temperature

[10]. In addition, Yang and Sun [24] suggested that the strength of PLA reduced significantly with heat treatments higher than 130°C. In contrast, no significant effect on bursting strength of UV-cured inkjet printed PLA fabrics was observed, presumably due to the ambient temperature curing conditions of the printed fabrics.

Abrasion resistance

The abrasion resistance properties of untreated and printed PLA fabric are illustrated in Figure 5. The poor abrasion resistance performance of untreated PLA fabrics improved significantly upon curing of both thermal and UV curable inks subsequently after inkjet printing. The abrasion resistance of Cyan and Magenta prints of UV curable inks was found to be higher than other types. The observed increase in abrasion resistance after printing could be attributed to the surface print films having better abrasion resistance than the underlying PLA filaments [22, 25].

KES-F analysis of PLA fabrics

The Kawabata Evaluation System indicated that the extensibility (EMT%) of PLA, Fig. 6, reduced significantly after printing with both thermal and UV-curable inks. The effect was more significant for thermal inks presumably because of the higher fixation temperature and possibly the greater rigidity of the thermally-cured polymer binder films, whereas the reduction in extensibility was relatively lower for UV inkjet printed fabrics. It is proposed that thermal curing provided a higher degree of cross-linking and rigid inter-fibre bonding which restricted the extensibility of the printed fabrics. Moreover, the cross-linking of the acrylates deposited through printing upon exposure to UV light reduced the extensibility of the fabrics, and the coating of hard LH-100 inks on the surface of PLA fabrics imparted restricted fibre flexibility [20]; thus imparting less extensibility than the other types of inks.

In contrast, the bending rigidity (B) and shear rigidity (G) of thermal inks, illustrated in Fig. 7 and 8, increased significantly with the application of printing inks and their subsequent fixation by thermal curing. In order to determine the effect of higher temperature curing on the rigidity of the fabrics, unprinted PLA fabric was cured at 150°C for 5 min and KES-F analysis was carried out. The shear rigidity of the unprinted thermally-cured PLA fabric was found to be 5.17 g/cm.deg, which is almost similar to that of inkjet printed thermally-cured PLA fabrics. However, the bending rigidity of the unprinted thermally-cured PLA fabrics was not obtained as it was not possible to bend the thermally-cured rigid fabrics. This result can be attributed mainly to increased inter-fibre and inter-yarn bonding forces, which were limited by the presence of the surface

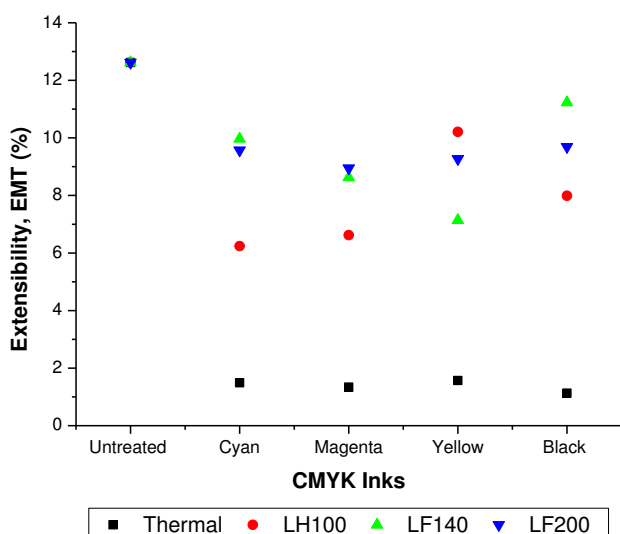


Fig. 6 Extensibility, EMT %, of untreated and printed PLA fabrics

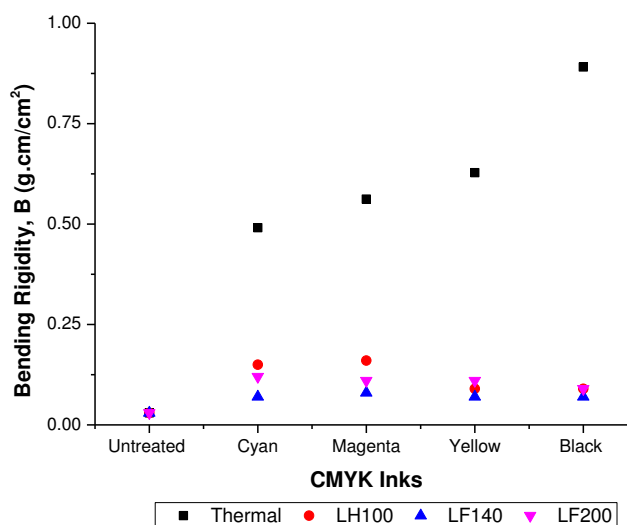


Fig. 7 Bending rigidity, B, of untreated and printed PLA fabric

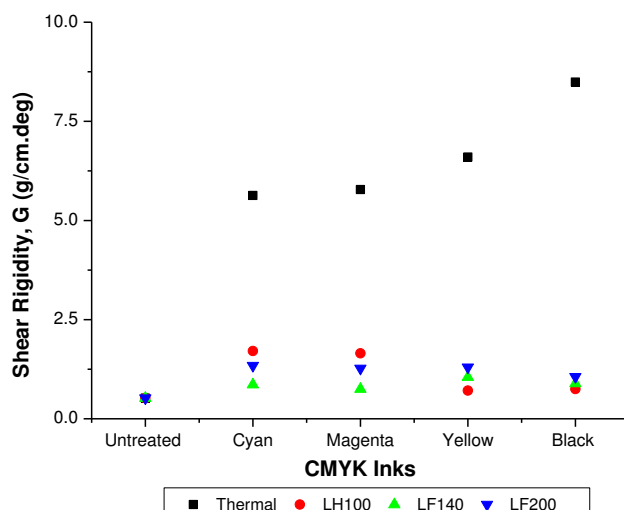


Fig. 8 Shear rigidity, G, of untreated and printed PLA fabrics

thermal inks on the fabrics at higher temperature; thus, higher rigidity was observed. The B and G for UV-cured inkjet printed fabrics also increased, however the effect was much lower than that observed with thermal inks. The overall effect of UV-curing on the increased shear rigidity and bending rigidity of the LF-140 inks printed PLA fabrics was lower than that of the other types of printing inks (Fig. 9).

Surface topography

SEM micrographs of unprinted and printed PLA fabrics, Figs 10, 11, 12, 13 and 14, indicate the presence of ink droplets on the fibre surfaces of both UV-cured and thermally-cured inkjet printed PLA fabrics. Inter-fibre bonding

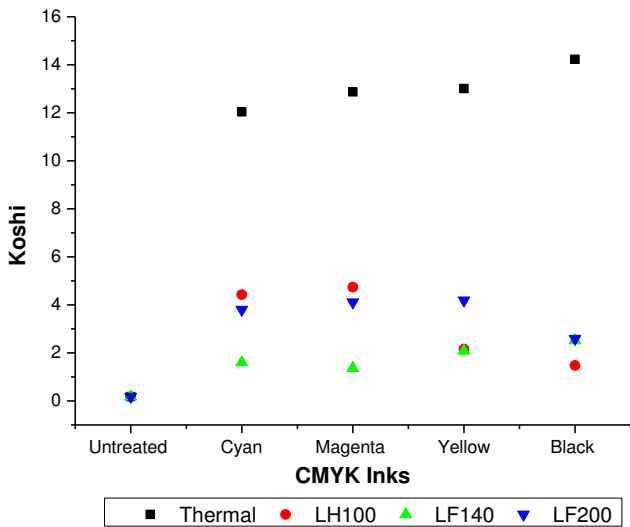


Fig. 9 Primary hand value, Koshi, of untreated and printed PLA fabrics

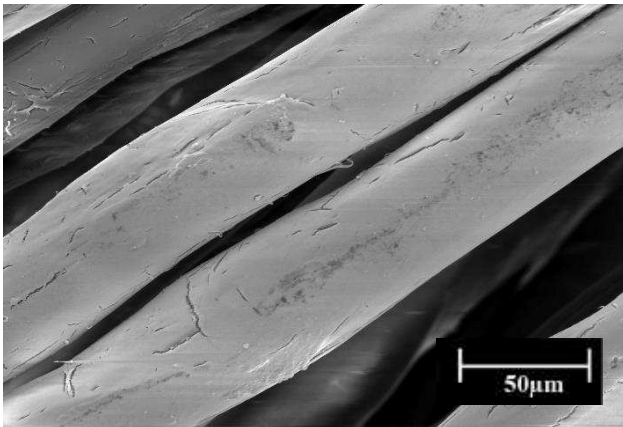


Fig. 10 SEM micrograph of control PLA fabric. Magnification $\times 2000$

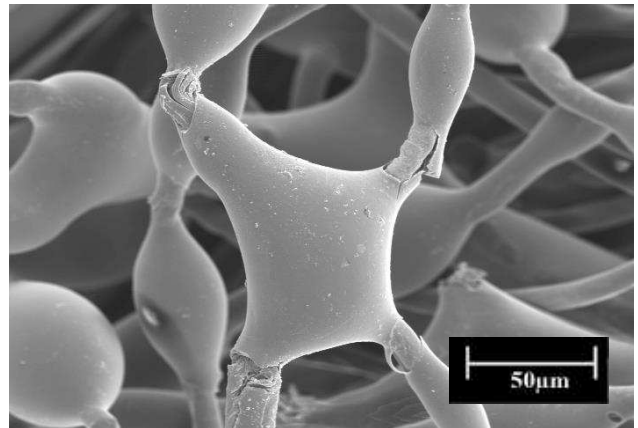


Fig. 12 SEM micrograph of after washed UV-cured inkjet printed PLA fabric. Magnification $\times 500$

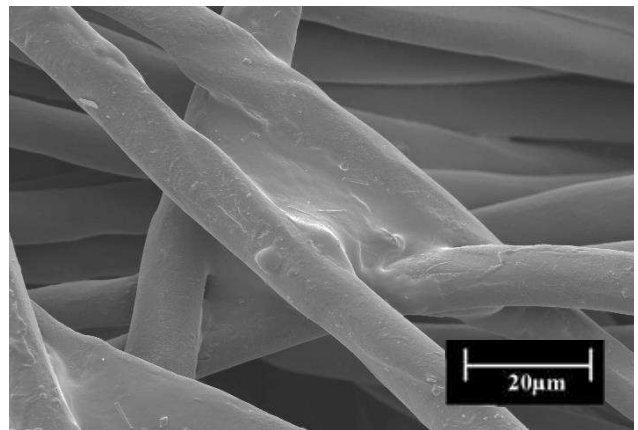


Fig. 13 SEM micrograph of thermally-cured inkjet printed PLA fabric. Magnification $\times 1000$

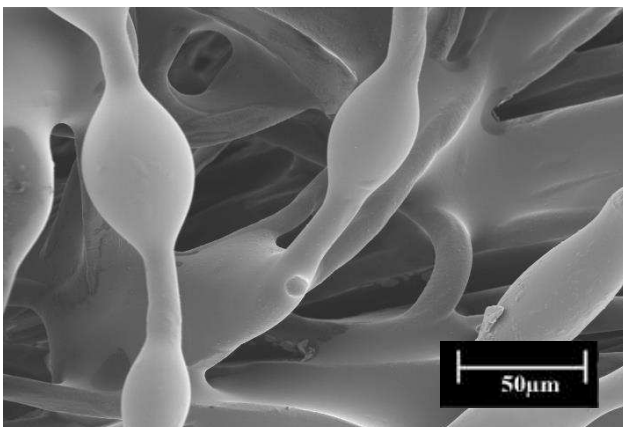


Fig. 11 SEM micrograph of UV-cured inkjet printed PLA fabric. Magnification $\times 500$

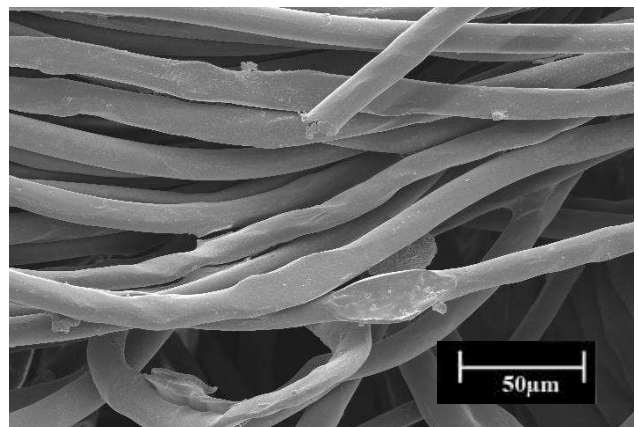


Fig. 14 SEM micrograph after washed UV inkjet printed PLA fabric. Magnification $\times 500$

achieved through photo-polymerisation of UV inks and thermal-crosslinking of Mexar inks was also observed and explains the observed increased in fabric rigidity. After a 5A washing of printed fabrics, the inter-fibre bonding was still observed but some surface film damage was detected, Figs. 12 and 14.

Conclusions

In this paper we have proposed a novel approach to print heat-sensitive biodegradable PLA fabrics using UV-curable inkjet inks to overcome the potential degradation at relatively higher curing temperature and longer processing time associated with thermal curing of pigment printing, most commonly used printing techniques for textiles. It was proposed that ambient temperature UV curing would cross-link pigment inks on the PLA fibre without any degradation of the thermal, mechanical and physical properties of the fabrics.

It was demonstrated that the UV-curable inks with higher acrylate functionalities in their formulation provided better overall colour fastness properties, higher colour strength and comparable colour difference to thermally cured system before and after washing. In addition the bursting strength of thermally-cured printed fabrics decreased significantly, whereas no significant effect was observed with UV inks. KES-F handle measurements indicated a decrease in flexibility provided by thermally cured prints presumably because of the reduction of extensibility after printing. Furthermore, bending rigidity, shear rigidity and stiffness of the printed fabrics increased after printing with thermal inks; however the effect of UV curable inks on the handle of printed fabrics was less significant than that of the thermally-cured prints.

TGA results indicated the thermal decomposition of untreated and printed PLA commenced at about 260 °C, with rapid decomposition occurring at 390 °C. Although there was no significant effect of UV curing on the thermal properties of the printed samples observed, the crystallinity of thermally-cured sample increased which might be attributed to thermal nucleation in the curing stage.

Following these initial encouraging results we believe UV-curable inkjet printing of PLA fabrics could be a possible solution to overcome the processing limitation of heat-sensitive PLA fibres. In addition, the proposed novel printing method would be an important step towards manufacturing commercial PLA textiles on large scale to meet growing demand of green materials and reduce environmental concerns with fossil fuel consumption and carbon emissions.

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