

## Abstract

With the growing awareness of environmental problems induced by plastic waste, great interest has been given to biodegradable polymeric materials. Until now, aliphatic polyesters have been found to be the most attractive biodegradable polymers. Although the aliphatic polyesters are available on the market, their thermal and mechanical properties do not favor their usage in many applications. Therefore the incorporation of aromatic units along aliphatic polyester chains appeared to be a good concept to merge biodegradability characteristic for aliphatic polyesters and good thermal and mechanical properties typical for aromatic polyesters. However, aliphatic-aromatic copolyesters (AAC) are biodegradable under condition of sufficiently short sequences of aromatic units which was shown by Witt et al [1]. Moreover, Witt et al. [2] drew a conclusion that AAC remain biodegradable provided the population of aromatic ester comonomers does not exceed 60 mol%. Up to now, there have been reports about copolyesters possessing from one up to three aliphatic units and one aromatic. However, none of them focused on the influence of chemical composition on nucleation of crystallization and on crystallization of AAC, especially that too short sequences of crystallizable units can significantly decrease crystallizability.

One of the aims of our studies, was to specify the chemical composition of AAC, that would optimally combine ability to biodegradation and good physical performance. Dr. Sławomir Dutkiewicz of Institute of Biopolymers and Man-Made Fibers, Łódź, Poland, was kindly asked to synthesize a range of aliphatic-aromatic copolyesters containing: butylene adipate, butylene succinate, butylene glutarate and butylene terephthalate esters (PBASGT), differing in composition [3]. Obtained PBASGTs were characterized by  $^1\text{H}$  NMR spectroscopy.

Using the assignment of  $^1\text{H}$  NMR [4, 5, 6] resonances due to homogeneous and heterogeneous dyads, the fraction of dyads, molar content of aliphatic and aromatic units, mean length of aliphatic and aromatic sequences and the randomness index were investigated for all copolyesters. All of the synthesized copolyesters having the content of aromatic component from 10% to 90% were nearly random copolymers. Surprisingly, it appeared that almost all PBASGTs are able to crystallize. It turned out also that in all the crystallizable copolyesters only butylene terephthalate (BT) blocks are able to crystallize in the crystallographic form characteristic of homo poly(butylene terephthalate). The increase of aromatic units' contents did not change the crystallographic structure, in contrary to the results obtained by Li et. al [7] for similar systems, however, with only one aliphatic ester, succinate. It is worth to underline that there are slight differences in several X-ray diffraction peak positions (not all) of synthesized copolyesters and aromatic homopolymer.

On the DSC heating traces for copolyesters with aromatic content less than 60% a broad peak of melting is observed, which becomes narrower and shifted to higher temperatures with the increase of aromatic units. The same phenomena is observed for the crystallization peak. The changes of glass transition temperature together with the increase of aromatic units content was also observed.

Mechanical properties of aliphatic-aromatic copolyesters in a range of compositions from 10 to 90% of aromatic component were studied by tensile deformation. Copolyesters with aromatic unit content below 60% deformed in an uniform manner characteristic for rubbers. With increasing aromatic units content the yield stress point becomes well-defined and the deformation manner changes. For copolyester with 80% of aromatic content a rubber deformation manner becomes stress-oscillating (or self-oscillating) due to jumping from uniform stable necking to neck propagation form of deformation and reverse. With further increase of aromatic content to 90% the deformation proceeds in a manner characteristic for semicrystalline thermoplastics with highly localized yielding, and formation of a well-defined neck or by simple brittle breaking, which is characteristic for aromatic homopolymer.

From the synthesized copolyesters the most promising composition with respect to biodegradability, thermal and mechanical properties was selected for further investigation of crystallization. It was revealed that PBASGT crystals form spherulitic aggregates filling the entire volume of the material with spherulites of average radius above 7  $\mu\text{m}$ , which are formed from few nanometers thick fibrous crystals while the crystallinity reached 20%. Fibrous crystals thickness appeared as the main factor influencing the depression of PBASGT melting temperature.

The studies showed that the crystallization behavior of PBASGTs is strongly driven by the presence of self-nucleation. Self-nuclei can survive the temperature up to 160°C. Self-nucleation studies evidenced the existence of three self-nucleating domains determined by the temperature at which PBASGT was melted.

The chemical structure, morphology and crystallization behavior of PBASGT were compared with commercial aliphatic-aromatic copolyester of butylene terephthalate and butylene adipate (PBAT), Ecoflex<sup>®</sup>.

It was expected that butylene adipate crystalline sequences in a random copolymer with butylene terephthalate would show much lower crystallization and melting temperatures than those of homopolymer. In order to check the possibility of crystallization of aliphatic component, samples of the copolymers were cooled down to 4°C and kept at this temperature for 24 h. On both heating thermograms melting endotherms were presented. Melting of crystals of aromatic components was observed at 110°C and 121°C for PBASGT and PBAT, respectively. In addition, a small endothermic peak at 39°C was seen on the thermogram of PBAT that is identified as melting of crystals of aliphatic sequences. No such peak can be detected for similarly treated PBASGT sample. Thus it appeared that, in contrast to aliphatic part of PBAT, aliphatic part of PBASGT is unable to crystallize, when annealed below room temperature.

Comparison of SAXS correlation function evolution of PBASGT and PBAT showed that the crystalline structure of aromatic component forms quickly in the case of PBAT, not in a step-wise manner as the structure of PBASGT. However, the final average thickness of crystals of PBASGT and PBAT is nearly identical (3.5 nm). The measured average crystal thickness closely corresponds to the length of 3 butylene terephthalate repeat units (3.48 nm) in the PBT crystal structure.

Strong and distinct self-nucleation phenomena led us to a conclusion that crystallization of PBASGT can be accelerated by introduction of nucleating agents. It was found that the nucleating agents that are effective for PBT are also effective for PBASGT. Two types of phthalocyanine and talk were found to be effective. For example, a nucleation of PBASGT with green phthalocyanine shifted the nonisothermal crystallization peak from 70°C to 84°C during cooling at the rate of 10°C·min<sup>-1</sup>. However, the crystallization peak temperature shift for most effective nucleating agent was significantly smaller than that for a sample with active self-nuclei (90°C).

## **Bibliography**

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