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Material behaviour

Increase in thermo-oxidation stability of conjugated polymers at high temperatures



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ABSTRACT

The effect of PCBM on the thermal stability of three conjugated polymers widely used in organic electronic applications, namely P3HT, MDMO-PPV and PFO, was studied under induced thermal stress (thermolysis and thermo-oxidation) using both dynamic and isothermal thermogravimetric analysis. The aim of this study was to test the potential anti-oxidant effect of PCBM on conjugated polymer:PCBM blends at high temperatures relevant to polymer melt techniques, and to evaluate the corresponding time and temperature windows of processability. Under thermolysis conditions (N_2 atmosphere), most of the blends are less stable than the pure compounds. However, all the blends considered showed increased thermo-oxidation stability (air atmosphere) in comparison to the pure conjugated polymers. These results show that PCBM can be used as an efficient anti-oxidant to increase the time and temperature windows of processability of conjugated polymers at high temperatures under a normal air atmosphere.

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1. Introduction

Conjugated polymers such as poly(3-hexylthiophene) (P3HT) [1], poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene (MDMO-PPV) [2] and poly(9,9-dioctyl fluorene) (PFO) [3] have been widely exploited in a broad range of (opto-)electronic applications, including polymer light-emitting diodes (PLEDs) [3,4], organic photovoltaics (OPVs) [5], organic field effect transistors (OFETs) [6,7] and lasers [8]. The fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is an electron acceptor which has also found, in the last two decades, widespread use in several organic electronic applications such as in OPVs [9] and OFETs [10,11].

Despite the fact that these systems used in devices have been until now mostly processed from solution, there is a growing environmental need for alternative processes that do not require solvents [12,13]. In the search for more eco-friendly as well as more industrially scalable

alternatives, both conventional polymer melt processing methods ($T > T_m$) [14] as well as solid state processing methods ($T < T_m$) have recently started to be exploited to produce fibers [13] and thin films [15]. However, one problem usually associated with the processing at high temperatures is the possible occurrence of thermal degradation (thermolysis and thermo-oxidation).

Although previous degradation studies have shown that conjugated polymers like P3HT, MDMO-PPV and PFO have a limited resistance to a simultaneous combination of oxygen, light, moisture and high temperatures, most of those studies have focused mainly on conditions relevant to device operation, namely presence of light, relatively low temperatures ($T \leq 150^\circ C$), either air or N_2 atmospheres and long exposure times to these conditions [1,2,16–18]. Studies of thermal degradation of these polymers focusing on conditions more relevant to melt processing ($T > T_m$) or solid state processing ($T < T_m$) techniques (absence of light, high temperatures, N_2 or air atmospheres and short exposure times to these conditions) are still very scarce in the literature [19]. We have previously shown, using a large set of different experimental characterization techniques,

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that the processing of pure P3HT in its molten state ($T \geq 250 \text{ }^\circ\text{C}$) is possible, without noticeable degradation, if carried out under nitrogen atmosphere and if the processing (residence) times are relatively short [19].

PCBM has been previously shown to stabilize π -conjugated polymers by reducing the degradation rate under photo-oxidation [16,20,21] and thermolysis [2]. Two mechanisms are usually invoked for the stabilizing effect of PCBM: exciton quenching [22,23] and radical scavenging [2]. Several reports in the literature addressed the increased photo- and/or thermo-oxidation stability of polymer/fullerene blends in comparison to the pure polymer at temperatures ranging from $40 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$ [1,2,16,20,23,24], that was also extended to the influence of type and number of adducts of the fullerene [17,25] and the number of carbons in the buckyball (C70 and C60) [26].

Although the use of anti-oxidants is pervasive in the polymer melt processing industry, in our previous study [19] we have addressed, as far as we know for the first time, the potential of PCBM as an anti-oxidant to prevent or delay the thermal degradation of a π -conjugated polymer (P3HT) in its molten state. In that study we have also shown that PCBM can be used to delay the P3HT oxidation under conditions relevant to melt processing.

In the present work, we have explored further the anti-oxidant effect of PCBM by conducting a detailed study on the impact of PCBM on the thermal stability of the three conjugated polymers P3HT, MDMO-PPV and PFO under induced thermal stress (thermolysis and thermo-oxidation) at relatively high temperatures ($T > 150 \text{ }^\circ\text{C}$), more relevant to polymer melt and solid state processing techniques [13]. The time and temperature windows in which these conjugated polymers and their PCBM blends can be processed in the dark, either in air or N_2 atmospheres, without noticeable degradation were tested in order to verify the feasibility of processing them by melt or solid-state techniques.

2. Experimental section

The polymers and carbon nanoparticles considered in this work were (Fig. 1): a) poly(3-hexyl-thiophene) (P3HT), ($M_w = 65.5 \text{ kg mol}^{-1}$, $M_n = 32 \text{ kg mol}^{-1}$, Ossila Ltd.), b) poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) ($M_n = 23 \text{ kg mol}^{-1}$, Sigma-Aldrich.), c) poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) ($M_w = 114.1 \text{ kg mol}^{-1}$, $M_n = 37.9 \text{ kg mol}^{-1}$, Ossila Ltd.) and d) phenyl-C61-butyric acid methyl ester (PCBM) (>99% purity, Solenne BV).

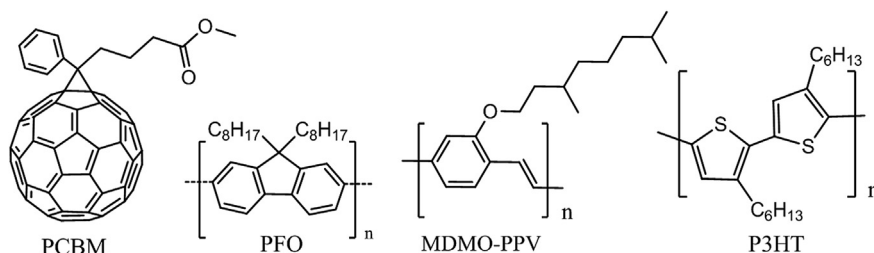


Fig. 1. Chemical structures of PCBM, PFO, MDMO-PPV and P3HT.

Toluene and methanol (both ACS reagents +99.8%) were purchased from Sigma-Aldrich.

Polymer:PCBM blends, with relative weight % compositions of 80:20, 60:40, 40:60 and 20:80, were prepared by solvent mixing for the three different polymers tested. In this preparation step, appropriate amounts of each polymer and PCBM were dissolved separately in toluene under heating and stirring until complete dissolution was achieved. PCBM and polymer solutions were mixed together and stirred for an additional 10 minutes. Each mixture was then added dropwise to cold methanol to precipitate the composites. The solids were filtered and dried under vacuum at $120 \text{ }^\circ\text{C}$ during 5 hours.

Thermogravimetric analysis (TGA) was carried out using a TA Q500 thermobalance which was calibrated with respect to indium and aluminum standards. Samples ($\sim 5 \text{ mg}$) were placed in platinum crucibles and both dynamic and isothermal tests were performed. In the dynamic tests, samples were heated from $40 \text{ }^\circ\text{C}$ to $600 \text{ }^\circ\text{C}$ using a heating ramp of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen (thermolysis conditions) and air flow (thermo-oxidation conditions) at 50 mL min^{-1} . The isothermal tests were performed at different test temperatures ranging from $150 \text{ }^\circ\text{C}$ to $350 \text{ }^\circ\text{C}$ with 60 minutes for each isothermal step, and only under air flow (thermo-oxidation conditions) at 50 mL min^{-1} . Isothermal tests were performed only for the pure components and for the polymer:PCBM blends with relative weight % composition of 80:20.

3. Results and discussion

3.1. P3HT:PCBM blends

Fig. 2 shows the derivative thermogravimetry (DTG) results and total mass percentage (inset) for the pure P3HT and PCBM and for the as-prepared P3HT:PCBM blends, obtained by solution precipitation, as a function of temperature under the thermolysis conditions in the dynamic tests. Our group has previously reported similar results for similar composites prepared by a different method, namely solvent casting from chloroform [19].

Pure P3HT is stable up to ca. $440 \text{ }^\circ\text{C}$ under oxygen-free conditions, i.e. nearly $200 \text{ }^\circ\text{C}$ above its melting temperature [27]. From ca. $440 \text{ }^\circ\text{C}$ until ca. $530 \text{ }^\circ\text{C}$ it shows a very fast and pronounced mass loss and, finally, when the maximum temperature of $600 \text{ }^\circ\text{C}$ is reached, the residual mass is ca. 30% of the initial mass, which is in accordance

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