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Difference in Glass Transition Behavior Between Semi Crystalline and Amorphous poly(lactic acid) Thin Films

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Summary: Semi crystalline and amorphous poly(lactic acid) (PLA) thin films exhibit different glass transition temperature and behaviour, as revealed by ellipsometry. For semi-crystalline poly(L-lactic acid) (PLLA) thin film (with crystalline content between 40 and 60%), the glass transition temperature (T_g) is found to decrease below a film thickness of 50 nm. This depression was interpreted in term of disentenglement effect which is likely to occur upon confining the amorphous PLA phase near a non interacting surface. New results performed on non completed films, *i.e.* isolated objects, also reveal the lower transition temperature, thus underlying the importance of the entanglement state of the polymer chains on their mobility. For amorphous PLA thin film, obtained from the L and D copolymer, two distinct glass transitions were observed, with the highest Tg attributed to the presence of some nano-phase domains, formed by a possible cooperation of the D and L blocks to form stereo-complexes sequences, within the film. Furthermore, if these T_g remained constant as film thicknesses decrease down to 50 nm, they were also found to slightly decrease for isolated objects, thus supporting the importance of the entanglement hypothesis on the glass transition.

Keywords: conformation; entanglement; glass transition; PLA; thin films

Introduction

In the past few years, the polymer community has drastically concentrated his research on the study of biodegradable polymers that could replace petroleum-based plastics in all kinds of applications. Among the most popular ones, poly(lactic acid) (PLA) has attracted much attention because it is easily produced from lactic acid but also because of its biocompatibility which makes it a good candidate in valuable biomedical applications. The glass transition (T_g) of polymer film is surely one of the most important parameter of polymeric materials. If many papers are devoted to the study of this parameter on bulk PLA materials, results are often found controversy, probably due to its semi-crystalline character. For example, the group of Mano found that the glass transition is shifted to higher temperature with an increasing crystalline content (X_c).[1] This result was interpreted by assuming the existence of dynamically heterogeneous environments in semi-crystalline PLA, with regions in which the mobility of the amorphous chains is restricted (higher T_g) near the rigid lamellar walls or within the intra-lamellar thickness. The opposite trend, *i.e.* a T_g depression with an increase of X_c for PLLA under constrained conditions, was also reported by Fitz and collaborators.[2] The authors proposed that the crystallisation process increases the net free volume in the amorphous phase. On the other hand, they also observed an increase of T_g with X_c for unconstrained Poly(L-lactic acid) (PLLA) samples. These two examples emphasize the complexity of the glass transition

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behaviour for semi crystalline samples and further investigations are still needed.

The T_g behaviour is also known to adopt a different behaviour when polymers are geometrically confined in thin film. In such case, surface-polymer interaction is often reported as a key controlling parameter for the T_g deviation[3]. Many papers[4,5] indicate that the reason why bulk properties deviates is not fully elucidated and is still sample dependant. Nonetheless, these studies are all supporting the idea of different layers in polymer thin films, including a less mobile layer at the solid-polymer interface in case of strong polymer-surface interactions or a more mobile one in case of polymer on a non interacting surface. It should be added that the mobility of the layer at the solid-polymer interface becomes predominant as the film thickness decreases. Specific conformations of polymer chains at the interfaces could yield modifications in chain packing and hence of the mobility of polymer chains at interfaces.[6]

Surprisingly, there is little information in the literature about the effect of confinement, either geometrically and/or induced by the crystallisation, on the glass transition for PLA systems. The only work that deals with the determination of the glass transition of PLA thin film was performed by Kikkawa *et al.*[7]. They measured the glass transition, using friction force microscopy (FFM), on crystallizable PLLA and uncrystallizable Poly(DL-lactic acid) (PDLLA) films of 300 nm thickness under vacuum and under aqueous condition. In this study, the authors investigated the effect of water on Tg of PLA surfaces according to the structure of the film (crystalline versus amorphous). They measured a lower Tg of uncrystallised PLA film under water (58 °C) in comparison with observation under vacuum (70 °C), as well as for crystallised sample (57 °C under water and 74 °C under vacuum) and suggested that the water act as plasticizers and enhance the molecular mobility of PLA molecules in thin films. It should be noted that the technique used in the study was particularly suited to probe the effect of water on the mobility of the polymer chains present at the outer surface of the film.

In the present study, we report the first ellipsometry study on the glass transition temperature of PLA thin film under film thickness reduction and we pointed out the different trends observed between amorphous and semi-crystallized PLA thin films.

Materials and Techniques

Poly(L-lactic acid) and Poly(D,L lactic acid) samples were kindly provided by PURAC Biochem BV (Gorinchem, The Netherlands) and used without further purification. The mean molecular weights M_n of the polymers is 200 kg mol^{-1} with a polydispersity index around 2, as measured by GPC. PLA solutions were prepared in dichoromethane at different concentrations and then spin-coated on cleaned silicon wafers. From this experimental set-up, films with thicknesses varying between 22 to 400 nm were prepared and analysed. Furthermore, experiments were also performed on isolated objects deposited on silicon wafers. Such samples were obtained from the deposition of highly diluted PLA solutions (100 g L^{-1}). For each sample, the glass transition temperature was measured on at least five different samples.

The so-formed samples were then thermally treated before ellipsometry measurements. PLA thin films were placed in a vacuum oven at the temperature of 120 °C for 5 hours. Below this temperature, the films were shown not to be equilibrated and no glass transition was clearly evidence on the ellipsometric graphs. Following this treatment, Raman spectroscopy was used to determine the samples crystalline contents, if any. This semi-quantitative procedure was previously described in another paper.[8] Micro-Raman experiments were performed on a Jobin-Yvon T64000 Raman spectrometer in single-monochromator mode using a Notch Rayleigh rejection filter, a 600 lines/mm diffraction grating, and a cooled CDD detector. The $\lambda = 514.5$ nm radiation of an argon-krypton ion laser was used for excitation with a limited power of 4 mW on the sample. The experiments were performed with a confocal microscope equipped with a ×100 objective which yields a spot diameter of less than 2 μm on the sample. For Raman experiments, thin films were initially scratched from silicon surface by razor blade and deposited on a clean glass slide to be studied under the microscope. The crystalline contents of the films were found to be about 60% for the homopolymer PLA films (either L or D) and around 0% for the D and L PLA copolymer. Figure 1 shows AFM images of the surface of the PLA films following the treatment. The presence of crystallites is clearly evidenced in the homopolymer film, whereas an homogeneous flat surface, representative of purely amorphous polymer films, is observed for the D,L copolymer film.

The glass transition of PLA thin films was characterised from the discontinuity in the ellipsometry parameter Δ, at 413 nm, as a function of temperature. T_g was then obtained at the intersection point at the discontinuity of the two linear least square regression lines fitting the responses variable (“cosΔ” vs. ellipsometry). Ellipsometry experiments were performed by using a Jobin-Yvon UVISEL AGMS M200 apparatus working in the wavelength range from 248 to 1700 nm, equipped with a hot stage. The incident and reflected angles were fixed at 70°. The polymer samples were placed on a hot plate mounted on the optical stage of the ellipsometer. The “CosΔ” ellipsometric angle was recorded at stabilized temperatures for 5 min and increased by 5 °C increments by manually adjusting the temperature controller. For ellipsometric measurements, reproducibility was verified by performing at least five measurements on each sample.

Results and Discussion

Glass Transition Temperature of Semi-Crystalline PLA Films

Figure 2 presents the glass transition temperature of PLLA thin films as the function of the thickness. It should be pointed out that the crystalline content of the film, as determined by Raman, were found between 40 and 60% over the whole range of thicknesses studied here.

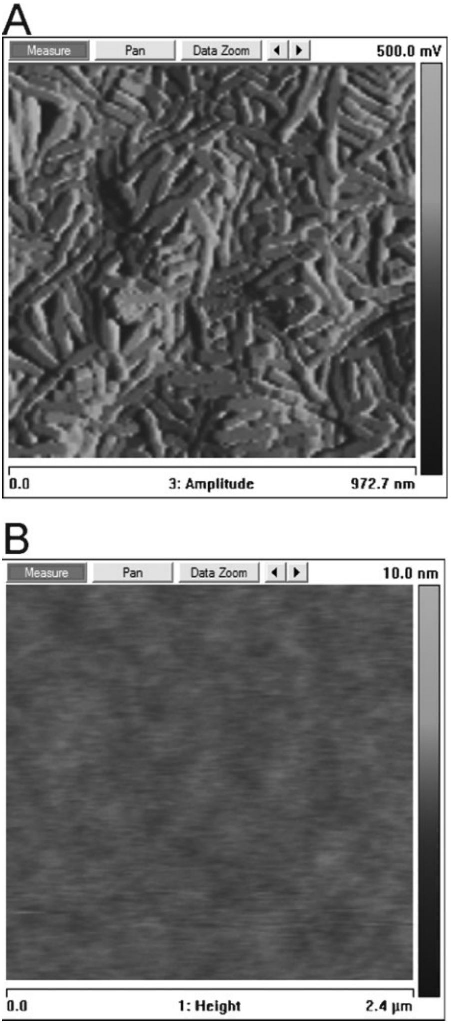

Figure 1.
AFM images of PLA thin films following a thermal treatment at 120 °C during 5 hours. A) PLLA thin film and B) PDLLA thin film.

It could be observed from Figure 2 that the T_g “bulk”, *i.e.* obtained for the largest film thicknesses, is around 65–70 °C. This value was further verified by DSC on bulk PLA samples that were submitted to the same thermal treatment. This value contrasts with the usual Tg values reported for

PLA systems (58 °C) but can be clearly attributed to the presence of crystallites within the thermally treated samples. This increase of T_g for a PLA sample with an X_c between 40 and 60% is well correlated with the work of Mano[1] and can be explained by either a geometrical effect induced by the presence of crystallites or by interaction with these surfaces. Figure 2 also reveals a new trend for this polymer since it could be observed that the T_g value is slightly decreasing, from 70 to 65 °C with decreasing film thicknesses down to 50 nm and then decreases more rapidly when the thickness becomes inferior to 50 nm. The lowest T_g, of 59 °C, was obtained for a PLLA film thickness of 22 nm. The decrease of T_g value with film thickness is a well known effect, largely documented in the literature, for amorphous polymer thin films. Such trend was, for example, reported for polystyrene (PS) or polymethylmethacrylate (PMMA) thin films.[3] Keddie and Jones measured the glass transition temperature of thin polystyrene films cast on silicon substrates as a function of film thickness using spectroscopic ellipsometry and found that the glass transition temperature decreased as the film thickness was reduced below approximately 100 nm. It was stated that the local chain mobility near an interface is changed, depending on the nature of the interaction between the polymer and the surface. In the case of polystyrene, weak polymer-surface interaction are expected, which in terms, lead to boundary conditions close to the one of free standing films, in which the dynamics of the confined systems will be faster than that of the bulk.

Our work also supports the concept of a polymer mobility increase when the polymer is confined near a non-interacting interface, *i.e.* when the polymer thickness decreases. Thus, from a dynamic point of view, the amorphous phase of semi crystalline PLA thin films could be seen as different phases, with different mobilities. For large thicknesses, the bulk amorphous phase is confined by crystallites and hence the overall mobility is decreased. As the thickness is reduced and for similar X_c, the geometrical confinement becomes important. Since the deposited surface is a non interacting one, the dynamics of PLA chains is enhanced and consequently T_g decreases. It was postulated by Si *et al.*[9] that an increase of the chain mobility near a non interacting surface could be attributed to a reduction of the entanglement effect. This statement was further confirmed by changing the surface properties.

The role of the entanglement parameter was further verified by performing T_g measurements on highly diluted polymer entities (inset Figure 3). Below a polymer concentration of 2 g L^{-1}, no PLA uniform film was formed on the surface but only densely packed macromolecules or isolated PLA entities can be observed on the silicon

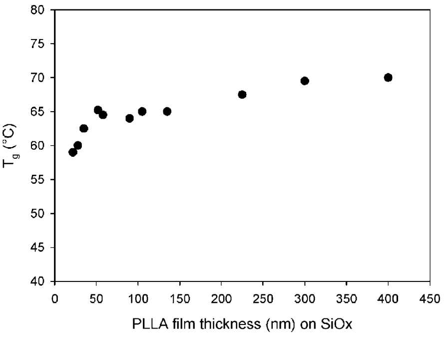

Figure 2.
Glass transition temperature of PLLA thin films as function of film thicknesses, as measured by ellipsometry (X_c for all PLLA films ranging from 40 to 60%).

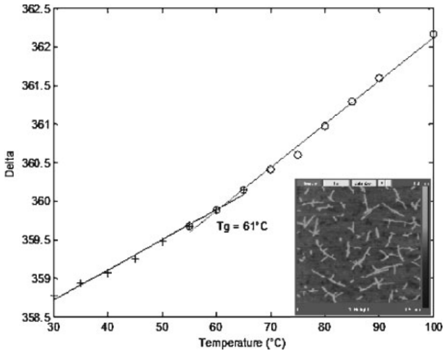

Figure 3.
T_g measurement on isolated PLLA macromolecules obtained from the deposition of polymer solution at a concentration of 100 mg L^{-1} on a silicon surface.

surface. The height values of these entities, between 8 and 10 nm, is in good agreement with the thickness of PLA lamellae reported in the literature, as measured by AFM and small angle scattering.[10] Figure 3 shows the T_g measurements on these isolated PLLA macromolecules. To the best of our knowledge, it is the first experiment of ellipsometry on isolated PLA macromolecules. A transition can be found around 60 °C for this low polymer concentrations. This value is found to be of the same order to the one obtained for the thinner 22 nm PLA thin film. This result is consistent with the entanglement hypothesis discussed. These samples are formed from highly diluted PLA solutions. Thus polymer chains may deposit on the surface with more pronounced and favoured disentanglements. As a consequence, the dynamics of the amorphous PLA part within these isolated entities may be enhanced, as experimentally observed here.

Glass Transition Temperature of Poly(D,L-Lactic acid) Film: An Amorphous PLA Film

Because of local disorder in its repeating unit, poly(D,L-lactic acid) is known to be an amorphous polymer. Figure 4 shows the ellipsometry signal obtained for a PDLLA Thin film of 225 nm.

Two clear transitions can be observed at 50 and 84 °C. This result indicates that the mobility distribution of the amorphous phase of the film is highly heterogeneous with a T_g difference around ~30 °C. This result can be probably explained by a phase separation that may occur within the film, due to the presence of L and D PLA sequences along the polymer backbone. These two sequences are known to interact each other to form stereocomplexes.[11] The higher Tg is thus attributed to the stereocomplexes phase and the lower one to the mobility of the homopolymer chains. It should be mentioned that the observation of two Tg for this type of copolymer was already reported in the literature.[12] This observation was done on a PLA that was exposed to a physical aging. The authors also interpreted the two glass transitions in terms of local phase separation. Moreover, it should be mentioned that other authors also reported the presence of 2 T_g's for confined homopolymers in thin films.[13] For example, Vignaud *et al.* measured 2 T_g for i-PMMA deposited on silicon wafer using Raman spectroscopy. In this latter case, the two transitions were attributed to a bulk T_g (for the lower one) and to polymer-polymer interaction for the higher T_g (105 °C). When the same authors performed the same measurement using ellispometry, they only measured one T_g, which was recorded at 107 °C. They suggested that the kink in the thermal expansion of the film recorded by variable temperature ellipsometry, and generally claimed to be the T_g (h) of the film is assumed to be an average of the different T_g's observed by Raman. To describe the presence of 2 T_g, models with different layers have been proposed.[13]

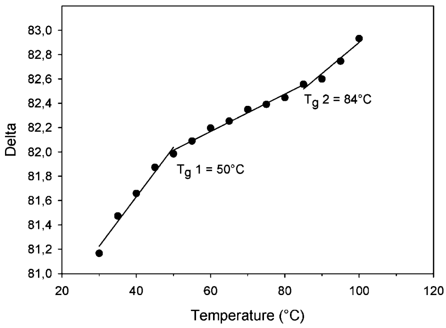

Figure 4.
Glass transition temperature of Poly(D,L-lactic acid) film (225 nm) measured by ellipsometry on a silicon surface.

It can be observed on Figure 5 that two T_g remain constant over the whole film thickness measured here. Since no thickness dependence is observed in our case, a simple model using 2 layers couldn't be used for example to argument the 2 T_g. Thus, another explanation could be the presence of cohesional entanglements within the films, as proposed by Liao *et al.*[12]. These entanglements would be formed by interactions between the D and L blocks of different chains to form some sort of "nano-domains", in which the

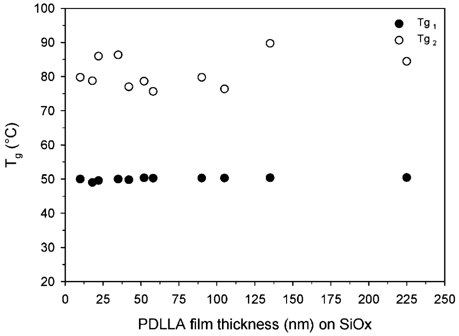

Figure 5.
T_g of Poly(D,L-lactic acid) as a function of film thickness.

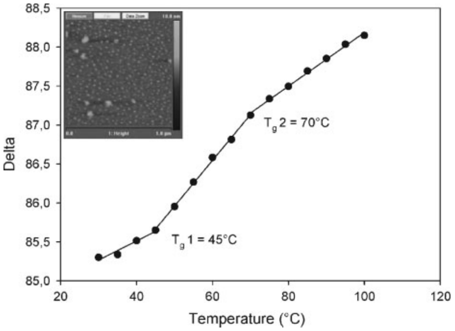

Figure 6.
Glass transition measurement on isolated PDLLA macromolecules by ellipsometry.

mobility will be reduced. We therefore assume a nano-phase separation of strongly interacting locally organized D and L blocks in PDLLA which yields a higher T_g whereas the other non organized phase results in a lower T_g.

Further experiments were also conducted on isolated objects (Figure 6). In this case, two T_g were still observed but both were obtained at lower values, respectively 45 °C and 75 °C. We may then conclude that the diluted solutions used to form such samples will enhance polymer chain disentanglements, which in term results in a higher mobility of the equilibrated materials. This effect can be observed on the two phases and thus emphasize the important aspect of the chain entanglement state on the final glass transition properties of materials.

Conclusion

We have investigated the glass transition of amorphous and semi crystalline PLA thin films. Different behaviours were observed. On the one hand, we found that the glass transition of semi crystalline PLA thin films, with crystalline content between 40–60%, is found to vary with thickness below 50 nm. This behaviour was attributed to a geometrical confinement effect of the amorphous PLA phase. Its mobility increases on a non interacting surface and this particular trend was explained by disentanglements effects which become important as the film thickness is reduced, owing to the film preparation step.

On the other hand, two glass transition temperatures were measured for the amorphous PDLLA thin film. The lower glass transition was located at 50 °C and the second glass transition was observed in the range of 75–85 °C. For such film, no geometrical confinement effect was observed within the thickness range investigated here, and the two glass transitions remain constant with decreasing film thichnesses. This behaviour was explained by a possible local phase separation, composed of weakly interacting chains. Nonetheless, these two glass transitions were found to decreased when measured on isolated entities, hence emphasizing the important role of the entanglement state ("or conformation") of polymers chains on their mobility.

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