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“Solid-state modification as a tool to control the chemical microstructure and the morphology of novel bio-based copolyesters”

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The aim of the performed study was to obtain knowledge on the structure-property relationship of two series of copolyesters. More specifically, the influence of a phase-separated morphology present in the amorphous phase of the copolyesters on the properties was studied. Besides, knowledge about the use of phase separation, in combination with SSPC, as a tool in the preparation of materials with novel properties would be obtained. To this end, two series of copolyesters were prepared based on a semi-crystalline polyester, i.e. poly(butylene terephthalate) (PBT), and a bio-based fatty acid dimer derivative (FADD). One series was prepared using solid-state polycondensation (SSPC), which was performed below the melting temperature of the semi-crystalline polyester. Hence, during SSPC the crystalline phase of the semi-crystalline polyester is retained and this would lead to copolyesters with a more blocky chemical microstructure. However, the morphology obtained in the the amorphous phase after SSPC could be phase separated or homogeneously mixed (Figure 1a and b), depending on the miscibility of the additional monomer and the PBT matrix. It was expected that these materials yielded a phase separated morphology if prepared by SSPC (shown using ^{13}C-NMR spectroscopy).

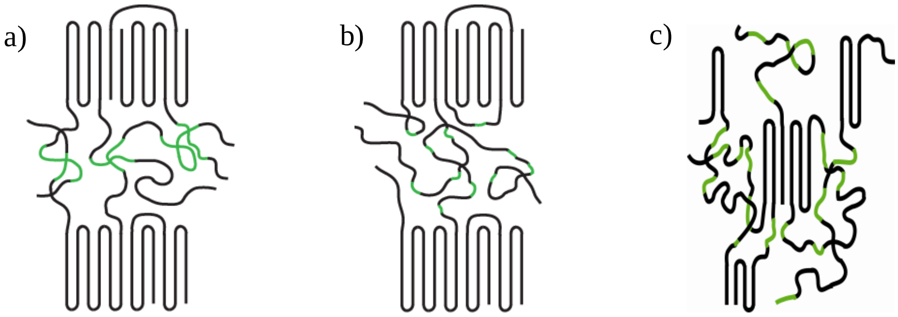

Figure 1. A schematic representation of the expected morphology obtained after incorporation of an additional monomer by SSPC yielding a a) phase separated or b) homogeneous amorphous phase and c) the random morphology as prepared by MPC.

A second series was prepared using conventional melt polycondensation (MPC) and this led to random copolyesters (Figure 1c). These materials were used as the benchmark for the materials prepared by SSPC. Each series consisted of five copolyesters with varying FADD content. Their phase structure and crystallization behavior was studied as a function of the temperature, composition and preparation method. This was performed by studying the Guinier’s region obtained from the previously mentioned material as function of the temperature. It was expected that the by SSPC prepared materials would show a phase-separated amorphous phase irrespective of the temperature. Moreover, these materials would have superior crystallization properties as a result of this phase separation. Besides, the stability of the phase separated morphology was studied in time by studying the Porod’s regime. This was performed in order to establish if these materials would randomize upon melting as materials would do exhibiting the structure shown in Figure 1b.

Various small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments were conducted on the previously mentioned samples. The samples were molten and subsequently recrystallized from the melt. This study was performed in order to analyze the influence of the FADD content on the crystallization behavior. Moreover, the influence of the morphology (random or blocky) on the crystallization behavior was studied. It was observed that samples prepared by SSPC with low FADD contents behave similarly to unmodified PBT samples. Copolymers prepared by SSPC with higher FADD contents, crystallized more slowly from the melt. This indicated even though phase separation was present the crystallization was hindered. The obtained SAXS results proved that a phase-separated morphology was present for the whole temperature range (25 – 260 °C) for the SSPC prepared copolymers with higher (≥ 20 wt%) FADD contents (Figure 2). No significant changes in the SAXS patterns were obtained during the heating of the copolyesters.

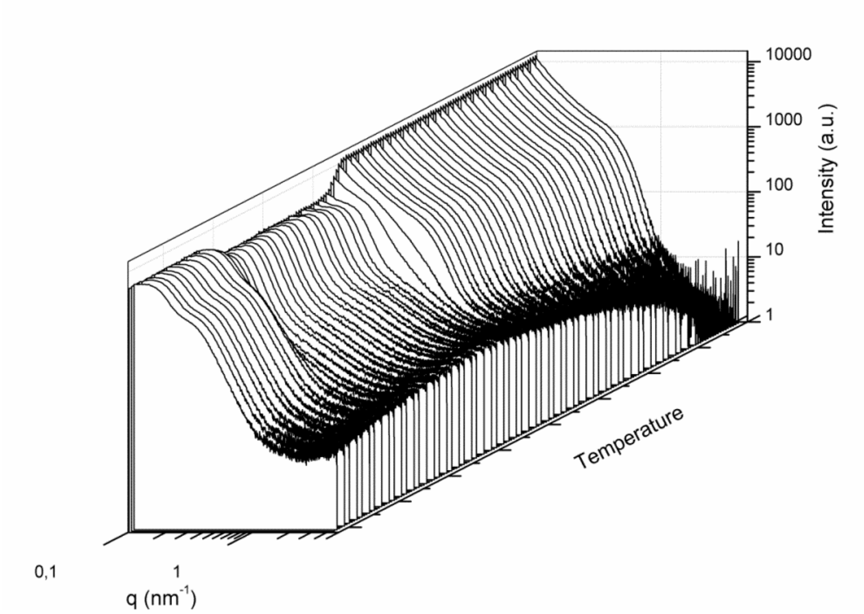

Figure 2. Temperature dependent SAXS results for a copolyester with 30 wt% FADD>

The resulting SAXS data after the recrystallization showed a shift in the long spacing of the crystalline-amorphous stacks. This could be explained by the fact that during SSPC the polyesters anneal and forms thicker crystals. It was not possible to obtain a similar crystalline phase just by cooling from the melt, something which was also observed by differential scanning calorimetry (DSC). The results obtained from the SAXS measurements were inconclusive and more time needs to be spent at analyzing the structure of the SSPC prepared copolyesters in the melt. The phase-separated structure was less significant or not present in the MPC prepared copolyesters, as observed from SAXS. The FADD in these copolyesters was more randomly distributed along the polymer backbone (Figure 1c). This yielded slower crystallization and not all the materials prepared by MPC did crystallize within the time frame of the experiment. This clearly showed the influence of the morphology exhibited by copolyesters with similar compositions. Moreover, the SAXS results were dependent on the temperature, as the temperature increased the long spacing of the crystalline phase started shifting to lower q-values. This was attributed to melting of a part of the crystalline fraction, because after the MPC less perfect crystals were obtained when compared with SSPC prepared materials. From the simultaneous temperature-dependent WAXD studies it was clear that no co-crystallization took place during cooling from the melt. Moreover, the addition of the FADD did not cause any changes in the crystal structure over the whole analyzed temperature range. This clearly showed that the FADD was exclusively present in the amorphous phase, which was expected.

From the obtained SAXS results the long spacing and related spacings from the copolyesters were studied as a function of FADD content and preparation method. As benchmark for this study the pre-polymers (before SSPC or MPC) were analyzed. It was observed that the long spacing of the pre-polymers increased and reached a plateau value at 37.5 wt% FADD, this proves that monomer swelling of the amorphous phase between the crystalline lamellae had occurred before the reaction. However, when the FADD content exceeded 20 wt% this FADD was excluded to the interspherulitic amorphous phase. The long spacing of the copolymers increased when more FADD was incorporated, caused by an increase in the thickness of the amorphous phase by swelling. When these results were compared with results obtained from the samples prepared by MPC it was observed that the thickness of the crystalline phase was much smaller. The result was ascribed to the random distribution of FADD residues along the copolyester backbone, which makes crystallization more difficult.

The thermal stability of the phase-separated morphology was analyzed by keeping a sample in the melt and continuously measuring SAXS on this sample. The results from this experiment were inconclusive because the sample moved from the beam and there was not enough time to repeat this experiment. It was believed that due to the phase separation (Figure 1a), randomization of the copolyester backbone would not occur on a significant scale. Copolymers prepared by SSPC which a random morphology in the amorphous phase (Figure 1b) would fully randomize upon melting and would give similar results as the copolyester prepared by MPC. Hence, phase separation could make these materials processable without the loss of the superior properties.

It can be concluded that some of the materials prepared by SSPC showed a phase-separated morphology (Figure 1a). The materials prepared by MPC did not or hardly showed any significant phase separation, proving the more random distribution of the FADD units along the backbone of the copolyester (Figure 1c). This was concluded from a study of the Guinier’s region from the SAXS results. The morphology of the materials prepared by SSPC did not change significantly over the temperature range during heating. Whereas, a shift in the value of the long spacing obtained from the crystal phase was observed for the MPC prepared samples. Moreover, it was observed that copolyesters prepared by SSPC with a low FADD content shown similar crystallization properties as the neat semi-crystalline polyester, when the FADD content is increase this changed. Even though there was a phase-separated morphology present, crystallization was hindered. However, all samples prepared by SSPC, crystallized more readily compared with the MPC prepared samples. This proved the use of SSPC as tool in the preparation of copolyesters with novel properties. Using WAXD it was observed that no co-crystallization took place as expected. Unfortunately, the experiments probing the stability of the phase-separated morphology were not successful. Hence, it is not possible to conclude if these materials could be processed in the melt. The role of the phase separation would have been that these materials would not randomize upon melting, this could not be proven but it is expected. A study towards the phase behavior as a function of time in the melt would be necessary. Nevertheless, it can be concluded that SSPC is a powerful tool in the preparation of copolymers with novel properties. Future studies should include the stability study and the study of the structure at very low angle. Moreover, the behavior of the morphology under shear stress could be studied.

On the above presented results in combination with previously obtained results, a scientific paper is being writing at the moment, aimed for the journal *Macromolecules*.