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MACROMOLECULAR MOBILITY OF CONFINED PLA LAYERS

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INTRODUCTION

Poly lactide (PLA) is today most produced biobased and biodegradable bioplastic in the field of food packaging, which remains nevertheless largely dominated by petrochemical polymers. Material structuring on the nanoscale offers novel tools to achieve the next level of innovation using polymer thin films^{4,5}. In particular, confinement of polymers, i.e. the reduction of geometric material length scales to the dimensions of the macromolecular chain can yield novel structures that impact bulk properties⁶. The layer-multiplying co-extrusion process can create multilayer architectures with thousands of alternating layers having themselves nanometric thickness [1]. This small layer thickness yields geometrical confinement of the polymer chains, which can change their macroscopic properties [2,3]. PLA can be used in this process as a barrier layer, but the impact of confinement on its macromolecular dynamics is largely unknown.

MATERIALS AND METHODS

In this work PLA (Corbion Purac, PLA REVODE 190) was confined with polystyrene (PS, Total Petrochemicals PS 1340), which has low compatibility with PLA with the help of the layer-multiplying co-extrusion process. The confined PLA layers were subsequently annealed in the aim to explore the impact of confinement on the crystallization behavior and macromolecular mobility. The analysis of the crystallization behavior was realized by in situ WAXS experiment. The analysis of the mobility landscape of the amorphous phases was done by MT-DSC in the light of the 3-phase model [4] and quantifying the size of the cooperatively rearranging region (CRR) according to Adam and Gibbs [5]. The CRR is a domain in which all molecules move cooperatively and measures therefore the heterogeneity of relaxation in the amorphous phase. The impact of the creation of confined PLA on macroscopic properties was analyzed with oxygen permeability measurements.

RESULTS

The figure 1 shows the confined PLA layers between PS layers obtained by the layer-multiplying co-extrusion process. The confinement of PLA slowed down the crystallization kinetics, which was quantified with Avrami's law. However, the final crystallinity degree, which could be reached was higher under confinement.

We showed that it was the confinement of PLA between PS layers allowed decoupling between the crystalline and amorphous phase of PLA, which had as a consequence that annealed PLA could be described by a two-phase model because of the absence of a rigid amorphous phase.

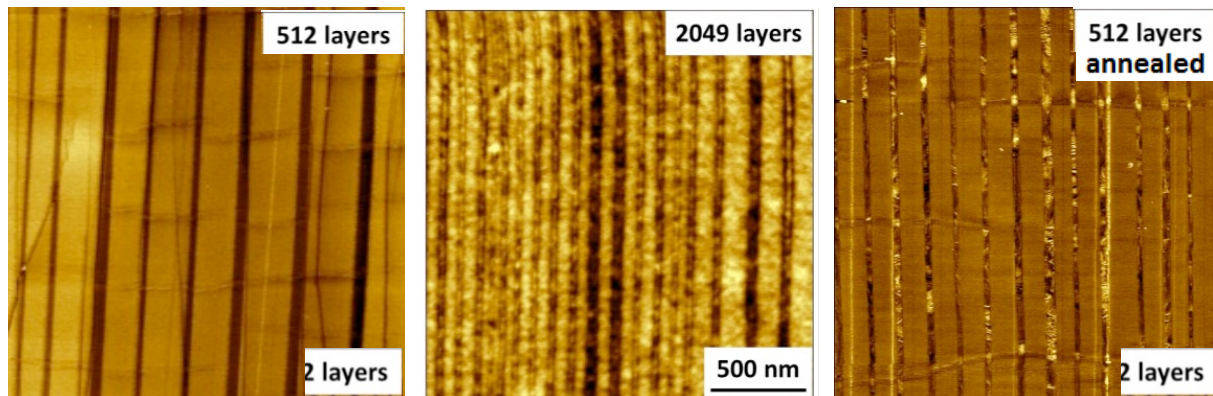


Figure 1 – Tapping mode AFM phase images of nanolayered amorphous PS/PLLA containing different number of layers as indicated.

Table 1 – Quantification of the 3-phase model for PLA multilayers with different layer thickness.

Sample	X_c (%)	X_{MAF} (%)	X_{RAF} (%)
30 μm annealed	28	33	39
300 nm annealed	36	55	10
20 nm annealed	44	59	0

X_c crystallinity degree; X_{MAF} Fraction of the mobile amorphous phase; X_{RAF} Fraction of the rigid amorphous phase

Furthermore, the decoupling of the crystalline and amorphous phase of PLA, which was beneficial for barrier properties.

CONCLUSION

This work constitutes a step towards the better understanding of the behavior of macromolecules under confinement in the aim to optimize materials properties using the layer-multiplying co-extrusion process.

References

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