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Characterization of the Amorphous and Semicrystalline Biodegradable Poly(lactic Acid) by Temperature-modulated Calorimetry

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A study of the thermodynamic properties of the biodegradable poly(lactic acid) (PLA) was carried out using quantitative thermal analysis and interpretation of the results on a molecular level. The quantitative thermal analysis in the glass transition region of the amorphous PLA and in the melting region of the semicrystalline PLA are examined using temperature-modulated differential scanning calorimetry (TMDSC) and standard differential scanning calorimetry (DSC). The apparent total, reversing, and non-reversing heat capacities of PLA with different thermal histories were evaluated on heating, using standard TMDSC, quasi-isothermal TMDSC, and standard DSC. The resulting information on hysteresis, in form of enthalpy relaxation, and the glass transition measured as the total heat capacity can be separated into the reversing and non-reversing heat-capacity components. The glass transition temperature, from the reversing heat capacity and the enthalpy relaxation peaks from the non-reversing component were both shifted to higher temperature for slowly cooled or aged PLA. Examination of the semicrystalline PLA by quasi-isothermal TMDSC and quantitative thermal analysis allows to separate any reversible and irreversible processes in the regions between the glass and melting transitions. Enthalpy relaxation and cold crystallization in the glass transition region, reorganization in the premelting region, as well as the major melting were found to be fully irreversible. Only a very small contribution from the reversing heat capacity can be observed within the melting peak by their time-dependent contribution. The fraction of excess reversible heat capacity is assumed to be due to local melting and crystallization of some fraction of the growth surface or fold surface of crystal that does not need molecular nucleation.

All quantitative thermal analyses of amorphous and semicrystalline PLA are presented in the frame of two equilibrium baselines of the heat capacities of the solid and liquid, using the Advanced Thermal Analysis System (ATHAS).