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Material properties

Melt processed polyethylene/fullerene nanocomposites with highly improved thermo-oxidative stability

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ABSTRACT

The thermo-oxidative stability of melt processed polyethylene composites with the two fullerenes C_{60} and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was studied with the aim of comparing the stabilization effect of both fullerenes on three different polyethylenes (PE). The results obtained show that, irrespective of the specific polyethylene being considered, C_{60} loadings as low as 1.0 wt% cause a dramatic increase in the thermo-oxidative stability of the corresponding composites (up to 64.8 °C at T2% and 113.8 °C at T5%, TX% being the temperature corresponding to a mass loss of X wt%), in agreement with previous reports. Furthermore, and more importantly, this work shows for the first time that the thermo-oxidation stability effect caused by PCBM is even higher than that of C_{60}, the difference between both being particularly significant in the early stages of degradation, i.e. for mass losses ≤ 2 wt%. For example, polyethylene composites with 1.0 wt% PCBM show T2% values which are systematically higher than those of the corresponding composites with 1.0 wt% C_{60}, the difference between the T2% values of the two composites being 38.8 °C, 67.1 °C and 26.4 °C in the three different polyethylenes considered. Therefore, when compared with C_{60}, PCBM is particularly more effective at delaying the beginning of the thermo-oxidative degradation. According to our results, PCBM loadings as low as 1.0 wt% can increase the thermo-oxidative stability of polyethylene composites by more than 130 °C and these are, as far as we know, the highest thermo-oxidative stability results induced by nanoparticles ever reported in the literature for polyethylene.

1. Introduction

Polyethylene (PE) is a very important commodity plastic, the global PE market being the largest polymer business (per volume) in the world today. Approximately forty percent of all the resins used in the world in a variety of applications, from bags for waste to automotive parts, are made from polyethylene.

Although polyethylene is a polymer with a simple chemical structure, its molecular structure depends on the polymerization technique used for its production. High-pressure polymerizations with radical initiation yield low density polyethylene with a large number of branches, while catalytic processes usually produce polyethylene with higher density as a result of linear chains with more regular structures.

PE can be processed using the main thermoplastic processing technologies available in industry such as extrusion, injection molding, rotational molding, blow molding, etc. During processing the polymer is subjected to the effect of heat, shear and oxygen and, as a consequence of these factors, chemical degradation may occur.

The thermal degradation of PE in oxygen-free environments is known to start with the random scission of the polymer chains to form alkyl radicals [1]. These radicals then participate in further reactions such as de-polymerization reactions through β-scission and hydrogen transfer reactions (both intra- and intermolecular).

In the presence of oxygen, the thermo-oxidative degradation is also a free radical chain reaction with formation of alkyl radicals which react with molecular oxygen forming peroxy radicals. The peroxy radicals form hydroperoxides on abstraction of hydrogen from the polymer chains. The hydroperoxides decompose fast giving rise to oxy and hydroxyl radicals. Chain termination occurs by recombination or disproportionation of radicals [2,3].

PE suffers from a relatively low thermal and thermo-oxidative stability and, therefore, with the purpose of improving this particular property, it has been previously compounded with a large number of different micro- and nanoparticles. Amongst the

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particle fillers considered are: clays (montmorillonite, silica, etc) [4–18], layered double hydroxides (LDHs) [10,19,20], calcium carbonate ($CaCO_3$) [21], carbon nanotubes (CNTs) [13,22–26] and the fullerene C_{60} [27–30].

Fullerenes have high electron affinity being good free radical scavengers and, therefore, as previous studies have shown, they can have a stabilizing effect in polymers which degrade through free radical degradation mechanisms. The few known studies on the thermal stabilization effect of C_{60} on polyethylene composites were all performed by Zhao et al. [27–30] using high-density polyethylene (HDPE). In the earliest report Zhao et al. [27] observed that, on the addition of 0.5 wt% C_{60}, the onset thermal decomposition temperature (T_{onset}) of HDPE increased by 70 °C in nitrogen and by 38 °C in air. Later, in a more detailed study [28] the same authors reported a much smaller increase of only 14 °C in the T5% in nitrogen and an increase of 91 °C in the T5% in air, on addition of 2.5 wt% of C_{60}, T5% being defined as the temperature corresponding to 5% of total mass loss. A study of the kinetics of the thermal and thermo-oxidative degradation of HDPE and HDPE/C_{60} nanocomposites [29] has shown that the addition of C_{60} increases the activation energy of degradation both in N_2 and in air atmosphere. In a more recent study [30], the same authors reported increases in T5% in air atmosphere of 43 °C on addition of 1 wt% C_{60} and 69 °C on addition of 2 wt% C_{60}.

The fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [31,32] is an electron acceptor with applications in organic photovoltaics [33]. PCBM has been previously shown to stabilize some pi-conjugated polymers, commonly used in organic electronics, by reducing their rate of degradation at high temperatures under thermo-oxidation conditions (air atmosphere) [34,35]. Our group has recently reported, for the first time in the literature, on the thermal stabilization effect of PCBM in common thermoplastic composites, namely in polystyrene/PCBM [36] and in poly(methyl methacrylate)/PCBM [37] composites prepared through solution blending. In the particular case of polystyrene composites, our studies have shown that the thermal stabilization effect of PCBM was clearly higher than the corresponding effect of C_{60}, and we attributed this higher thermal stabilization effect of PCBM to the better dispersion of the PCBM nanoparticles in the polystyrene matrix when compared to the C_{60} nanoparticles. The impact of PCBM on the thermal stability of polyethylene composites has still not been reported on the literature.

In the present work, we conduct a detailed comparative study on the impact of the two fullerenes, C_{60} and PCBM, on the thermal and thermo-oxidative stability of the corresponding polyethylene composites prepared by melt processing. Three different polyethylenes were considered as well as several fullerene loadings in the range 0–3 wt%. Our goal is to help elucidate how the functionalization of the fullerenes affects the thermal stability of the corresponding polyethylene composites.

2. Experimental section

2.1. Materials

Three different polyethylenes, hereafter simply referred to as PE-1, PE-2 and PE-3, were considered in this work and with the following specifications: a) PE-1 is a medium density (0.934 g/cm^3) metallocene polyethylene from Total Petrochemicals (Product name: M3583UV), commonly used in rotational molding and with Melt Flow Index (MFI) = 8 g/10 min (190 °C, 2.16 kg – ISO 1133); b) PE-2 is a low density polyethylene (0.920 g/cm^3) from Carmel Olefins (Brand Name: Ipethene; Grade Name: 323), film extrusion grade with MFI = 2 g/10 min (190 °C, 2.16 kg – ISO 1133) and c) PE-3 is a low density polyethylene (0.906 g/cm^3) from Sigma–Aldrich (catalog # 427799), with average Mw~35.000, average Mn~7.700 and MFI = 2250 g/10 min (190 °C/2.16 kg – ISO 1133).

The two fullerenes considered in this work were: a) C_{60} (>99.5% purity, Solenne BV, M_w = 720.64 g mol^{-1}) and b) phenyl-C61-butyric acid methyl ester (PCBM) (>99% purity, Solenne BV, M_w = 910.88 g mol^{-1}).

The chemical structures of all the materials (polymer and fullerenes) used in this work are shown in Fig. 1.

2.2. Experimental procedure

PE-1, PE-2 and PE-3 were melt compounded with C_{60} and PCBM in a Microlab Twin Screw extruder from Rondol, using the experimental conditions indicated in Table 1. In this preparation step, appropriate amounts of each polymer and each fullerene were mixed in powder form and then fed into the twin-screw extruder. The extruded samples were then stored for subsequent characterization.

Nanocomposites with the following compositions were prepared: PE-1 nanocomposites containing 0.1 wt%, 0.5 wt%, 1.0 wt% and 3.0 wt% of C_{60} and 1.0 wt% of PCBM; PE-2 nanocomposites containing 1.0 wt% of C_{60} and 1.0 wt% of PCBM; PE-3 nanocomposites containing 1.0 wt% of C_{60} and 1.0 wt% of PCBM.

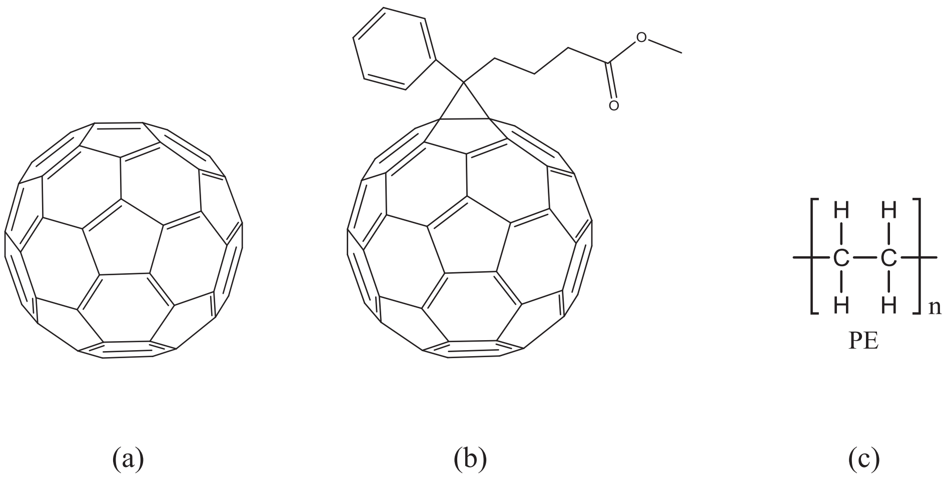

Fig. 1. Chemical structures of: (a) C_{60}; (b) PCBM and (c) Polyethylene (PE).