

# STUDY OF THE STRUCTURE MODIFICATION DURING THE DYEING PROCESS OF *INGEO*<sup>TM</sup> FIBERS OF POLY(LACTIC ACID)

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Ten years ago when they were first introduced into the market, PLA fibers had great potential as they are in nature hydrophobic, similarly to PET as well as they are classified as biodegradable fibers. Some current challenges and limitations associated with PLA fibers have constrained their popularity. The PET fibers are commonly blended with cotton. The preparation of the fabric is carried out in an alkaline medium, and the degradation of the PLA is important. That means that PLA cannot substitute the PET in cotton PET mixture. In this study with pure PLA fabrics, the dyeing behavior of these fibers and the modification of structure during dyeing were investigated. The differential scanning calorimetric data shows an increase in the crystallinity of PLA fibers during dyeing but this increase is due to the hydrolysis of the amorphous fraction which explains the low saturation rate of fabrics, compared to the saturation rate of PET fibers. Furthermore, the wash fastness is poor, when the temperature exceeds 60°C, and that may be attributed to the polymer hydrolysis during the dyeing process or during the washing process which results a change in the pH of the dyeing bath and in some cases the stability of the dye dispersion.

## 1. Introduction

The petroleum-derived textile fibers will be affected by the crisis of oil depletion estimated between 2010 and 2050[1]. These fibers count 53.52% of all world textile fiber market in 2005[2]. On the other hand, the pollution results from many million tons of packages incinerated every year increase the earth temperature by realizing greenhouse gases. These synthetic polymers are non-degradable and non-renewable, and with oil depletion considerations, the raw materials of fiber will be changed. Consequently, many researches have been made to find another source of the synthetic fibers that reduces the environment impact. A possible solution is the biodegradable polymers such as Poly(lactic acid) (PLA). These biodegradable plastics have found their applications especially in the biomedical applications, packaging materials, and textile fibers. Sorona® from DuPont, polyhydroxyalkanoates (PHAs), and *Ingeo*<sup>TM</sup> from NatureWorks LLC are examples of the biodegradable polymers which may be successfully commercialized. *Ingeo*<sup>TM</sup> are poly(lactic acid) fibers, and they are the first biodegradable polymer made from 100% annually renewable natural resources, such as corn.

PLA are wonderful fibers. They have the performance of both natural and synthetic materials. Their properties like low flammability, excellent UV stability, high resilience, excellent wicking, and moisture management are remarkable.

But they did not become common fibers. Its magnificent biodegradable property that gives PLA fibers their importance seems to be their weak point.

The PET fibers are commonly blended with cotton. The preparation of the fabric is carried out in an alkaline medium, and the degradation of the PLA is important. That means that PLA cannot substitute the PET in cotton/PET mixture. In this study, with a pure PLA fibers, the correlation between dyeing behavior and structural modifications of these fibers was investigated.

## 2. Experimental

This paper aims to elucidate some phenomenon associated with PLA dyeing process such as structural modification. Before dyeing, all samples were pretreated in warm water for 20 min at 60 °C with a 10:1 liquor ratio at pH 5. A 1[g/L] non-ionic surfactant was used as a dispersing agent. After this treatment, the samples were rinsed with cold water and dried at room temperature.

### 2.1. Materials

#### 2.1.1. PLA samples:

A circular single jersey knit fabric with a weight of 0.13 kg/m<sup>2</sup> was provided by NatureWorks LLC. PLA fabric was knit with a staple yarn of 20 tex.

#### 2.1.2. Dyestuff:

The total comprehension of the mechanism of dye up-take on PLA fibers is still incomplete. Dyeing theory research has consumed substantial resources invested by dye makers and academic institutions, but many of these studies have failed to yield useful data that could be applied directly in practical dyeing systems[3]. Karst et al. have investigated the disperse dyes behavior in studying the solubility parameters. They suggested that dyes should contain at least one phenyl, -NHR, -NR, -COR, -OR, or -COOR functional group for each -OH, -NO<sub>2</sub>, -CN, -NH, or halide group present in the molecule. The R groups should be -CH<sub>3</sub>, -(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub>, or phenyl. These dyes seemed to have a moderate to good exhaustion on PLA[4]. In another study, Karst & Yang have found that most anthraquinone dyes do not have solubility parameters close to that of PLA, except if they contain only the functional groups with an R group, which should be a large -(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> group[5]. Yiqi et al. have found that there was no obvious pattern as to which energy level or which structure class provided better dye exhaustion[6]. Dye class has no effect on the exhaustion of disperse dyes, and not related to energy level either [7].

In this study, four dyes, Samaron Red HBSL, Terasil Red 3BL, Samaron Pink FRL and Samaron Brilliant Yellow HRL, were used. These dyes have a

large alkyl chain which supposed to act an essential role in the dye uptake on the fabric. Characteristics of these dyes are summarized in Table I.

There is no explication of the differences between the high exhaustion rate on PET while it is bad on PLA. As there are some dyes with a high exhaustion rate and possess a long alkyl chain (C.I.Disperse Red 167, 98.4%[8]), there are some dyes without this chain having a good exhaustion rate on PLA (C.I.Disperse Yellow 42, 85.4%[9]).

### 3. Experimental

#### Dyeing procedures

Samples of 3.00 g were dyed with 2.00 % owf of a disperse dye and a liquor ratio of 20:1. Dyeing baths were pH adjusted at 5 by acetic acid. Two drops of Lyocol (non-ionic surfactant; Clariant) have been added. The dyeing was performed in the AHIBA NUANCE Top speed from Datacolor. Dyeing curve was started at 50°C. After heating up to dyeing temperature with ramping rate of 2°C.min<sup>-1</sup>, they held for 30 min supposed to be sufficient to reach the equilibrium[10, 11], then the bath was cooled to 50°C with cooling rate of 2°C.min<sup>-1</sup>. For more consistency, the experiments were reproduced 2 times. After dyeing, the samples were rinsed in warm water (50°C) then in cold water until no color bleeding was happened and finally allowed to dry at room temperature. The linearity of the calibration curves indicated adherence to Beer–Lambert’s law. The quantity of dyestuff fixed within the fibers was calculated from the absorbance measurements made with the spectrophotometer.

Table 1. Characterization of the four disperse dyes used in this study.

| Commercial Name              | Maker | C.I. Generic Name      | Structural Data | Constitution Number | Family        |
|------------------------------|-------|------------------------|-----------------|---------------------|---------------|
| Samaron Red HBSL             | CAS   | C.I.Disperse Red 167   |                 | 62175               | Azo           |
| Terasil Red 3BL              | CGY   | C.I. Disperse Red 82   |                 | 11140               | MonoAzo       |
| Samaron Pink FRL             | CAS   | C.I.Disperse Red 91    |                 | 60753               | Anthraquinone |
| Samaron Brilliant Yellow HRL | CAS   | C.I.Disperse Yellow 58 |                 | 56245               | Aminoketone   |

## Crystallinity of the fibres

Crystallinity measurements provide a good image for some structural changes inside the fibers, and how macromolecules arrangement has been developed during the heat treatment. The dye is only able to penetrate between macromolecules in the amorphous phase within the fibers. Any changes in this phase will have, in consequence, an influence on the fibers dyeing behavior. So, it is necessary to measure the crystallinity in order to compare the adsorption rates. Differential scanning calorimeter technique has been chosen to measure the crystallinity because this technique indicates the perfect and imperfect crystals. A Universal V3.4C Modulated Differential scanning calorimeter MDSC was used to determine the thermal transitions of the PLA samples. The DSC cell was calibrated with indium 99.999% pure. Sample size was about 2.7 mg. Heating rate of 5 °C/min was chosen. Atmosphere of nitrogen was used. All temperatures and enthalpies were determined thanks to program integrated with the DSC. The crystallinity was calculated as follows:

$$\% \text{ Crystallinity} = 100 \cdot (\Delta H / 93) \quad (1)$$

Where: 93 J/g is the heat of fusion of an infinitely large crystal[12], and  $\Delta H$  is the area of the melting peak calculated thank to program integrated with the DSC.

## 4. Results and Discussion

### 4.1. Dyeing rates:

The effect of Dyebath temperature on the exhaustion of the four dyes is outlined in the figure 1. No exhaustion was seen for all the tested dyes before 70 °C. Disperse Yellow 58 exhibited the optimum exhaustion at 100 °C with 14%, whereas the exhaustion of the others was increasing as temperature of the dyebath increase. As their exhaustion values at 110°C were 45%, 75% and 91% for Disperse Red 91, Red 82 and Red 167, respectively. Dyeing rate was seen to increase slightly after 70°C.

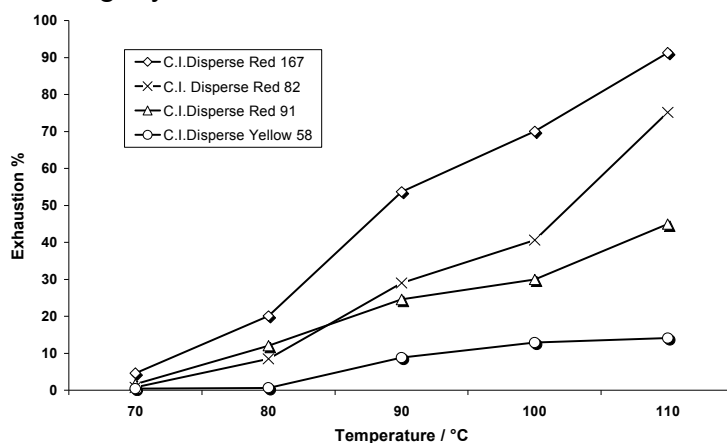


Figure 1. Dye exhaustion rate of Disperse Red 267, Yellow 58, Red 91 and Red 82 on PLA fabric, at 2% owf, and pH 5.

These changes in dyeing behavior have to be correlated with the PLA fiber structure and its relation with the dye structure. The first observation was a dramatic decrease in the dyebath pH after dyeing as the dyebath temperature increases figure 2. Previous study has found that the pH of the dyebath decreased with increasing dyeing time [13].

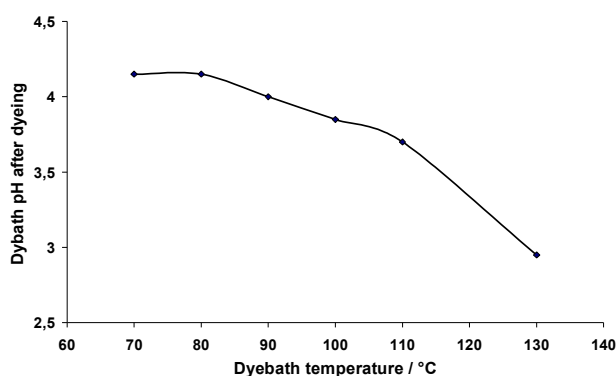


Figure 2. Relationship between dyebath pH and dyebath temperature.

To investigate this decrease during the dyeing process, three samples  $S_1$ ,  $S_2$  and  $S_3$  were annealed at 110°C for 30 min in a bath at pH 4.5. The different treatments are summarized in Table 2.

Table 2. bath pH of different samples of PLA at 110°C for 30 min.

|       | Treatment   | pH before | pH after |
|-------|---|-----------|----------|
| $S_1$ | as-received sample  | 4.5       | 3        |
| $S_2$ | mild scouring at 60°C for 20 min with 1 g/l non-ionic wetting agent                           |           | 3.3      |
| $S_3$ | scouring at 60°C for 20°C with 1g/l $\text{Na}_2\text{CO}_3$ and 1g/l non-ionic wetting agent |           | 3.4      |

It was noticed that the dyebath pH for  $S_1$  became more acidic than the others. This may be because  $S_2$  and  $S_3$  was suffered different degree of hydrolysis during the previous scouring. This pH drop is not attributed to traces of chemicals which remained from the latest process. This decrease suggests depolymerisation by hydrolysis of the PLA fiber. The generated oligomers and lactic acid help in enhancing the acidity in the simulated dyebath [13].

The pH change has many effects on the dyeing behavior of PLA. Shah and Yang have found that the shade depth increased as dyebath pH increased from pH 5 to pH 8 [8, 14]. This high dye uptake was explained by the alkaline hydrolysis of PLA polymers leading to an increase in the accessible area in the

fiber. Moreover, many disperse dyes are unusable or unstable in extremely acidic or basic dyebaths, therefore a pH in the range of 5-6 is generally used [15]. In all way, dyebath pH has to be controlled for consistent result. Many papers have confirmed that PLA exhibit different increases in crystallinity after dyeing or annealing. Lowe and Negulescu have reported that crystallinity of low crystalline PLA was doubled after annealing at 100°C from an initial 20.6% to 44% while the crystallinity of high crystalline PLA annealed in water at 70°C was increased to 57.3% from an initial crystallinity of 49.9% [12]. Actually, this increase in apparent crystallinity may be to the detriment of the amorphous phase of PLA fibers, and this explains that PLA becomes brittle after dyeing[9]. This increase in crystallinity suggests a decrease in dye uptake of PLA due to the decrease in amorphous phases in PLA fibers where the dye molecules have to penetrate. For this reason, a DSC analysis was performed for samples treated in a simulated dyebath without dyes with the same parameters of the first experiment.

#### **4.2. Crystallinity Changes:**

The thermograms obtained on the DSC are shown in the Figures 3 and 4. The double melting behavior is seen in all cases except in the second scan of as-received PLA sample, and PLA sample treated at 130°C. The double melting phenomenon in synthetic polymer fibers is quite common due to processing conditions, and it is well documented and widely studied in the literature[16-23]. Common mechanisms that have been proposed include:

1. Melt-recrystallization model that has been proposed by Yasuniwa *et al.*[17]. According to this model, the low-temperature and high-temperature peaks were attributed to the melting of some amount of the original crystals and the melting crystals formed through a melt-recrystallization process during the heating scan, respectively. The exothermic peak between the double-melting peaks is attributed to the recrystallization [16, 17].
2. The presence of more than one crystallographic form (chain folded versus extended chain crystals) [16, 19], or (heat treatment (heat setting) causes a different additional crystalline form) [22].
3. Changes in morphology, such as lamellar thickening and crystal perfecting. The lower-temperature peak is due to the melting of less thick crystals than crystals corresponding to the high temperature[21].
4. Entropy restriction in the structural units as the temperature nears the melting point leads to a super-heating effect on some of the crystallites, which is the reason for the higher temperature melting endotherm[16].

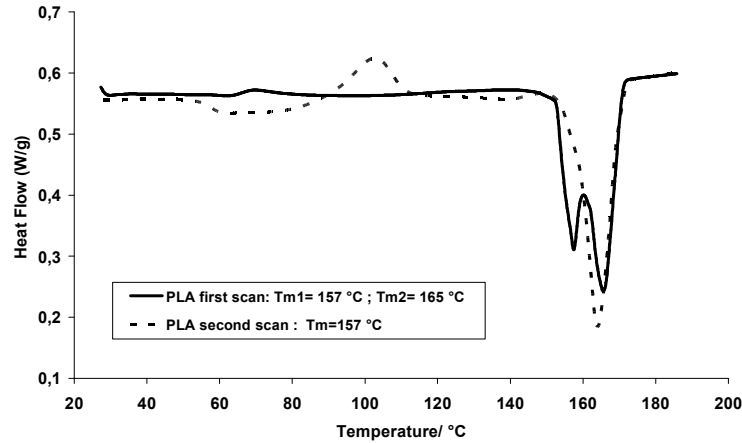


Figure 3. DSC analysis curve of as-received PLA fibers for first and second scan.

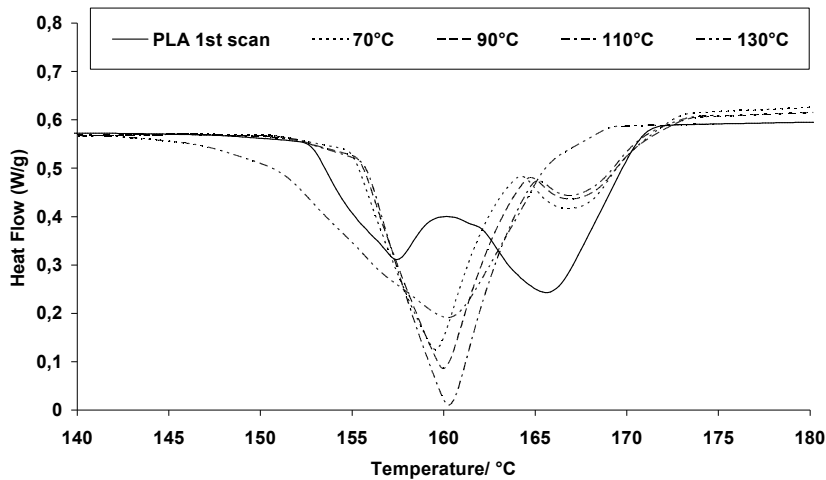


Figure 4. Double melting behavior for different samples treated at different temperatures.

The highest peak is due to the perfection of crystals during heating scan. The ratio between the peak area of low temperature peak and of high temperature increases with increasing treatment temperature from 70 °C up to 130 °C. This means that the percentage of imperfect crystals increases with increasing the dyeing temperature and the amorphous phase will be more accessible by the dye molecules. Furthermore, during the treatment in hot water, the combination of heat treatment and hydrolysis leads to the formation of small imperfect crystallites.

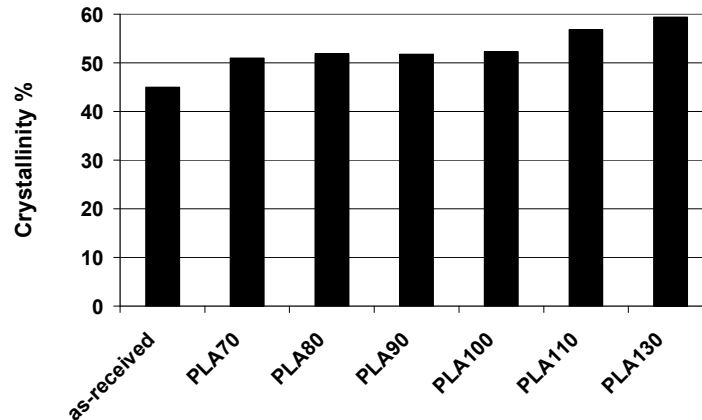


Figure 5. Crystallinity of PLA fibers for as-received sample and for the samples dyed at 70, 80, 90, 100, 110 and 130°C.

The crystallinity (including the whole crystalline fraction, perfect and imperfect) increased from 45% to 59% with increasing dyeing temperature in the simulated bath from 20°C to 130°C, figure 5. However, Kalb *et al.* suggested that PLLA crystallinity might not exceed 60%[24]. Therefore, PLA130 is assumed to have the maximum crystallinity. Since the dye is only fixed within the amorphous phase of the fiber, presumably PLA130 will show a minimum dye uptake. But, PLA130 has shown the maximum dye exhaustion. As the high temperature during the dyeing breaks up the molecular chains, the molecular arrangement into crystallites will be less probable, and this will provide more dye accessible area within the fibers. Furthermore, the high temperature increases the disperse dye solubility and the small dye particles can enter easily between the small crystallites. Actually, the amorphous domains are easily attacked by water molecules and degrade first accordingly. Initial mass loss occurred in the amorphous domains and causes an apparent crystallinity increase. As the polymer degrades further, the crystalline domains also degrade, which leads to drastic decrease in melting point and mechanical properties, and finally leads to the disintegration of the entire material [25]. So, the unique peak of the PLA130 presents 100% of this imperfect crystalline form or small crystallites which is produced during the simulated dyeing process.

## 5. Conclusions

PLA are promising fibers. They can reduce the releasing of greenhouse gases. Their magnificent biodegradable property that gives PLA fibers their importance seems to be their weak point. PLA are very water sensitive, and it is starting to hydrolysis is the dyebath directly after reaching its glass transition



temperature. Crystallinity increase during the dyeing was observed in the differential scanning calorimeter, whereas dyebath pH dramatically decreases with increasing dyebath temperature. This crystallinity increasing suggests a decrease in dye uptake of PLA due to the decrease in amorphous phase in PLA fibers where the dye molecules have to penetrate. The high temperature during the dyeing breaks up the molecular chains, consequently the molecular arrangement into crystallites will be less probable, and this will provide more dye accessible area within the fibers.

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