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Material behaviour

Impact of fullerenes on the thermal stability of melt processed polystyrene and poly(methyl methacrylate) composites

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ABSTRACT

The impact of the two fullerenes C_{60} and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) on the thermal and thermo-oxidative stability of the corresponding melt processed composites with the two polymers polystyrene (PS) and poly(methyl methacrylate) (PMMA), was studied using both dynamic and isothermal thermogravimetric analysis (TGA). For each polymer, three different composites with C_{60} loadings of 1.0 wt% and 3.0 wt% and PCBM loadings of 1.0 wt% were considered. The aim of this work was to compare the stabilization effect of both fullerenes on PS and PMMA. The results obtained show unequivocally that, although PCBM has lower thermal and thermo-oxidative stability than C_{60}, the PS-PCBM and PMMA-PCBM composites have higher thermal and thermo-oxidative stability than the corresponding PS-C_{60} and PMMA-C_{60} composites. These results corroborate our previous reports, on showing that PCBM is better than C_{60} at improving the thermal and thermo-oxidative stability of polymers which degrade through radical degradation mechanisms.

1. Introduction

In the last few decades, a large number of studies have been performed aimed at improving the thermal and thermo-oxidative stability of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by compounding them with different micro- and nanoparticles as well as with chemical antioxidants. Amongst the particles considered are: clays (montmorillonite, etc) [1–14], layered double hydroxides (LDHs) [15–18], cadmium sulfide [19], aluminum hypophosphite [20], silica [21–25], polysilsesquioxanes [26], calcium carbonate [27], alumina oxides [28,29], antimony oxide [30], iron oxide [10,31], titanium oxide [10,31,32], zinc oxide [29,33], magnesium dihydroxide [34], silver [35], titania [36], zirconia [37], phenolic phosphite antioxidants [38], photoinitiators [39], graphite [40,41], carbon nanotubes [42] and the fullerenes C_{60} [43–52] and PCBM [46,52].

Troitskii et al. [43] observed that the addition of 0.04 mol% of C_{60} to PS caused an increase of ca. 30 min in the induction period that precedes the beginning of mass loss under an oxygen atmosphere at 238 °C. Zeinalov et al. [44] observed that the addition of 1% wt of C_{60} to PS increased the thermo-oxidative stability of PS from >270 °C to > 300 °C. Kim et al. [45] prepared C_{60}/PS nanoparticles by emulsion polymerization which also showed increased thermal stability when compared to the pristine PS.

The addition of small quantities of C_{60} ($\leq$0.2 mol%) to PMMA was also shown by Troitskii et al. [43,47] to retard considerably the polymer's thermal degradation both in vacuum [47] and in the presence of oxygen [43]. The authors attributed this effect to the interaction of C_{60} with macro-radicals, which are generated in the thermal degradation of PMMA, with formation of less reactive species. An increase in the thermo-oxidation stability of PMMA upon addition of 1 and 10 wt% C_{60} has also been reported by Ginzburg et al. [48]. Zhogova et al. [49] found that C_{60} increases the temperature of thermal degradation of PMMA when exposed to ionizing radiation. Zuev at al [50] have also reported on the stabilizing effect of C_{60}, in concentration of ca. 1 wt%, responsible for increasing the thermal stability of acrylic polymers. According to these authors, the addition of C_{60} hinders the random scission reactions of the main chain which occur through a radical pathway, but does not influence the non-radical reactions in the side chains, which occur at higher temperatures. Similar observations were made more recently by Zhao et al. [51] in the study of PMMA composites containing 1 and 2 wt% loadings of C_{60}.

C_{60} has also been shown to increase the thermal stability of other polymers such as polyethylenes [51,53,54], high-density polyethylene (HDPE)/ethylene vinyl-acetate copolymer (EVA) [55]

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and polypropylene (PP) [51].

The fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is widely used as an electron acceptor in polymer photovoltaic applications [56]. Our group has previously shown that PCBM, when blended with some π-conjugated polymers commonly used in organic electronics, can increase their thermo-oxidation stability at high temperatures [57,58]. Furthermore, and despite the fact that the fullerene PCBM has a lower thermal and thermo-oxidation stability than the unfunctionalized C_{60}, our group has recently reported for the first time in the literature that PCBM, when blended with some commodity thermoplastics (such as polystyrene [46], poly(methyl methacrylate) [52] and polyethylene [54]), can impart to the corresponding composites a higher thermal and thermo-oxidative stability than the unfunctionalized and chemically more stable C_{60}. This apparent contradiction stems, most likely, from the fact that PCBM disperses better in the corresponding polymer matrices due to its organic ligand.

In our two previous studies with PS [46] and PMMA [52], the composites were prepared using solution blending followed by precipitation in a non-solvent, and the minimum fullerene loadings considered were 5 wt%. However, in the commodity plastics industry, melt processing is the ubiquitous technique for mixing and forming of polymers and polymer composites. Furthermore, the still high prices associated with the fullerene nanoparticles make the large scale production of thermoplastic composites containing fullerene loadings as high as 5 wt% economically unfeasible. Therefore, at least from a practical perspective, there is obvious interest in exploring the impact of very small amounts (~1 wt% loadings) of these fullerenes (C_{60} and PCBM) on the thermal and thermo-oxidative stability of melt processed PS and PMMA composites.

In the present work, we conduct a comparative study on the impact of the two fullerenes C_{60} and PCBM, on the thermal and thermo-oxidative stability of the corresponding PS and PMMA composites, prepared by melt extrusion. Two different fullerene loadings were considered, namely 1.0 wt% (C_{60} and PCBM) and 3.0 wt% (only C_{60}). Our goal is to understand how the functionalization of the fullerenes affects the thermal and thermo-oxidative stability of the corresponding PS and PMMA composites.

2. Experimental section

2.1. Materials

The two polymers considered in this work were: (a) polystyrene from Sigma Aldrich (catalog # 430102) with average Mw~192.000 and MFI = 6.0–9.0 g/10 min (200 °C/5 kg) and (b) poly(methyl methacrylate), Plexiglas 7H extrusion grade, with MFI = 1.4 cm^3/10 min (230 °C, 3.8 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 (polymers and fullerenes) used in this work are shown in Fig. 1.

Table 1
Experimental conditions during melt compounding in a twin-screw extruder. T1 to T4 are the temperatures along the extruder, being T1 the temperature in the region closer to the hopper and T4 the temperature in the region closer to the die.

Polymer	Temperatures	Screw velocity (rpm)	Feeding screw velocity (rpm)
PS	T1 = 135 T2 = 190 T3 = 200 T4 = 210 Tdie = 220	71	20
PMMA	T1 = 135 T2 = 200 T3 = 215 T4 = 230 Tdie = 245	71	20

2.2. Experimental procedure

PS and PMMA 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 fiber samples were then stored for subsequent characterization.

PS and PMMA nanocomposites were prepared containing 1.0 wt% and 3.0 wt% of C_{60} and 1.0 wt% of PCBM.

Thermogravimetric analysis (TGA) was carried out using a TA Q500 thermobalance. The instrument was calibrated with respect to indium and aluminum standards. Extruded samples (~5 mg) were placed in platinum crucibles and dynamic tests were performed by heating the samples from 40 °C to 600 °C using a ramp of 10 °C min^{-1}, under nitrogen and air flow at 50 mL min^{-1}. Isothermal tests of the extruded pure polymers as well as of the 1.0 wt% C_{60} and 1.0 wt% PCBM composites were also performed for 1 h under nitrogen and air flow at several different temperatures.

3. Results and discussion

3.1. Thermal stability of PS/fullerene nanocomposites (N_2 atmosphere)

Fig. 2 shows the thermogravimetry (TG) and the derivative thermogravimetry (DTG) results (inset) for the pure PS, and for the as-prepared melt compounded PS:C_{60} and PS:PCBM composites, as a function of temperature under nitrogen.

The thermal degradation of PS and of all the PS-fullerene composites, occurs in a single step, as evidenced by the single peak observed in the corresponding DTG curves. This degradation begins, for all the composites, at ca. 340 °C and is slow until ca. 380 °C.

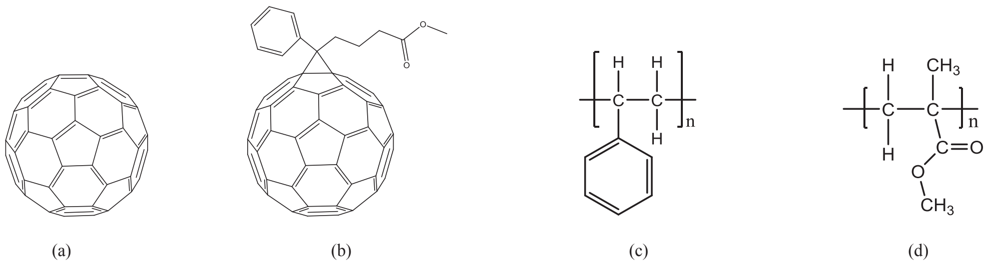

Fig. 1. Chemical structures of: (a) C_{60}; (b) PCBM; (c) Polystyrene (PS) and (d) Poly(methyl methacrylate) (PMMA).