

## Enhanced Performance of Polylactide Film via Simultaneous Biaxial Stretching and Silane Coupling Agent as a Thermal Shrinkable Film

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### Abstract

Biaxial stretching technique has been known to improve the toughness of polylactide (PLA) film. Furthermore, blending with an additive is another way to control the mechanical properties of the product. The integrated effect of simultaneous biaxial stretching and blending with silane coupling agent on the properties of PLA film is examined in this study. The PLA pellets are melt compounded with various amounts of 3-aminopropyltriethoxy silane (APS). Then, the films are prepared by cast film extrusion and simultaneous biaxial stretching process with a stretching speed of  $75 \text{ mm s}^{-1}$ . The relationships among the crystallinity, tensile properties, and thermal shrinkage of the prepared films are investigated. The crystallinity of PLA is significantly induced in the film by the stretching technique. An increase in the additive content also facilitates the polymeric crystallinity. The elongation at the break of the biaxially stretched film increases with the additive content, which corresponds with the PLA crystallinity. Compared to the pristine PLA film, the addition of 1% APS improves tensile strength in a transverse direction of the film about 10 times. The thermal shrinkage of the obtained films was evaluated to assess their applications as heat-shrinkable films. The prepared films show a thermal shrinkage of 45%, which are comparable to that of a commercial shrink film.

**Keywords:** Polylactide, Shrinkable film, Biaxial stretching, Silane coupling agent

### 1 Introduction

Plastic films have been utilized in various applications, especially packaging [1]. For product cover or protection, thermal shrinkable films or shrink films, which are shrunk and deformed to wrap into a product shape under heating conditions are utilized mostly for single-use applications, for example, labels, food wraps, and cap seals. Such films are made from polyethylene (PE), polypropylene (PP), and poly(vinyl chloride) (PVC), which are petroleum-based plastics,

hence, they cause environmental issues after disposal. Bioplastics have been investigated as substitutes for commercial plastic products that are currently in use.

Poly lactide, which is abbreviated as PLA, is a biodegradable polymer that has been developed for many plastic products as a potential substitute for petroleum-based/commercial plastics [2]. However, the main disadvantages of PLA are its brittleness and low crystallization rate. To overcome its limitations, several methods, such as copolymerization, blending with soft materials, and controlled processing

techniques, have been reported [3]–[5]. Strain-induced crystallization has been observed for PLA [6], [7]. In this way, stretching is another factor to enhance the mechanical properties of the PLA.

Biaxial stretching is a processing technique that has been applied to films to increase film toughness. Many commercial products have been used worldwide in the plastic film industry due to their strength and toughness, such as biaxially oriented polypropylene (BOPP) and biaxially oriented poly(ethylene terephthalate) (BOPET). The obtained films are mostly utilized as flexible packaging, barrier films, and shrink films. The biaxial stretching technique is also applied to PLA, which is a brittle material [8].

Processing factors, such as the stretching temperature, heating time, stretching rate, and draw ratio apparently affect the mechanical properties of PLA films [9]. Jariyasakoolroj *et al.* reported that simultaneous biaxial stretching at 90 °C and high speed (75 mm s<sup>-1</sup>) to 5 times the original length in both a machine direction (MD) and a transverse direction (TD) significantly increased the toughness of the PLA film (75%), which was due to the isotropic distribution of small crystalline lamellae in the machine and transverse directions [10]. Chemical modification of PLA to obtain high-toughness PLA has been proposed. PLA was chemically modified by using polyglycidyl ether and pyromellitic anhydride to obtain long-chain-branched PLA [11]. Biaxial stretching of the long-chain-branched PLA film was possible up to a draw ratio of 6 × 6. The tensile strength and elongation at the break of this film reached 208 MPa and 85%, respectively [12]. However, this preparation was complicated and many steps were required. Biaxial stretching technique has been integrated with additive blending to control the microstructure of the polymer, which influences many properties of the films.

A silane coupling agent is one of the promising additives. It has various functions in many types of materials, for example, an adhesion binder, a compatibilizer, or a crosslinking agent. Since this coupling agent, after hydrolysis, reacts chemically with other substances, condensation, grafting and crosslinking will feasibly occur [13], [14]. As an example, a silane coupling agent that contained a vinyl group was grafted onto PLA by using dicumyl peroxide as an initiator. The thermal stability, tensile strength, and hydrolysis resistance of the PLA film were enhanced,

but the elongation at break was decreased due to silane crosslinking in the PLA film [15]. Another example is the synergistic effect of stereocomplex PLA and an alkoxy silane that contains isocyanate end group, which results in a PLA-grafted silane hybrid gel. The tensile strength and modulus were preserved, whereas the elongation at the break of the film was increased dramatically from 16% to 120% with a small addition (2.5%) [16]. Aminopropyltriethoxysilane (APS), which is a type of silane coupling agent that contains an amino group at the end chain, is applied mostly in biocomposite materials since the hydrogen bond interaction between amino groups or hydroxyl groups of APS and carboxylic or hydroxyl groups of a polymer can form and strengthen the product properties [17], [18]. For instance, a supertough PLA film with 130% elongation at break was prepared by the addition of 0.5% APS in dichloromethane [19].

Inspired by previous studies, to increase the toughness of PLA, various approaches have been developed, which include not only controlled processing techniques but also additive selection, such as a core-shell rubber [20], a modified thermoplastic starch [21], and an ethylene-vinyl acetate copolymer [22] with consideration of many factors. These also strongly influence the mechanical properties of the film product. In this work, the silane coupling agent with amino functional group was selected, which might alter the film toughness via a partial network structure from self-condensation, chemical reaction, and intermolecular interaction [23].

This study focuses on the synergistic effect of simultaneous biaxial stretching and blending with APS on the properties of PLA film as a thermal shrinkable film. The thermal stabilities and mechanical properties of the prepared film were investigated via thermogravimetric analysis (TGA) and tensile testing, respectively. The change in PLA crystallinity, which might be related to other properties of the film was characterized via X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The relationships between the effect of the APS and the properties of the prepared film, such as the heat shrinkability, were identified.

## 2 Experimental

### 2.1 Materials

Poly lactide, PLA, (Ingeo™ 2003D) was purchased

from NatureWorks LLC. 3-Aminopropyltriethoxy silane (APS) was supplied by Alfa Aesar, Thermo Fisher Scientific.

## 2.2 Film preparation

After drying at 60 °C for overnight in a hot air oven, PLA pellets were mixed with various amounts of APS in a twin-screw extruder (L/D 25:1) (Thermo Electron Prism TSE 16 TC, UK) at 145–160 °C with a screw speed of 5 rpm. The sheet sample was prepared by using a chill-roll cast film extruder (Labtech LE25-30/C and LCR-300, Thailand). The silane concentrations added in PLA were 0.5, 1, and 5 percent by weight, called PLA\_APS0.5, PLA\_APS1, and PLA\_APS5, respectively. The cast sheet was simultaneously biaxially stretched in two perpendicular directions (the machine direction (MD) and the transverse direction (TD)) 5 times at a speed of 5, 35, and 75 mm s<sup>-1</sup> by using a biaxial stretching machine (Ryuu, Japan) at 100 °C. After the desired draw ratio was obtained, the sample was held while it was cooled to room temperature. The biaxially stretched PLA and PLA\_APS films were referred to BOPLA and BOPLA\_APS, respectively.

## 2.3 Characterization

### 2.3.1 Thermal properties

The thermal stability of the prepared sample was determined via thermogravimetric analysis (TGA) (Mettler Toledo TGA/DSC1, Switzerland). The sample was heated from 40 to 700 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

The glass transition temperature ( $T_g$ ), cold crystallization temperature ( $T_{cc}$ ), and melting temperature ( $T_m$ ) were determined by a differential scanning calorimeter (DSC) (TA Instruments DSC Q2000, USA). The sample was heated from 20 to 200 °C, cooled to 0 °C, and reheated to 200 °C at a rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

### 2.3.2 Crystallinity

The degree of crystallinity ( $\chi_c$ ) was calculated from the DSC data by the following Equation (1):

$$\chi_c (\%) = (\Delta H_m - \Delta H_{cc}) / (f \times \Delta H_0) \times 100 \quad (1)$$

where  $\Delta H_m$  is the melting enthalpy of the sample,  $\Delta H_{cc}$  is the cold crystallization enthalpy of the sample,  $f$  is the weight fraction of PLA, and  $\Delta H_0$  is the melting enthalpy of 100% crystalline PLA, which is 93.1 J g<sup>-1</sup> [24].

The X-ray diffraction (XRD) pattern of the film was recorded by an X-ray diffractometer (Rigaku SmartLab, Japan) using Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) that was operated at 40 kV and 30 mA. The prepared film was scanned in the  $2\theta$  range of 5–50° with a scan rate of 1° min<sup>-1</sup>.

### 2.3.3 Morphological study

Morphology of the biaxially stretched films was observed by a scanning electron microscope (FEI Quanta 450 SEM, USA). The film samples were submerged in liquid nitrogen, then fractured and coated with gold before SEM analysis. The cross-sectional area of the samples was scanned with magnification of 1,000 and 5,000 at 10 kV.

### 2.3.4 Mechanical testing

The tensile strength, Young's modulus, and elongation at break of the stretched film were determined by using a universal testing machine in a tensile mode (Instron 55R1123, USA) according to ASTM D882-12. The film had been stretched in both the MD and the TD. Each sample was measured in quintuplicate.

### 2.3.5 Thermal shrinkage testing

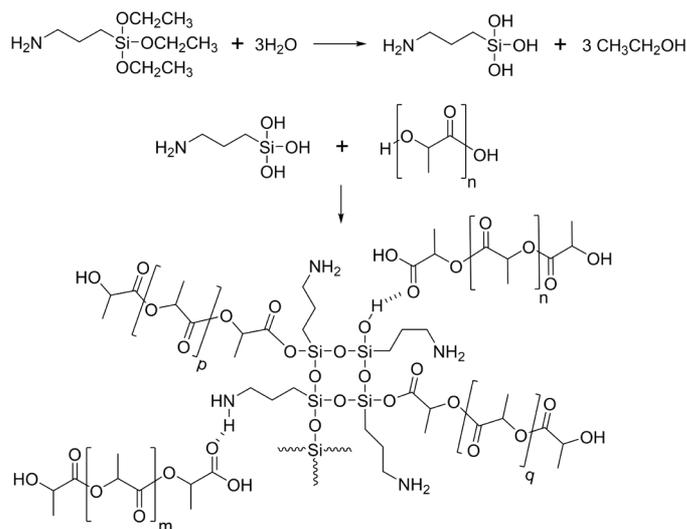
The film shrinkage was evaluated in an oil bath at 100 °C. The film size after soaking in the oil bath ( $L$ ) at 100 °C was measured and compared with the initial size ( $L_0$ ). The average values were calculated from triplicate sample measurements [Equation (2)].

$$\% \text{ shrinkage} = (L_0 - L) / L_0 \times 100 \quad (2)$$

## 3 Results and Discussion

### 3.1 Presence of silane coupling agent in the sheet

In order to prove the existence of silane coupling agent in the PLA sheets, the trace of Si was determined by TGA in a nitrogen atmosphere. According to Table 1,



**Figure 1:** Proposed feasible reaction of APS and PLA.

the onset degradation temperature ( $T_{d,onset}$ ) of the PLA sheet is 336 °C. Blending APS 1% with PLA (PLA\_APS1) hardly affected  $T_{d,onset}$  but mixing APS 5% into PLA (PLA\_APS5) reduced  $T_{d,onset}$  by approximately 5 °C. This might be due to the short chains generated by hydrolytic degradation during processing [25].

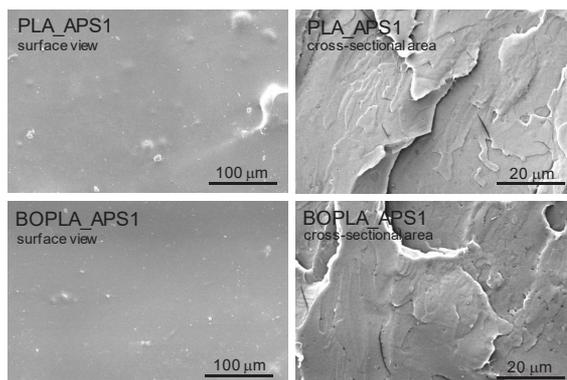
After heating to 600 °C, the PLA sheet showed a one-step degradation and only 4.1% remained, whereas, in the PLA\_APS1 and PLA\_APS5 sheets, 6.9% and 13.0%, respectively, remained. This might relate to the carbon and silicon contents left. Comparing the remaining content of the PLA\_APS with that of the PLA sheet, the amount of residue obtained exceeded the added APS content. This implied partial crosslinking of APS in the PLA sheet (Figure 1) and clearly supports the presence of APS in the PLA sheets.

**Table 1:** Onset degradation temperatures and residues at 600 °C of PLA and PLA\_APS sheets

Sample	$T_{d,onset}$ (°C)	Residue at 600 °C (%)
PLA	336	4.1
PLA_APS1	336	6.9
PLA_APS5	331	13.0

### 3.2 Microstructure of the biaxially stretched film

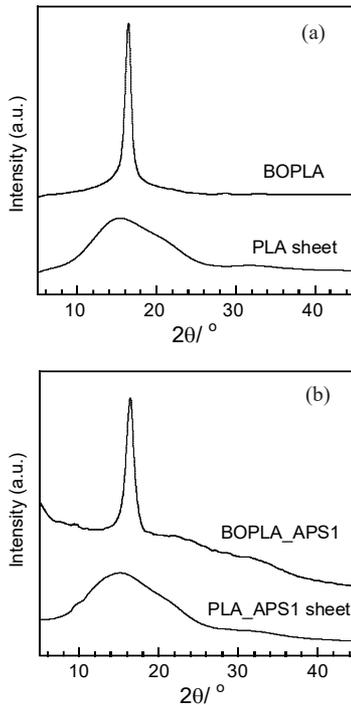
Morphology of the PLA blended with APS was observed by SEM. Figure 2 compares the surface and the cross-sectional area of the PLA\_APS sheets and the



**Figure 2:** Surface and cross-sectional morphology of the PLA\_APS1 sheets and the biaxially stretched films.

BOPLA\_APS films. Both the sheets and the biaxially stretched films gave smooth surfaces with some small defects in micron scale. For the cross-sectional images, the cracks with some nanoscale pits dispersed throughout the area were observed. This might relate to a good distribution of APS in the PLA matrix.

To study the microstructural change after biaxial stretching in detail, X-ray diffraction measurements were conducted. XRD patterns of the PLA sheets (before stretching) and the biaxially stretched films that were obtained at a stretching speed of 75 mm s<sup>-1</sup> are compared in Figure 3. The PLA sheet showed a broad peak; hence, an amorphous part was a major component. In contrast, the BOPLA film showed a



**Figure 3:** XRD patterns of (a) PLA and (b) PLA blended with APS 1% in the forms of sheets and biaxially stretched films taken at stretching speed of 75 mm s<sup>-1</sup>.

sharp peak at 2θ~16.5°, which corresponded to a highly crystalline α-form [26]–[28]. This supported the effect of simultaneous biaxial stretching, as already reported elsewhere [29]. A similar trend was observed for the PLA\_APS film. A sharp peak at 2θ~16.5°, which belonged to the (110/200) planes of the α-form of PLA, was observed for the biaxially stretched PLA\_APS film. This confirmed the increment of the crystalline part by the simultaneous biaxial stretching at the high stretching speed [10]. Also, the results were stable after the addition of APS.

The crystallinity degree of the bulk sample can be determined via DSC analysis. The PLA sheet exhibited three distinct peaks that corresponded to a glass transition at 62.5 °C, a cold crystallization peak at 125.3 °C, and melting peaks at 148.5 °C. The effect of biaxial stretching was observed in the first heating scan of the DSC thermograms. The biaxially stretched PLA film (BOPLA) showed only T<sub>g</sub> and T<sub>m</sub> (at 64.9 °C and 147.9 °C, respectively) without cold crystallization. A similar result was also found in uniaxially stretched

film [6]. This implied that the high crystallinity in the biaxially stretched films from the beginning so the PLA could not crystallize anymore during heating. After biaxial stretching, the degree of crystallinity (χ<sub>c</sub>) of the PLA was significantly increased from 1.9 to 32.0%, as presented in Table 2. In another word, a strain-induced crystallization of PLA occurred during biaxial orientation [10].

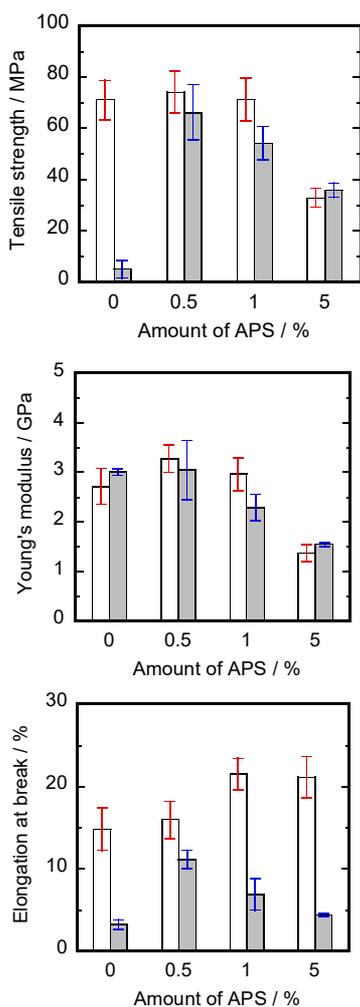
Regarding the addition of APS, the degree of crystallization of the obtained film (BOPLA\_APS) tended to increase with increasing APS content, as shown in both first heating and second heating data. Thus, APS may act as a nucleating agent. In order to indicate the actual effect of APS in the PLA films without thermal history, the results from the second heating were considered. Cold crystallization temperature (T<sub>cc</sub>) of the BOPLA film was 126.5 °C but T<sub>cc</sub> of the BOPLA\_APS films was reduced to 115.9–119.5 °C. These results showed that APS induced PLA crystallization and confirmed the nucleating function of APS in the PLA film, which was similar to an example case of titanium dioxide addition [30].

**Table 2:** Thermal properties of the biaxially stretched films

Sample	T <sub>g</sub> (°C)	T <sub>cc</sub> (°C)	T <sub>m</sub> (°C)	χ <sub>c</sub> (%)
<i>First heating</i>				
PLA sheet	62.5	125.3	148.5	1.9
BOPLA	64.9	-	147.9	32.0
BOPLA_APS0.5	66.5	-	148.2	31.5
BOPLA_APS1	63.3	-	148.7	34.6
BOPLA_APS5	64.0	-	148.1	40.2
<i>Second heating</i>				
BOPLA	55.8	126.5	149.1	1.2
BOPLA_APS0.5	56.7	115.9	146.9	4.2
BOPLA_APS1	56.6	119.1	147.4	4.6
BOPLA_APS5	57.1	119.5	147.2	5.0

### 3.3 Mechanical properties of the BOPLA\_APS film

As already reported, simultaneous biaxial stretching at high speed (more than 35 mm s<sup>-1</sup>) leads to high-strength and tough PLA [10], and blending APS into PLA might affect the mechanical properties. Figure 4 presents the tensile properties of the biaxially stretched PLA film with various contents of APS. The tensile strength in the MD and the TD of the BOPLA film were 71.0 ± 7.8 and 4.9 ± 3.5 MPa, respectively. After



**Figure 4:** Tensile properties in both MD (white) and TD (grey) of the biaxially stretched PLA films with different amounts of APS stretched at  $75 \text{ mm s}^{-1}$ .

blending with APS, the tensile strength of the obtained film in the TD was substantially improved, while that of the film in the MD was almost unchanged. Tensile strength in the TD of the BOPLA film was increased to  $66.0 \pm 10.7 \text{ MPa}$  for the addition of APS 0.5%. This increment clearly related to the effect of APS. Not only the silanol functional groups created siloxane linkage [13], but the primary amine groups possibly reacted with PLA via aminolysis [17] and hydrogen bond interaction [19], contributing to accumulate favorable interaction in the TD. However, the tensile strength in both the MD and the TD of the film decreased with a

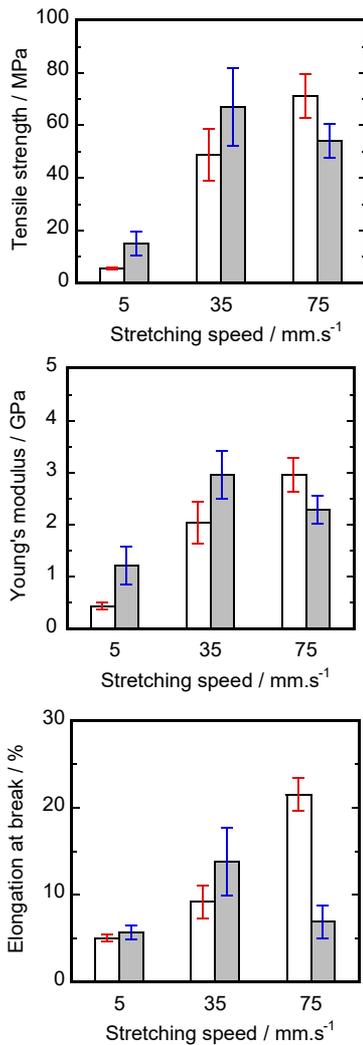
large amount of APS. This might be attributed to the effect of aminolysis, which leads to chain scission and degradation of PLA [19], [25]. Young's modulus, referring to the elasticity, of the BOPLA\_ APS film exhibited a similar tensile strength trend.

In the case of the toughness, the elongation at break in the MD and the TD of the BOPLA film were  $14.8 \pm 2.6$  and  $3.2 \pm 0.6\%$ , respectively. After APS loading, the elongation at the break of the obtained films in the TD was increased but decreased as a result of high APS. This was the similar trend to the tensile strength and Young's modulus obtained. However, the elongation at break of the film in the MD increased with increasing APS content, although no difference in the elongation at the break between BOPLA\_ APS1 and BOPLA\_ APS5 was observed.

Generally, coupling by silane coupling agent increases tensile strength but reduces elongation [15]. However, combining with simultaneous biaxial stretching technique leads to tough PLA film. This is in agreement with the increase in elongation at break of biaxially stretched PLA film with soft materials such as a core-shell rubber [20], modified thermoplastic starch [21], and ethylene-vinyl acetate copolymer (EVA) [22]. Considering the tensile data of the obtained films, adding 0.5% APS into PLA gave higher strength than adding 1% APS but the percentage of elongation at break of BOPLA with 1% APS is much higher than that of BOPLA with 0.5% APS. Therefore, the selected amount of APS to be applied into PLA is 1%.

The tensile results could be summarized that, by using a small amount of APS, a stiffness of the biaxially stretched PLA film in TD was improved. This might be due to bond strengthening between PLA and APS. Nevertheless, when the APS content was increased, the mechanical properties tended to be decreased, similar to a reduction of  $T_{d,onset}$  as reported previously. These results might be influenced by three factors; (i) chemical reaction (either grafting or crosslinking), (ii) hydrogen bond interaction between PLA and APS [19], and (iii) hydrolytic degradation of PLA [25].

To reinvestigate the effect of the simultaneous biaxial stretching speed, the BOPLA\_ APS1 film was prepared with various stretching speeds. The tensile strength, Young's modulus, and elongation at break of the biaxially stretched film differently increased when the stretching speed exceeded  $5 \text{ mm s}^{-1}$  (Figure 5). This supports the finding that the simultaneous biaxial

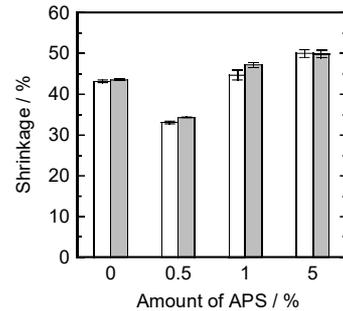


**Figure 5:** Tensile properties in both MD (white) and TD (grey) of the biaxially stretched PLA films with APS 1% with different stretching speeds.

stretching at high speed increases the toughness of both the PLA and blended PLA films, especially in the MD [10], [21].

### 3.4 Thermal shrinkage of the biaxially stretched film

Stresses remain in the product after the stretching process, which leads to shrinkage of the film when it is heated. The film shrinkage was evaluated in an oil bath at 100 °C. The PLA sheet (before biaxial stretching) showed a shrinkage of  $5.5 \pm 0.5\%$ . After simultaneous



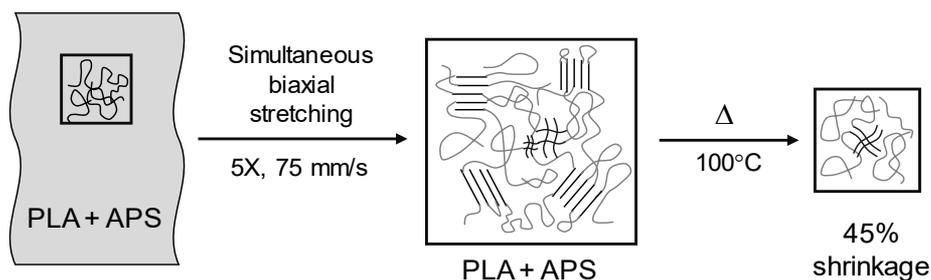
**Figure 6:** Thermal shrinkage of the biaxially stretched PLA films (stretched at  $75 \text{ mm s}^{-1}$ ) in both MD (white) and TD (grey) taken in an oil bath at 100 °C.

biaxial stretching, the BOPLA film was substantially contracted by heat, and the film shrinkage was approximately  $43.3 \pm 0.2\%$ . This could be explained that the high crystallinity obtained by biaxial stretching was in a low entropy state, thus, when the heat was applied to an unconstrained film, the polymer chains would return to a high entropy state resulting in a shortened length of the film [31].

Figure 6 compares the shrinkage percentages of the BOPLA\_APS film after being stretched at a speed of  $75 \text{ mm s}^{-1}$  with various amounts of APS. The addition of a small amount of APS decreased the shrinkability, relating to the high strength of the obtained film. This might be because the APS somehow releases the acquired stretching force after reacting with PLA. However, the higher the APS content, the higher the shrinkage. The BOPLA\_APS1 film showed a higher shrinkability percentage than the BOPLA film at about 3%. Blending 5% APS into PLA gave as high as 50% shrinkability. The results corresponded to the modulus of elasticity of the films. Also, this suggests that the stress absorption in the film might be related to the crystallinity degree and the resulting structure of PLA with APS.

## 4 Conclusions

In this study, an integrated application of the biaxial stretching technique and blending with APS was conducted for PLA film to obtain a heat shrinkable film (Figure 7). The occurrence of the chemical reaction of APS and PLA was supported by TGA. The film samples were biaxially stretched with a stretching speed of  $75 \text{ mm s}^{-1}$ , which led to high crystallinity and



**Figure 7:** Schematic draw of proposed shrinkable PLA film blended with APS.

high tensile properties. Additionally, the reacted APS improved the toughness and the strength, especially in a transverse direction, of the film. This might be because the interactions of APS and PLA, e.g. self-condensation, esterification, and hydrogen bond formation, were strengthened in all directions. However, the tensile properties were distinctly decreased in the case of PLA blended with 5% APS, which might be influenced by hydrolytic degradation of PLA. Compared to the biaxially stretched PLA film, the optimal amount of APS to be added into PLA is 1%. The tensile strength in a transverse direction and the elongation at break in a machine direction of the developed films were improved at about 50 MPa and 7%, respectively.

Moreover, the shrinkage of the film occurred due to stress relaxation during heating. The film shrinkability, which is proportional to the APS content, corresponds to the crystallinity of the biaxially stretched film. The biaxially stretched PLA film with 1% APS showed a thermal shrinkage of 45%. Hence, this developed film is comparable to a commercial shrink wrap film, which has shrinkability from 40 to 60%.

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