Piezoelectric properties of roll-to-roll fabricated polylactic acid films

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***Abstract*— In this work, we report functionality of polylactide acid (PLA) as piezoelectric degradable material, which has given in the preliminary studies the piezoelectric sensitivities are on the range of 10 pC/N, depending on PLA film details. However, this is very promisingly close to commercial alternatives, such as fluoropolymer polyvinylidene fluoride (PVDF), which is expensive fluoropolymer, not biodegradable or recyclable. Further, we have demonstrated the manufacturing of PLA films in roll-to-roll pilot line, which gives the promise that this type of sensors could act as elements in the future trillion sensors vision, where the large number of individual sensors are required.**

Keywords—Piezoelectric sensor material, polylactic acid, roll-to-roll film coating

I. Introduction

In the future scenarios, such as Internet of Things (IoT), embedded wearable and flexible electronics, energy harvesting, there is a need for sustainable, low-cost, disposable, bio-degradable sensors. These needs can only be fulfilled by developing new functional materials, which are not further degrading our environment. In this context, bio-based piezoelectric sensors are highly desirable.

Polylactic acid (PLA) has been widely used in many applications, e.g. plastic films, bottles, and biodegradable medical devices. The advantage in PLA based sensors would be the usage of renewable raw materials and thus, decrease of plastic waste production, which will be an issue in the future trillion sensor visions including ambient sensoring, food transport monitoring or IoT applications.

We have previously extensively studied piezoelectric bio-based material, such as wood nanocellulose [1], bacterial cellulose [2], chitosan [3] and their nanocomposites [4], which show promising levels of piezoelectric sensory action. There are very few reports in the literature about the piezoelectric properties of PLA [5, 6]. Here, we report the results of direct piezoelectric measurement performed in normal compression mode and in bending mode for in-house roll-to-roll fabricated PLA films and commercially available PLA films.

II. Materials and Methods

A. Commercial PLA films

The commercial PLA films were obtained from Taghleef Industries S.p.A. (Taghleef Industries S.p.A., San Giorgio di Nogaro, Italy). These films were from NATIVIA® product family, which are biodegradable and based on renewable raw materials. The thicknesses of the tested foils varied between 17 μm and 30 μm. Also, the composition of the foils differed from each other. The first tested foil had a PLA core with non heat sealable PLA layers on both sides of the film (called NTNS). The second tested foil had a PLA core with heat sealable PLA layers on the both sides (called NTSS). The third tested foil had voided (air) PLA core structure in the film with heat sealable PLA layers on the both sides of the film (called NELD) and the fourth tested foil had a PLA core with an evaporated aluminum layer on the one side and a heat sealable PLA-layer on the other side (called NZSS). The piezoelectricity properties of samples were tested such than each of the sample was measured three times in normal and shear mode configuration. The tested samples with their respective thicknesses are listed in Table 1. The structures of the tested commercial PLA films are illustrated in Figure 1.

TABLE I. Commercial PLA film properties.

Film label	***Thickness (μm)***	***Film properties***
NTNS	*20*	*Transparent, non sealable, biodegradable*
NTSS	*17*	*Transparent, both sides heat sealable, biodegradable*
NZSS	*20*	*Metallized film, heat sealable*
NELD	*30*	*White voided film, both sides heat sealable, biodegradable*

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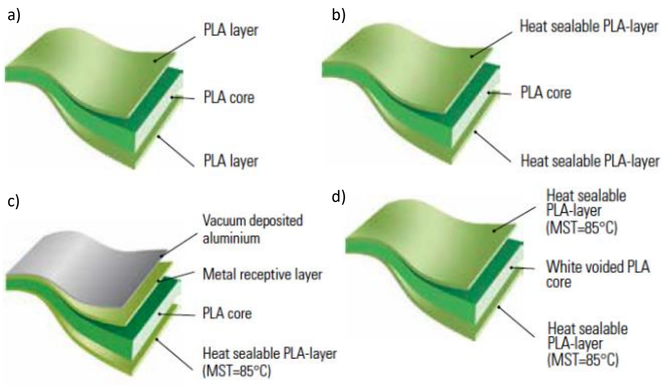

Fig. 1. Structure of the different commercial PLA- films, a) NTNS, b) NTSS, c) NZSS, and d) NELD. Figure is adapdet from Taghleef product data sheet.

B. *PLA film preparation in roll-to-roll*

Roll-to-roll (R2R) PLA films were produced at Tampere University, Paper Converting and Packaging Technology pilot line. PLA granulates were purchased from Nature Works LLC. PLA films were extrusion coated onto paperboard substrate. Prior to extrusion coating process, silicon paper sheets were attached onto paperboard in order to avoid adhesion and ensure easy separation of the PLA film samples. Extrusion coating and lamination pilot-line is presented in Fig. 2.

Fig. 2. R2R extrusion coating pilot line at Tampere University premises.

The target coating weight of the PLA samples were 20 and 30 g/m^2. Screw speed of the extruder was set to constant 120 rpm and the two different coating weights were achieved by adjusting line speed. During extrusion coating of the PLA film, mass temperature was set to 265°C and pressure 96 bar. Coating weights of 20 and 30 g/m^2 were produced with line speeds of 100 m/min and 75 m/min respectively. Casting of the polymer film is illustrated in Fig. 3. The dried PLA films were peeled off from the silicon paper coated paperboards to obtain freestanding PLA films for piezoelectric sensitivity measurements.

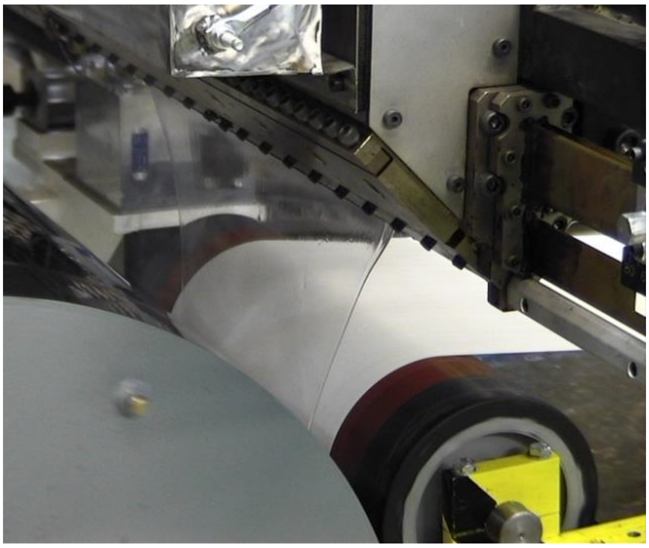

Fig. 3. Casting of polymer films at the pilot line.

C. *Piezoelectric measurements*

Measurements for the piezoelectric sensitivity were conducted with a custom-built in-house measurement setup, which contains mechanical shaker equipped with static and dynamic force sensors. The measurement system is described in more details in the previous publication [1]. The sample films were sandwiched between two electrodes (shown in Fig. 4) and subjected to 2 Hz sinusoidal compressive excitation. This included compressive and bending mode measurements. With the former, sample and the electrodes were laying flat on the sample bed and the exciting force was perpendicular to their surface plane. With the latter, sample and the electrodes laid on top of a PDMS ring with a 10 mm diameter hole in the center (used in previous paper [4]). Exciting force direction was the same, but due to the ring it allowed sample bending and created a shear stress in it.

Fig. 4. Photograph of used evaporated silver electrodes on polyethylene terephthalate (PET) film and example of two in-house prepared PLA films.

III. RESULTS AND DISCUSSION

A. *Properties of PLA films*

Extrusion process is a conventional and reproducible processing way to produce PLA coatings and films. Visually produced PLA film samples appeared of uniform and high quality. Notable defects were not discerned. PLA films were easily separated from the silicon paper. The exact coating weights of the samples were 18.0 and 27.3 g/m^2 with standard deviation of 1.30 and 0.75 g/m2 respectively. The corresponding film thicknesses were 17 ± 3 and 24 ± 2 µm as 20 measurement averages.

B. *Piezoelectric sensitivity measurement results*

With all the measured films, bending mode showed higher sensitivity values in comparison to normal compressive mode results. Results of piezoelectric sensitivity measurements for in-house prepared PLA film are shown in Fig. 5. In-house prepared PLA film resulted in about 3 pC/N sensitivity in normal compressive mode measurement. In the bending mode, sensitivity difference between 17 µm and 24 µm thick films was higher, but around 10 pC/N was reached in the case of thicker film. However, the standard deviations were also relatively high.

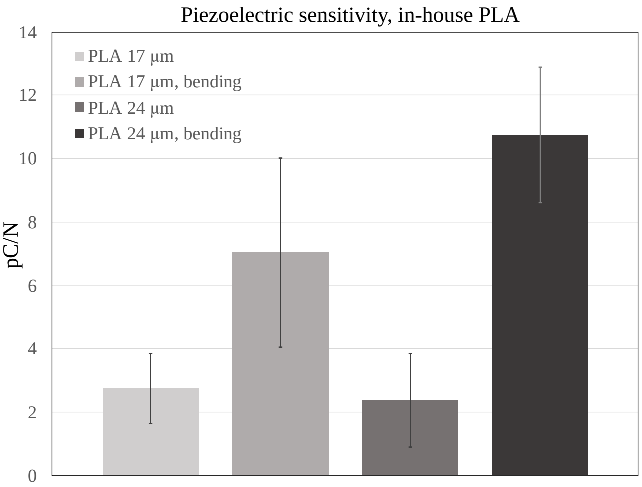

Fig. 5. Piezoelectric sensitivity results for two in-house roll-to-roll fabricated PLA films in normal compressive mode and bending mode.

Piezoelectric sensitivity measurement results for commercial PLA films are shown in Fig. 6. Similarly to in-house made films, commercial PLAs showed significantly higher sensitivity in bending mode in comparison to normal more, but also standard deviations were high. In comparison to the in-house made films, commercial films had similar normal mode sensitivity (3–5 pC/N) but significantly higher bending mode sensitivity (30–80 pC/N). In the case of transparent, both sides heat sealable and biodegradable NTSS film, bending mode values exceeded 80 pC/N. Metallized NZSS films showed the lowest sensitivity values among commercial films (about 30 pC/N).

We suggest that the significantly higher bending mode sensitivity in the case of commercial films is related to differences in the film manufacturing techniques. PLA molecules may orient differently in these processes, which would mostly influence to bending mode sensitivity, but not as much to normal compressive mode values.

In relation to film thicknesses, for in-house prepared film, thicker PLA showed slightly higher bending mode sensitivity. On the contrary, in the case of commercial films, where thicknesses varied from 17 to 30 µm, thinnest film showed the higher sensitivity. However, the commercial film structures were quite different from each other (see Figure 1). For example, metallization of PLA film can yield of degradation of piezoelectric behavior, if the film is heated during the metallization process.

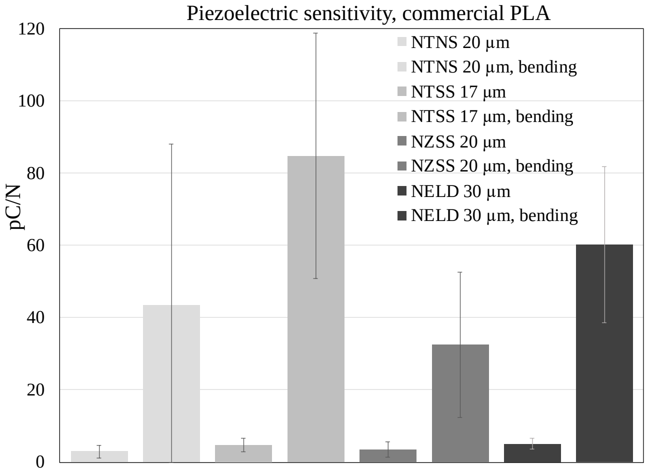

Fig. 6: Piezoelectric sensitivity results for four commercial PLA films in normal compressive mode and bending mode.

In the previous literature, there are only a few studies of PLA piezoelectricity. In 1991, Fukada estimated sheer mode piezoelectricity constant d_{25} = 10 pC/N [5]. In 2017, Curry *et al*. reported shear constant value d_{14} ~11 pC/N [6]. These constants are closely related to our bending mode type measurements, and the values are very close to our in-house film results.

IV. Conclusions

Here, we report direct piezoelectric measurement performed for in-house roll-to-roll fabricated PLA films and commercially available PLA films. Piezoelectric sensitivity measurement has been performed in both normal compression mode and bending mode. Normal mode sensitivities were about 3–5 pC/N for both in-house and commercial PLA films. In bending mode, sensitivities were significantly higher, about 10 pC/N for in-house made films and for commercial films even higher, from 30 to 80 pC/N. Based on our results, we suggest that PLA is a suitable material for force sensor applications, especially when used in the bending type sensor.

References

[1] Rajala, Satu, et al. "Cellulose nanofibril film as a piezoelectric sensor material." ACS applied materials & interfaces 8.24 (2016): 15607-15614.

[2] Mangayil, Rahul, et al. "Engineering and characterization of bacterial nanocellulose films as low cost and flexible sensor material." *ACS applied materials & interfaces* 9.22 (2017): 19048-19056.

[3] Hänninen, Aleksi, et al. "Nanocellulose and chitosan based films as low cost, green piezoelectric materials." *Carbohydrate polymers* 202 (2018): 418-424.

[4] Sriplai, Nipaporn, et al. "Enhancing piezoelectric properties of bacterial cellulose films by incorporation of MnFe2O4 nanoparticles." *Carbohydrate Polymers* 231 (2020): 115730.

[5] Fukada, E. "Piezoelectric properties of poly-L-lactic acid." *Rept. Prog. Polym. Phys. Jpn* 34 (1991): 269-272.

[6] Curry, Eli J., et al. "Biodegradable piezoelectric force sensor." *Proceedings of the National Academy of Sciences* 115.5 (2018): 909-914.