CRystallization behavior of clay nanocomposites prepared from a degradable alternating copolyester constituted by glycolic acid and 6-hydroxyhexanoic acid

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Introduction
Aliphatic polyesters constitute nowadays the main family of degradable polymers due to the presence of hydroxylable ester groups. However, in general mechanical and thermal properties are not adequate to satisfy the requirements for their use in applications such as packaging materials. Properties of materials can also be considerably modified by the incorporation of layered silicates into the polymer matrices. The resulting biodegradable nanocomposites possess several advantages generally attained at low silicate content (less than 5%). Although, biodegradable nanocomposites have very strong future prospects the present low level of production and high costs still restrict them form a wide range of applications.

The aims of this work are to prepare an exfoliated nanocomposite from a new biodegradable copolyester with an alternating distribution of glycolic acid and 6-hydroxyhexanoic acid units, and to study the influence of clay particles on the isothermal crystallization process. Thus, overall crystallization rate, crystal growth rate and change of morphological parameters during crystallization are analyzed for both the pristine and the nanocomposite samples by using different techniques.

Nanocomposite Preparation
An exfoliated nanocomposite was prepared by the film-casting technique from the C25A organo-modified clay and a new biodegradable polyester derived from glycolic acid and 6-hydroxyhexanoic acid. This polymer has a sequential monomer distribution and high crystallinity, allowing a detailed study of its isothermal crystallization.

X-ray diffraction and Transmission Electron Microscopy

The samples were studied by means of X-ray diffraction and transmission electron microscopy. It was obtained an exfoliated structure by the film-casting technique from the addition of C25A organoclay.

FTIR Analysis

Absorption FTIR spectra (1500-1000 cm⁻¹) of the neat polyester at the beginning and at the end of isothermal crystallization at 50°C

FTIR is highly sensitive to molecular conformation and packing density, hence its usefulness in polymer crystallization studies. Characteristic bands can be correlated to the crystalline and amorphous phases of the bulk and typically remain distinguishable over the course of crystallization. Different bands in this region can be assigned to the crystalline and amorphous phase (1282 and 1196 cm⁻¹) and the crystalline phases (1420, 1234 and 1222 cm⁻¹) were chosen.

Optical microscopy studies and Calorimetric Data.

Primary nucleation and crystal growth rate decreased significantly with the incorporation of nanoparticles. The overall crystallization rate of the nanocomposite was lower than that of neat polymer. A similar equilibrium melting point was derived from both samples.

Crystalline morphology and isothermal crystallization from SAXS/WAXD data

Deconvolution of the WAXD profile of poly(glc-alt-6HH)/C25A at 50°C

Evolution of crystallinity determined from WAXD at 50°C of the neat polymer (•) and its nanocomposite (○)

SAXS/WAXD 3-dimensional profiles of poly(glc-alt-6HH)/C25A during isothermal crystallization at 54°C

Time evolution of invariant (○). Bragg spacing (□), long period from the correlation function (●), crystal thickness (∆) and amorphous thickness (▲) during isothermal crystallization at 54°C of poly(glc-alt-6HH)/C25A.

Correlation functions at the end of crystallization at 50°C of the neat polymer (●) and its nanocomposite (○). The inset shows the final Lc (○) (△) and Ll (●) (□) spacings at various crystallization temperatures for the neat polyester (full symbols) and its nanocomposite (empty symbols).

Conclusions

X-ray and TEM observations revealed full dispersion of silicate layers and suggested a high miscibility between the polymer matrix and the clay.

Incorporation of C25A decelerated the mechanism of primary nucleation and crystal growth of poly(glc-alt-6HH), a trend commonly observed when high homogeneous dispersion of silicate layers occurs. A slight increase in the secondary nucleation constant was also inferred for the nanocomposite by considering the Lauritzen and Hoffman treatment.

SAXS data showed significant changes in the morphology of constituent lamellae since a dramatic decrease in the amorphous layer thickness was observed for the nanocomposite.