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Study of crystallinity and thermomechanical analysis of annealed poly(ethylene terephthalate) films

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Abstract

The objective of this article was the determination of the degree of crystallinity of a series of heat-set poly(ethylene terephthalate) (PET) films and their study by thermomechanical analysis (TMA) in order to elucidate a peculiar behaviour that takes place around the glass transition region. For this purpose, amorphous cast Mylar films from DuPont were annealed at 115 °C for various periods of time. Four methods were used to study the crystallinity of the samples prepared: differential scanning calorimetry (DSC), density measurements (DM), wide-angle X-ray diffraction (WAXD), and Fourier transform infrared spectroscopy (FT-IR). From the results obtained, the following conclusions are drawn: amorphous PET Mylar films can be crystallized in a degree of about up to 30% after thermal treatment for 30 min (cold crystallization) above glass transition temperature. When these semicrystalline samples are subjected to TMA, they show a two step penetration of the probe into them, which decreases with the increase of the degree of crystallinity. The first step of penetration was attributed to the shrinkage of the amorphous or semicrystalline sample, which takes place on the glass transition temperature, while the second step was attributed to the continuous softening of the sample, and the reorganization of the matter which takes place on heating run due to cold crystallization.

Keywords: Poly(ethylene terephthalate); MAF; RAF; Crystallinity; Glass transition temperature; Thermomechanical analysis

1. Introduction

Poly(ethylene terephthalate) (PET) is a semicrystalline alipharomatic thermoplastic polyester possessing interesting thermal and mechanical properties, such as tensile strength and elongation at break, chemical resistance, high ability to form fibers, low permeability in O_2 and CO_2 and melt processability [1]. Because of the excellent combination of the aforementioned properties, PET has found many applications in packaging materials, fibers, electrical equipment (mainly capacitors) and even the automotive and construction industries.

The properties of PET are due mainly to its chemical alipharomatic structure, but also depend on its crystallinity, orientation, molecular weight, etc. The

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crystallization of this polyester, or even of the polymer matrix in composite materials, may cause a volume reduction up to 20%, which in turn results in generation of mechanical stresses. So, it is a pressing need to know its crystallinity in any case, since this physical property affects generally its behaviour. In this work we tried to obtain, by thermal treatment at 115 °C of amorphous PET films, a series of samples with different degree of crystallinity and to determine their crystallinity by four well known analytical methods [2]. These techniques were: differential scanning calorimetry (DSC), density measurements (DM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). All these techniques were used in the past for the study of PET and other similar polymers taking into account that the semicrystalline polymer consists of a two-phase system. According to the two-phase model, it is assumed that any semicrystalline polymer is composed of an amorphous part (W_a) and a crystalline one (W_c), that is

$$W_a + W_c = 1$$

According to Craig et al. [3] for most pharmaceutical compounds, there does appear to be general acceptance of this model for a semi-crystalline material containing discrete crystalline and amorphous regions of uniform behaviour equivalent to that of “perfect” crystals and “perfect” glasses. However, the examination of the polymer science literature suggests that there may be alternative approaches to this issue. More specifically, it is now recognized that a proportion of amorphous material in semicrystalline polymers may exist in a distinct state, whereby molecular mobility is restrained to a greater extent than in the “perfect” glass. This material, known as “rigid amorphous fraction” (RAF), is believed to be associated with the interface between the crystalline and the mobile amorphous phases and has properties that are intermediate between them [4–9]. As the material is cooled from the melt through the crystallization temperature a proportion remains completely amorphous (the mobile amorphous fraction, MAF), while a further proportion forms a crystalline solid. However, associated with this crystalline solid is the RAF that does not undergo a mobility change on subsequent cooling through the glass transition temperature. Consequently, this fraction does not contribute to heat capacity change at the glass transition. This leads to discrepancies between the degree of crystallinity calculated from ΔC_p and the figure calculated from, for example, melting or crystallization behaviour or from data obtained using such techniques as X-ray diffraction, NMR or Raman spectroscopy [10]. During the last few years, various independent studies in the literature, employing different experimental techniques such as FT-IR spectroscopy [11], temperature modulated differential scanning calorimetry (TMDSC) [12,13] and X-ray scattering techniques [14,15] have shown that a three-phase model is more appropriate to describe the microstructure of PET. According to this model the previous relation is transformed to the following,

$$W_{\mathrm{MAF}} + W_{\mathrm{RAF}} + W_c = 1$$

where W_{MAF} is the mobile amorphous phase, W_{RAF} is the rigid amorphous phase and W_c is the crystalline phase.

So, all the above methods have to be reexamined if they are reliable according to the three-phase model, since the relative constants for RAF are unknown.

The whole study of this work consists of two parts: the first one is the above mentioned preparation of the series of semicrystalline samples and their characterization for crystallinity and the second one is the thermomechanical analysis of these samples in order to elucidate the peculiar behaviour that was observed in the last few years in our research [16–19].

As it is known, in the solid state all amorphous polymers are stiff and glassy, the macromolecular chains are randomly arranged in space and are entangled without any possibility of changing their conformations and consequently the morphology of the polymer. The only movement that takes place in this state is the stretching, bending and rotating of macromolecular bonds. This glassy or vitreous state exists for a polymer up to the glass transition temperature (T_g). On heating, polymers soften in the aforementioned characteristic temperature range known as the glass–rubber transition region. In this region polymers behave in a leathery manner, because the additional energy induces the movement of macromolecular segments in the free volume. This new state is the rubbery state.

The glass transition temperature is usually determined by DSC or by dynamic thermomechanical analysis (DMTA or DMA), or even by thermomechanical analysis (TMA). The latter is a very useful thermal technique, because it allows detection and resolution of transitions that other techniques cannot see or separate and it is used to measure variations in