Research and Reviews in Materials Science and Chemistry
Vol. 3, Issue 2, 2014, Pages 115-122
ISSN 2319-6920
Published Online on June 2, 2014

http://jyotiacademicpress.net

INFLUENCE OF HUMIDITY ON GLASS TRANSITION OF PLA FILMS

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Abstract

PLA has a relative low point of glass transition, which can limit its application. The aim of the study was to observe the effect of humidity on glass transition. The glass transition of PLA films was determined under three different climates (nitrogen-atmosphere, wetted, and room conditions) by dynamic mechanical analysis with a tensile testing setup. The point of glass transition was calculated by interpretation of storage modulus (E') and tan δ curve as well. Although the applied humidity levels showed high variation, significant differences were observed. The glass transition temperature changed from 57.8 ± 1.5°C (E')/

Keywords and phrases: biopolymers, DMA, glass transition, humidity, PLA.
Communicated by Jiliang Wang.
Received November 15, 2013; Revised March 14, 2014

62.5 ± 1.9°C (tan δ) under dry condition to 46.5 ± 3.5°C (E')/53.2 ± 3.1°C (tan δ) at medium and 41.9 ± 4.8°C (E')/45.2 ± 4.1°C (tan δ) at high humidity.

Abbreviations: CA (Contact Angle); DMA (Dynamic Mechanical Analysis); DSC (Differential Scanning Calorimetry); Tg (Glass Transition Temperature).

1. Introduction

The use of bio-based and biodegradable polymers for food packaging has a great potential to avoid ecological problems caused by non-biodegradability of the common oil-based polymers. Polylactic-acid (PLA) is one of the most promising bio-based polymers for eco-friendly applications due to its biodegradability, processability, lightness and transparency [1, 2, 3]. According to the forecast of European Bioplastics, the production of PLA will increase from 186.953 in 2011 to 294.703 metric tons in 2016, which equates an increase of 63%.

Glass transition (Tg) characterizes the softening behaviour of polymers and determines the area of application. The Tg is usually determined by thermo-mechanical analysis, DMA, and DSC [3, 4, 5, 6]. Both methods work commonly under nitrogen atmosphere. The high purity of nitrogen establishes a climate with very low relative humidity. As mechanical properties of natural polymers are much more affected by humidity data from DMA and DSC measurements under nitrogen does not reflect properties under real conditions. Especially in food packaging higher humidity could occur.

Although several studies about ageing and degradation of PLA were published, only little information about the effect of humidity on glass transition temperature is known. Until now, only the change in Tg of PLA after storage at different relative humidity or after absorbing water is reported [4, 5, 7]. The aim of the study was to characterize the influence of humidity on the in situ softening behaviour of PLA films.

2. Experimental

PLA films with a thickness of 0.15 ± 0.01mm were purchased from NaKu (Wiener Neustadt, Austria). The films were stored at 20 ± 2°C and 65 ± 5% relative humidity for at least two weeks. Nitrogen 5.0 from Messer (Austria, Schwechat) with purity of 99.999% was used for DMA experiments. Contact angle of PLA films was measured by means of a self-made setup composed of a camera (Sony 93D, Model XC-77CE, 2/3 Zoll CCD, $11 \times 11\mu m$ pixel size) and an adjustable background lighting at 23 ± 2°C and 50 ± 5% relative humidity. The measurements were performed with deionized water. The drop was applied statically with a syringe. The angle between water drop and surface was determined with a drop shape analysis software DSA1 (KRÜSS Optronic GmbH, Hamburg, Germany). Each measurement consisted of ten test series and was done in triplicate.

Thermal-mechanical characterisation was performed by DMA (Netzsch DMA 242 C, Germany) measurements with a tension build up. A heating rate of 3K/min from 30 to 90°C was applied. Measurements were done at a strain sweep frequency of 1Hz. The static load was 0.2N, whereas the dynamic force applied during frequency sweep was 0.3N. For equilibration, films were placed in the test chamber for 30 min before the measurement was started. The different humidity levels were established by using N_2, ambient air and piping air through washing bottles filled with hot water. The lab was conditioned to 23 ± 2°C and 50 ± 5% relative humidity. The washing bottles were heated in a water bath to about 100°C. The relative humidity was recorded with an external HT2 sensor from Sensirion (Staefa, Switzerland).

The storage modulus (E') as well as the loss factor tan δ = E"/E', with E" being the loss modulus were recorded. All measurements were done at least in triplicate. Data analysis was performed with Proteus software from Netzsch (Selb, Germany). Tg was determined by interpretation of

the maximum of tan δ and the transition onset of E' as well. Statistical analysis was accomplished by means of a *t*-test ($P < 0.05$) with SPSS software (Version 18, IBM, New York, United States).

3. Results and Discussion

The measured contact angle of PLA films was 74.48 ± 3.21^{o}. This value correlated well with results of other studies [3]. Due to this contact angle, PLA can be assigned as relatively hydrophobic [7]. Furthermore, PLA lacks on reactive side chains and is quite inert [1, 2].

The relative humidity during thermal-mechanical characterization for each climate is given in Figure 1. The use of N_2 gained a very dry climate; the maximum recorded humidity was only about 50%, which equated the moisture content of the lab. During heating the relative humidity was reduced quickly to 4%. Turning off the N_2 supply gained a moderate level of moisture, which ranged between 18 and 55%. By piping air through boiling water into the test chamber of the DMA equipment a very wet climate with over 90% relative humidity was established. Not until temperatures above $60^{o}C$ were reached, decrease in the moisture content was recorded. Generally, the humidity profiles showed quite high variation, except under N_2 atmosphere.

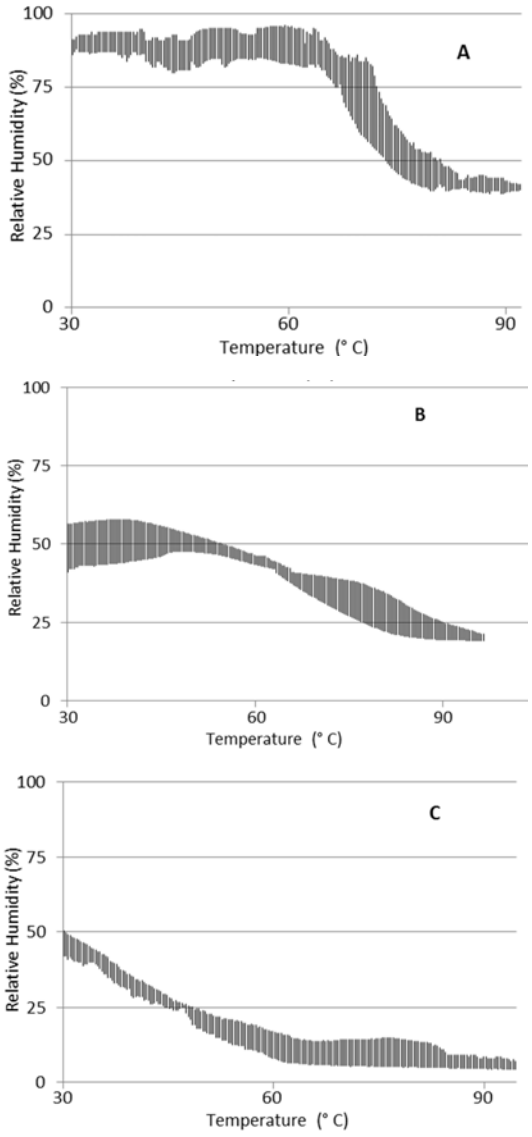

Figure 1. Humidity profiles during DMA testing (A) with additional moistening; (B) room climate; and (C) under nitrogen atmosphere. Curves represent maximum and minimum values of three measurements, respectively.

The DMA curves (E' and tan δ) and determined Tg are given in Figure 2 and Table 1. Tg temperature under standard condition with N_2 as inert gas was 57.8 ± 1.5°C (E') and 62.5 ± 1.9°C (tan δ). Tg of PLA usually ranges between 50 and 72°C depending on the purity and degree of crystallinity [2]. Thus determined range of Tg was confirmed. Already under room condition, the Tg was strongly affected and decreased to 46.5 ± 3.5°C (E') and 53.2 ± 3.1°C (tan δ), respectively. At high humidity determined Tg temperatures showed the lowest values of 41.90 ± 4.78°C (E') and 45.20 ± 4.08°C (tan δ), respectively. Statistical analysis showed significant differences between all groups, except between the Tg at medium and high humidity based on the interpretation of E' curve. One reason could be the relative high variation of relative humidity under these climates due to the simple self-made setups. Furthermore, alternating humidity during testing obviously restrained complete equilibration of PLA films. Also, the different conditions referring the surrounding atmosphere (ambient air or N_2) could have affected Tg. Nevertheless obtained results were in sound correlation with other studies, in which increased water absorption also led to lower Tg values [4, 5, 7].

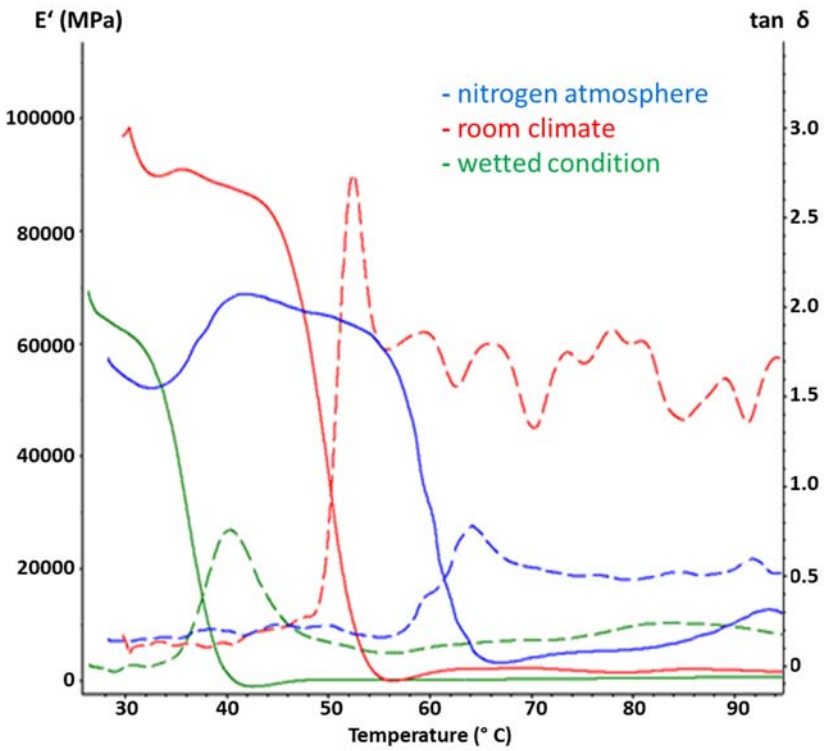

Figure 2. DMA curves of E' and tan δ (dashed line) with a heating rate of 3K/min from 30 to 90°C at different humidity levels (1) with additional moistening; (2) room climate; and (3) under nitrogen atmosphere.

Table 1. Tg of PLA films determined under different climates

Testing condition	Tg based on E'	Tg based on tan δ
N_2	57.77 ± 1.46°C[a]	62.47 ± 1.92°C[a]
Indoor climate	46.47 ± 3.48°C[b]	53.20 ± 3.14°C[b]
Wetted climate	41.90 ± 4.78°C[b]	45.20 ± 4.08°C[c]

Mean values and standard deviation were based on three measurements. Letters indicate group differences determined by means of a *t*-test ($P < 0.05$).

Several methods were commonly used to determine Tg by means of DMA, the transition onset or inflection point in the E', the loss modulus peak or the tan δ peak. The inflection point in the storage modulus is known as the most accurate procedure for Tg determination by DMA [6]. However, the mentioned procedures were used for determination of Tg in order to cover and observe a broader range. Generally, the Tg calculated based on the maximum of tan δ is much higher compared to Tg calculation based on the E' curve because of the phase shift [6].

4. Conclusion

Results of this study showed a strong effect of humidity on Tg of PLA. Already a moisture content of about 50% in the testing chamber decreased Tg significantly. Although PLA films were not completely equilibrated during the measurements due to varying moisture levels, useful findings were generated. Summing up, the usual determination of Tg for PLA is not sufficient in respect to most applications like food packaging. However, further studies with other bio-polymers have to be conducted.

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