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Evidence of a monoclinic-like amorphous phase in composites of LDPE with spherical, fibrous and laminar nanofillers as studied by infrared spectroscopy

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ABSTRACT

Well-dispersed nanocomposites of LDPE with spherical silica and laminar and fibrous silicates have been prepared by melt compounding with nanofiller compositions ranging from 50 to 5 wt%. Spatial dispersion and size domains of the aggregates in the composites series have been evaluated by electron microscopies (SEM and TEM). The methylene rocking (700–740 cm^{-1}) and bending (1400–1480 cm^{-1}) modes of LDPE in these composites were studied by FTIR spectroscopy. When the nanofiller is present in a 40 or 50 wt%, the amorphous phase of polyethylene adopts a monoclinic arrangement. This arrangement is due to the confinement induced by the nanofillers on the polymer matrix. When the fibrous silicate or the spherical silica are used as nanofillers, a dilution of the concentrated composite or annealing bring about a relaxing of the amorphous structure of the polymer, and the monoclinic-like conformations disappear. When the nanofiller is a laminar silicate, dilution or annealing only partly eliminate the monoclinic-like structure, which remains in all cases an important fraction of the polymeric matrix.

1. Introduction

Since in 1993 nylon-montmorillonite composites with highly enhanced mechanical and thermal properties were prepared by in-situ polymerization in the Toyota Laboratories [1], time and resources have been devoted to develop similar improved materials and to understand the origin for such behaviour. For some time, it was given for granted that the inorganic component of the nanocomposite reinforces mechanically and locally the structure, and less attention was paid to the structure of the polymeric matrix in the nanocomposite. In the last years, the situation has changed and it is frequent to find research work dealing with the importance of the modification produced in the polymer matrix by the introduction of nanofillers. For example, it has been shown that the origin of the excellent mechanical properties of the nylon-montmorillonite composite is the development of a γ crystalline phase stabilised by the surface of the silicate [2]. Inorganic surfaces modify dramatically the polymer crystallization behaviour, and so many examples of changes in the semicrystalline morphology of the polymeric matrix of a nanocomposite can be found [3–5]. It is now borne in mind by the researchers in the area that together with the possible reinforcing effect of the nanofiller, the modifications in the semicrystalline morphology have to be considered very carefully.

Together with the semicrystalline morphology, modifications of the conformational structure of the polymer matrix amorphous fraction may also occur as a direct consequence of the presence of the inorganic nanofiller, though work in this connection is still really scarce. A priori, one can expect that the behaviour of the polymeric phase in nanocomposites will show strong resemblance to the behaviour of the polymeric phase in thin films and surfaces, where modifications in the conformational structure are reckoned and their effect on properties, for example on the glass transition temperature, proved [6].

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In this work, a study of the conformational structure of the polyethylene matrix in a series of composites with nanofillers of different geometries is undertaken, and strong conformational changes have been found, namely the presence of a monoclinic-like phase, at least partly non-crystalline, which is by far the most abundant structure in some of the composites. That polyethylene crystals can be monoclinic is well-known. Though orthorhombic is thermodynamically favoured under most crystallization conditions, plastic deformation of the polymer can make monoclinic the most stable of them both. This was demonstrated by Walter and Reding [7] and other authors [8,9] in cold-drawn polyethylene, and has been also detected more recently in rolled polyethylene [10], in battered polyethylene samples [11] and in ethylene containing copolymers [12]. This monoclinic structure, disappears almost completely if the stress disappears [7,8], and also if a sufficient annealing is produced between 50 and 80 °C [13].

The identification of the monoclinic crystalline form is not straightforward by X-ray diffraction [11], and so other techniques such as solid state ^{13}C NMR or infrared spectroscopy are used [11–13]. Since the pioneering works by Snyder [14] and Painter [15], infrared spectroscopy has been extensively used to detect and characterise the conformational structure of polyethylene by the study of the rocking, bending, and wagging modes of the methylene groups. When no preferred orientation or ordered chain arrangement exists, the methylene rocking modes of a polyethylene chain appear at 721 cm^{-1}; this is the case of either polyethylene in the molten or in a glassy disordered state. When the chains are not randomly placed, and a short range order exists, the possibility of interchain interaction appears and splitting of the band takes place: in the case of orthorhombic crystal unit cell, two bands appear at 719 and 731 cm^{-1} [15–19], in the case of a monoclinic arrangement a unique band at 716 cm^{-1} is seen. A very clear illustration of the rocking modes in the orthorhombic and monoclinic structures is shown by Painter et al. [15].

Methylene bending modes, due to long *all-trans* conformations, appearing in the range from 1450 to 1473 cm^{-1} and wagging modes in the range of 1300–1440 cm^{-1} are also sensible to the conformational structure [9,15,21]. 1455 cm^{-1} corresponds to short trans amorphous sequences, 1463–1461 cm^{-1} to trans sequences in the orthorhombic form and parallel to b-axis, 1466–1467 cm^{-1} to long trans disordered/amorphous sequences, 1471 cm^{-1} to trans sequences in the orthorhombic form and parallel to a-axis [9,22,23] and 1473 cm^{-1} to trans monoclinic arrangement [20]. Though most authors give for granted that bands at 715–717 cm^{-1} and 1472–1473 cm^{-1} indicate the existence of a *crystalline* monoclinic structure, it is important to bear in mind that a monoclinic arrangement of the chains does not necessarily imply the existence of well-developed monoclinic crystals [15,24].

The results presented in this work deal with a series of composites made up of a low density polyethylene and three nanofillers of different geometries: a spherical nanosilica, a fibrous silicate and a laminar silicate. Composites of concentration varying from 50 wt% (masterbatches) to 5 wt% were prepared with each of these nanofillers, which had been previously organophilised. The CH$_2$ rocking and bending modes of the polymeric matrix in the composites and of the aliphatic chains incorporated to the nanofillers are studied.

2. Experimental

2.1. Materials

The polymer matrix used in this study was LDPE Alcudia® 003: a film application grade polymer supplied by REPSOL YPF. The polymer main features are melt flow rate 2 g/10 min (190 °C, 2.16 kg), density 0.920 g cm^{-3} (23 °C), Vicat temperature 91 °C (under load of 10 N), melting temperature 111.6 °C (DSC) and calculated intrinsic viscosity 101.3 mL g^{-1}.

Silica nanoparticles (AEROSIL 200 from Degussa) and the fibrous phyllosilicate (PANGEL from TOLSA) have been organically modified following previously reported methods [25] and using octyltrimethoxysilane (Lancaster, 90%) as organic reagent. The organic content (determined by thermogravimetric analysis) in the nanoparticles after the modification reaction was about 7 wt%. The organophilised silica nanoparticles and phyllosilicate will be called hereafter SPH and FIB, respectively.

An organically modified laminar phyllosilicate, (CLOISITE 15A from Southern Clay Products) was subjected to an additional ionic exchange reaction by using tetraoctadecyl ammonium bromide as ionic salt. The as-modified montmorillonite had an organic content of 72 wt% measured by thermogravimetric analysis and will be named as LAM in what follows. Small angle X-ray diffraction (SAXS) was used to evaluate the gallery distance in LAM compared to the original CLOISITE 15A. The layer spacing of the compounds was calculated from the measured reflection angles using the Bragg equation. The measured *d*001 spacing of the CLOISITE 15A suspended in water was determined to be 1.23 nm. LAM shows a single reflection at 2.2° corresponding to a layer spacing of 4.01 nm.

2.2. Composite preparation

The composites were prepared in the melt by using a Haake Rheocord model 9000. The most concentrated composites (50 wt% for FIB and 40 wt% for SPH and LAM) were prepared by physical mixing in the solid state and subsequent shearing at 20 rpm for 10 min at 130 °C. These three samples will be called hereafter LDPE-SPH-40, LDPE-LAM-40, and LDPE-FIB-50, where, according to the nanofiller geometry, SPH, FIB, and LAM stand for spherical nanosilica, fibrous silicate or laminar silicate, respectively, and the number at the end stands for the weight fraction of the nanofiller in the composite.

Dilutions of these concentrated composites were prepared by mixing them with an adequate amount of LDPE at 130 °C for 10 min at a shear rate of 40 rpm to obtain composites with a 25 wt% of nanofiller content. These samples have been called LDPE-LAM-25, LDPE-SPH-25, and LDPE-FIB-25. Finally, composites with a 5 wt% of nanofiller were prepared by kneading the 25 wt% composites with an adequate amount of LDPE in the mixer at 160 °C and