Role of molecular mixing on the stiffness of polymer:fullerene bulk heterojunction films

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ABSTRACT

Bulk heterojunction films, which typically comprise a polymer donor and fullerene acceptor, are considerably stiffer than films of the neat polymer. The increase in stiffness upon blending is dependent on the miscibility of the polymer and the fullerene, and potentially on the details of molecular mixing, in particular, intercalation of the fullerene molecules between the polymer side chains. This paper describes the effects of molecular mixing on the tensile modulus of polythiophenes in 1:1 blends with [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$). A series of four polymers and their blends with $PC_{61}BM$ are tested using mechanical, spectroscopic, and photovoltaic device-based measurements to determine if it is possible to predict trends in the tensile modulus based on the extent of molecular mixing. The four polymers are poly-2,2′:5′,2″-(3,3″-dihexyl-terthiophene) (PT2T), which forms an amorphous, molecularly mixed composite, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), which forms a well ordered blend with bimolecular crystallization, and regioregular poly(3-hexylthiophene) (P3HT) and poly(3-heptylthiophene) (P3HpT), which form a ternary blend with an amorphous mixed phase. The tensile moduli are measured by the buckling technique and correlations are found between the modulus of the neat polymer and the blends. Although spectroscopic and photovoltaic device-based measurements of $P3HT:PC_{61}BM$ and $PT2T:PC_{61}BM$, along with literature precedent, suggest completely different extents of molecular mixing, they were found to have similar moduli (2.75 ± 0.59 GPa and 2.61 ± 0.39 GPa, after annealing). A strong correlation between the moduli of the blended films and the moduli of the neat polymers suggest that the stiffness of the blend is determined to a large extent by that of the polymer, and is unexpectedly insensitive to the details of molecular mixing, at least for the materials investigated.

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1. Introduction

The pursuit of low-cost, flexible and stretchable organic electronics requires an understanding of the ways in which state-of-the-art electronic properties can coexist with mechanical resilience. Bulk heterojunction (BHJ) photovoltaic devices, which have a photoactive layer comprising donor and acceptor phases mixed on the molecular scale or nanoscale, are the most commonly studied organic photovoltaic (OPV) devices because of their high efficiency and easy processability [1–4]. The extent of molecular mixing (or the size of the phases) in BHJs influences the molecular packing and interfacial interactions, which in turn, greatly affects exciton dissociation, recombination, and charge transport [5,6]. While the relationship between molecular mixing and electronic properties has been studied extensively, the effect of the extent of mixing on the mechanical properties and stability against fracture is not well known. Improving the mechanical resilience of active materials and interfaces will improve the yield of working devices in roll-to-roll manufacturing, and the lifetime in outdoor, portable, and wearable applications [7–9].

The goal of our experiments was to understand the influence of molecular mixing on the stiffness – i.e., tensile modulus – of BHJ films. In particular, we measured the tensile moduli of four different blends of polymers with main-chains comprising thiophene rings and the methanofullerene [6,6]-phenyl C_{61} butyric acid methyl ester ($PC_{61}BM$), (Fig. 1) whose behaviors in a blend are known in the literature to span a range from an amorphous, molecularly mixed composite ($PT2T:PC_{61}BM$) [10,11], a well ordered blend with bimolecular crystallization ($PBTTT:PC_{61}BM$) [12,13], and two ternary blends with pure or enriched phases separated by mixed phases ($P3HT:PC_{61}BM$ [14,15] and $P3HpT:PC_{61}BM$ [16,17]). The ternary blends are differentiated primarily by the relationship of the glass transition temperature (T_g) of the pure polymer to ambient temperature: T_g for P3HT is close to room temperature [18,19] and is generally reported as stiff (tensile modulus ~ 1 GPa) [20,21], while T_g is below room temperature for

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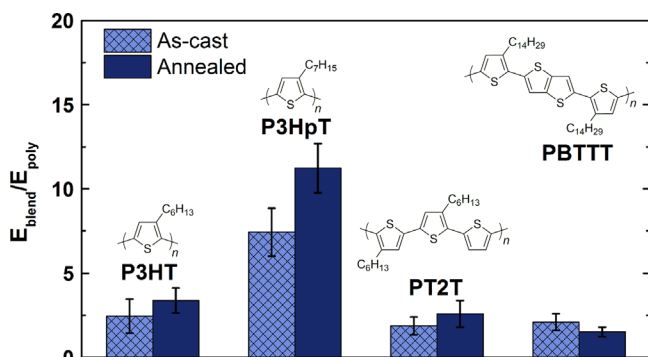   *E-mail address:* dlipomi@ucsd.edu (D.J. Lipomi).

Fig. 1. The ratios of the tensile moduli of as-cast/annealed 1:1 polymer:fullerene blends to as-cast/annealed neat polymers and the chemical structures of the conjugated polymers examined in this work: regioregular poly(3-hexylthiophene) (P3HT), regioregular poly(3-heptylthiophene) (P3HpT), poly-2,2′:5′,2″-(3,3″-dihexyl-terthiophene) (PT2T), and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno [3,2–b]thiophene) (PBTTT).

P3HpT [16] and is highly elastic (tensile modulus ≤ 0.1 GPa) [16]. While all polymer:fullerene blends reported so far have greater elastic moduli than do the neat polymers [9,11,16,20–22], the factor by which the blend is stiffer than the neat polymer varies over a wide range (Fig. 1). Our goal was to understand the role of molecular mixing by combining our mechanical measurements with knowledge of the well studied microstructures of these four systems. Understanding the effects of molecular mixing on the compliance of BHJs will provide the insight necessary for the selection of materials with mechanical properties appropriate to the application and to mitigate mechanical forms of degradation.

2. Background

The first organic solar cells (OSCs) had a planar heterojunction between a layer of pure donor and a layer of pure acceptor in direct contact [23,24]. This architecture exhibited relatively low efficiencies because of the limited interfacial area between the donor and the acceptor [25]. The discovery of the bulk hetero-junction (BHJ) – an intimately mixed blend of donor and acceptor, which are frequently a conjugated polymer and a soluble fullerene derivative – led to devices exhibiting much higher efficiencies [1–4,26,27]. The advent of BHJs generated significant interest in understanding the extent of molecular mixing to elucidate the relationship between microstructure and electronic performance [5,14,28]. Of equal interest, in terms of the yield of functional devices and their stability in outdoor and portable environments, are the ways in which the morphology of the bulk heterojunc-tion influence the mechanical properties of the composite film [7–9,29,30]. The mechanical aspects of the stability of organic electronic devices have, until recently, received relatively little attention.

The most extensively studied bulk heterojunction blend is P3HT:PC$_{61}$BM [9,14,20–22,31–37]. The current model for this system comprises a ternary blend of a pure polymer phase, a pure (or enriched) fullerene phase, and an amorphous mixed phase of polymer and fullerene [38]. These ternary blends form because PC$_{61}$BM exhibits high solubility in amorphous P3HT, and is excluded from the pure polymer phase, which is well ordered [33,39]. For efficient charge transport, pure phases of both polymer and fullerene are required so that, once separated, charges can travel to the electrodes [14]. Without these percolated networks, losses due to recombination reduce the efficiency. In P3HT: PC$_{61}$BM, the segregated polymer and fullerene phases are believed to account for most of the charge transport in BHJ devices; the

presence of the mixed phase is regarded as deleterious to the efficiency due to the disruption of contiguous pathways for charge transport to the electrodes [14]. Like P3HT, P3HpT – a polythio-phene with a side-chain longer than P3HT by one methylene unit ($n=7$) – is also believed to form ternary blends with PC$_{61}$BM [17]. P3HpT is of particular interest because it has previously been shown to simultaneously display excellent compliance and good photovoltaic characteristics [16].

Very little is known about what, if any, specific molecular interactions are responsible for the solubility of PCBM in amor-phous P3HT. On the other hand, some conjugated polymers, which exhibit lower densities of side chains than do P3HT, contain notches along the polymer chain into which fullerenes can sit [10,13]. This outcome – intercalation – either prevents crystal-lization or produces bimolecular crystallites; the morphology depends on the dimensions of the fullerene compared to the dimensions of the free volume between side chains. For example, the poly(terthiophene) PT2T is similar to P3HT except that every third thiophene in PT2T is without a side chain (and also that the coupling between 3-alkylthiophene rings is tail-to-tail in PT2T and head-to-tail in P3HT, Fig. 1). In neat form, the side chains of PT2T interdigitate, and a highly ordered film is obtained [10]. In bulk heterojunction films, due to the notch between side chains, PT2T is hypothesized to allow intercalation of fullerene along the main chain [10]; intercalation forces the formation of a largely amor-phous molecularly mixed phase. Intercalation of the PC$_{61}$BM likely inhibits cofacial π-stacking as well as lamellar stacking, and this disruption in order produces lowered efficiencies of devices [10,11]. This hypothesis is supported by the much lower power conversion efficiency (PCE) demonstrated in PT2T:PC$_{61}$BM devices when compared to those of P3HT:PC$_{61}$BM, even though the relative positions of the frontier molecular orbitals of PT2T to PC$_{61}$BM suggest that this system might be more efficient than P3HT:PC$_{61}$BM [10].

Miller et al. studied the intercalation of fullerenes between the alkyl solubilizing groups of PBTTT and found that the fullerene solubilizing groups were critical in determining if [13,40]. Mono-functionalized fullerenes, such as PC$_{61}$BM and PC$_{71}$BM, readily intercalated between the side chains of PBTTT, while some multi-functionalized fullerenes, such as bis-PC$_{61}$BM and bis-PC$_{71}$BM, did not intercalate between the side chains due to steric hindrance [13]. The absence of intercalation of multifunctionalized fullerenes was not a generalizable rule, though. Because of its less bulky solubilizing groups, indene-C$_{60}$ bisadduct (ICBA) was found to intercalate [40]. (It should be noted that photovoltaic devices made with ICBA underperformed those made with PC$_{61}$BM because the ICBA preferentially aligned with its side groups parallel to the polymer backbone, which prevented efficient charge transport between fullerenes [40].) In the cases where the fullerene intercalated – such as with PC$_{61}$BM and PC$_{71}$BM – an excess of fullerene was required to make efficient devices. At a ratio of 1:1 PBTTT:fullerene, the fullerene completely intercalated between the side chains of the polymer; the absence of pure fullerene domains prevented the formation of a percolated net-work to transport electrons to the cathode. The efficiency of PBTTT:PC$_{71}$BM devices was optimized at a ratio of 1:4 [5,41,42]. That is, an excess of fullerene was necessary to form a percolated network of pure (or enriched) phases. While a large volume fraction of fullerene improved electronic performance, it also had a deleterious effect on the mechanical properties. Dauskardt, McGehee, and coworkers studied the effect of intercalation on the cohesion of poly(3,3‴-didodecyl quaterthiophene) (PQT-12) and PBTTT and found that high ratios of fullerenes (1:4) produced BHJ films with decreased cohesive energy compared to 1:1 blends [8]. A lower cohesive energy was also found in 1:1 blends with fullerene that did not intercalate (bis-PC$_{71}$BM) when compared to