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Shear-induced crystallization of biodegradable polymers

Abstract in English

Within the frame of the doctoral dissertation, the shear-induced crystallization of a series of polylactides (PLA)s was investigated, including commercial PLAs with similar molar masses, with weight average masses, M_w, of 128 kg /mol and 109.5 kg/mol, but with different D-lactide content, 2.8% and 1.5%, respectively, as well as optically pure poly(L-lactide)s (PLLA)s synthesized in CBMiM PAN. In the latter case, PLLAs with a star structure with different molar masses as well as their linear counterparts were investigated. The crystallization of the commercial random copolymer poly(butylene adipate-co-terephthalate) (PBAT) with M_w of 67 kg/mol and the content of aromatic and aliphatic repeating units of 48.4 mol% and 51.6 mol%, respectively, was also investigated. The non-isothermal crystallization of these polymers during cooling at rates of 10 °C/min i 30 °C/min, induced by shearing at different rates at different temperatures, was studied. The crystallization kinetics was analyzed by the light depolarization method. The structure and thermal properties of crystallized materials were investigated by: differential scanning calorimetry, light microscopy and scanning electron microscopy, X-ray methods and small angle light scattering. In the case of star PLLAs and their linear counterparts with similar molar masses, static isothermal and non-isothermal crystallization was also studied with differential scanning calorimetry and light microscopy. In particular, the dependence of the growth rate of spherulites on temperature was determined.

The shear induced crystallization of commercial PLAs as well as PLLAs during cooling at rates at which static crystallization did not occur, 10 °C/min and 30 °C/min for PLAs, and 30 °C/min for PLLAs. Moreover, it enhanced crystallization of PLLAs during cooling at a rate of 10 °C/min, which was reflected in an increase of the temperature of the maximum crystallization rate and the achieved crystallinity.

Although the shear-induced crystallization depended on the shearing conditions as well as the cooling rate, in the case of commercial PLAs the lower content of D-lactide intensified the crystallization, although the maximum crystallinity achieved in these polymers was similar and

equal to 39 wt%. Moreover, in these polymers, shear mainly caused an enhancement of point-like nucleation, which resulted in the absence of crystal orientation.

It has also been shown that during static crystallization, the star structure of PLLA macromolecules significantly slowed down the growth of spherulites in the polymers with M_w of about 120 kg/mol, in the temperature range of (120−145) °C. The growth rate of spherulites of PLLAs with M_w > 200 kg/mol was smaller than that of spherulites of PLLAs with M_w of about 120 kg/mol, but was not affected by the star structure. Moreover, only in linear PLLA with M_w of 121 kg/mol the I regime of crystallization was observed. Under isothermal conditions, PLLAs with M_w of about 120 kg/mol achieved higher crystallinity than PLLAs with M_w > 200 kg/mol. The differences in the spherulite growth rates of PLLAs were reflected in their kinetics of isothermal crystallization, as well as in the temperatures of non-isothermal crystallization during cooling and the achieved crystallinity.

Although the crystallization of PLLAs was influenced by the shearing conditions and the cooling rate, the influence of the shear depended on the molar mass as well as the structure of the macromolecules. The shear more intensified the crystallization of PLLAs with M_w > 200 kg/mol than the crystallization of PLLAs with M_w of about 120 kg/mol. In the case of the latter, the shear more intensified the crystallization of star PLLAs than that of linear PLLA. On the other hand, the crystallization of linear PLLA with M_w of 240 kg/mol was similar or even slightly stronger than its star counterpart with similar M_w but a lower z- average molar mass, M_z. Moreover, orientation of the crystals and polycrystalline aggregates nucleated on fibrillar nuclei were observed in PLLAs. Thus, there was not only an intensification but also a change in the nature of nucleation.

In the case of PBAT, shear elevated the temperature of the maximum crystallization rate, whereas the degree of crystallinity only slightly increased, which was accompanied by a marginal increase in the average lamellae thickness. The study of the structure did not show the orientation of the crystals but only a reduction in the size of the spherulites, which indicated that there was only an intensification of point-like nucleation.