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When Electronically Inert Polymers Meet Conjugated Polymers: Emerging Opportunities in Organic Photovoltaics

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Abstract Insulating polymers (commodity plastics in particular) are a major category of polymeric materials widely used in our daily life, but they exhibit abysmal electrical conductivity. Instead, conjugated polymers are gaining tremendous interest due to their excellent electrical properties and versatile applications in organic electronics. In this perspective, we provide a concise account of the added value in organic solar cells, as brought by the combined use of conjugated and insulating polymers. The challenging tasks and prospective directions are given to the potential benefits of employing insulating polymer additives, which spans from common commodity plastics to high-temperature resistant resins and thermoplastic elastomers. Particularly, the inert polymers can improve many important properties such as mechanical and thermal robustness but not sacrifice optoelectronic performance.

Keywords Organic solar cells; Insulating polymers; Photovoltaic polymers; Miscibility; Morphology

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INTRODUCTION

As fossil fuels—coal, oil, and natural gas are getting less, energy and environmental problems are becoming more and more serious, and the development of new clean energy is always a hot topic in the research field. Solar cells have attracted much attention because they can convert solar energy into electricity. Traditional inorganic solar cells such as silicon are limited by the preparation complexity of monocrystalline silicon and high cost. Organic solar cells, using organic and polymer conjugated materials as active layers,[1−7] can be prepared by simple methods such as solution processing, which has great potential for commercial application in modern greenhouses, buildings, internet of things and so on.[1,8−15] At present, the top efficiency of single-junction organic solar cells has reached over 19%[16−18] and the best operation lifetime of a polymer:small molecule blend has surpassed 30 years.[19] However, the present high-performance organic solar cells also face some issues such as poor strechability,[20−22] costly photovoltaic materials,[23] and insufficient operation lifetimes[24−27] under heat or light.

Insulating polymers exhibit intrinsically low charge carrier concentration and poor electrical conductivity, which are considered detrimental to the optoelectronic performance of organic electronics. Many of the pioneering reports[28−30] of blending insulating polymers with polymer semiconductors in organic thin-film transistors and organic photovoltaics (OPVs), however, appears to challenge this thought. Strikingly, the addition of up to ~50 wt% electronically inert components to the organic semiconducting system does not significantly degrade the OPV performance.[28] Importantly, the combination of insulating polymers with organic photovoltaic materials can significantly reduce the production cost of OPVs, as these insulating polymers are much cheaper than organic photovoltaic materials. In recent years, a growing number of studies devoted efforts to this direction and have achieved new successes. The library of insulating components for OPVs has been enriched over recent years. It is possible to gain a deeper understanding of the structure-property relationships in these multi-component blend systems from the viewpoint of polymer physics. Though a few reviews[28,31] summarized the applications of commodity plastics in OPVs, a more general perspective covering all kinds of insulating polymers (beyond commodity plastics) has not been established yet. Moreover, the prior reviews concentrated heavily on the polymer:fullerene systems, while the most recent nonfullerene systems (for instance, PM6:Y-series acceptors) were not much covered. Thus, a timely guide on selecting the third component with abysmal electrical properties for the high-performance OPVs is particularly needed.

To fill the above knowledge gap, we provide an updated status and critically assess the recent advances of high-performance OPVs enabled by incorporating insulating poly-

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mers over a span of ten years. These insulating polymers span from common commodity plastics widely used in our daily life to high-temperature resistant resins and thermoplastic elastomers in many industries like aerospace and automobiles. Attratively, they can improve many important properties of OPVs such as flexibility and thermal stability but not sacrifice their optoelectronic performance. According to their different functions, insulating polymers can be mainly divided into three categories, namely, commodity plastics, high-temperature resistant resins and elastomers. Commodity plastics can be produced in large quantities and at a very low price, but they usually do not have special functions. High-temperature resistant resins mainly refer to polyesters containing aromatic rings and ether bonds in the backbone which have good high-temperature resistance, are expected to improve the thermal stability of solar cells. Elastomers are polymers with viscoelasticity and with weak intermolecular forces, having good mechanical properties, low elastic modulus and high elongation at break, which can be used as aids to improve the flexibility of the devices. The representative examples of these electronically inert polymers are summarized in Fig. 1.

COMMODITY PLASTICS

Nowadays, commodity plastics such as polyethylene (PE), polypropylene (PP), and polystyrene (PS) are cheap and have permeated almost everywhere in our daily life. Using commodity plastics in OPVs can greatly cut the cost of the device which is beneficial to commercial applications. The most notable example is the organic semiconductor:insulator ternary blend constructed by Ferenczi *et al*. in 2011.[29] They applied a common insulator of high-density PE to the benchmark P3HT:$PC_{61}BM$. The introduction of high-density PE up to 50 wt% did not significantly degrade the electronic properties of the P3HT:$PC_{61}BM$ system, but greatly cut down on the amount of P3HT and $PC_{61}BM$ materials used in this ternary system. As a result, the cost of device processing can be reduced without sacrificing the device performance. They unveiled the occurrence of this phenomenon, which was ascribed to the forming of percolating network with lower fractions of organic semiconductors.

In addition to the cost of the active layer, film thickness is also an important factor affecting the printing scalability of OPVs and commercial application.[32] Generally, the thickness of the active layer in top-notch OPVs is about 100 nm, which is not compatible with large-area printing processes. Nevertheless, larger thickness often results in severe charge recombination and reduced efficiency. Thus, the development of high-performance OPVs with thick active layers is an inevitable requirement for industrailization. To address this issue, Hao *et al*.[33] found that the addition of PP can increase the device efficiency for much thick active layers (PBDB-T:$PC_{71}BM$ and PTB7:$PC_{71}BM$). What's more, the ternary blends with thick films are beneficial to achieve better photocurrent and require less rigorous printing setups than thin films. PBDB-T:$PC_{71}BM$:PP (2 wt%) ternary system obtained the highest power conversion efficiency (PCE) of 7.46% at a film thickness of 280 nm. PTB7:$PC_{71}BM$:PP (4 wt%) devices exhibited higher PCE at the same thickness than those without PP (Fig. 2a). Grazing-incidence wide-angle X-ray scattering (GIWAXS) data showed that the addition of PP improved the crystallinity of PBDB-T with high crystallinity in the blend film, which is beneficial to charge transport (Fig. 2b). As shown in Fig. 2(c), the presence of PP can be analogous to fixing PBDB-T molecules to form more ordered crystalline structure, and the self-aggregation of $PC_{71}BM$ would also be reduced. However, it has little reverse effect on PTB7 with low crystallinity, which can

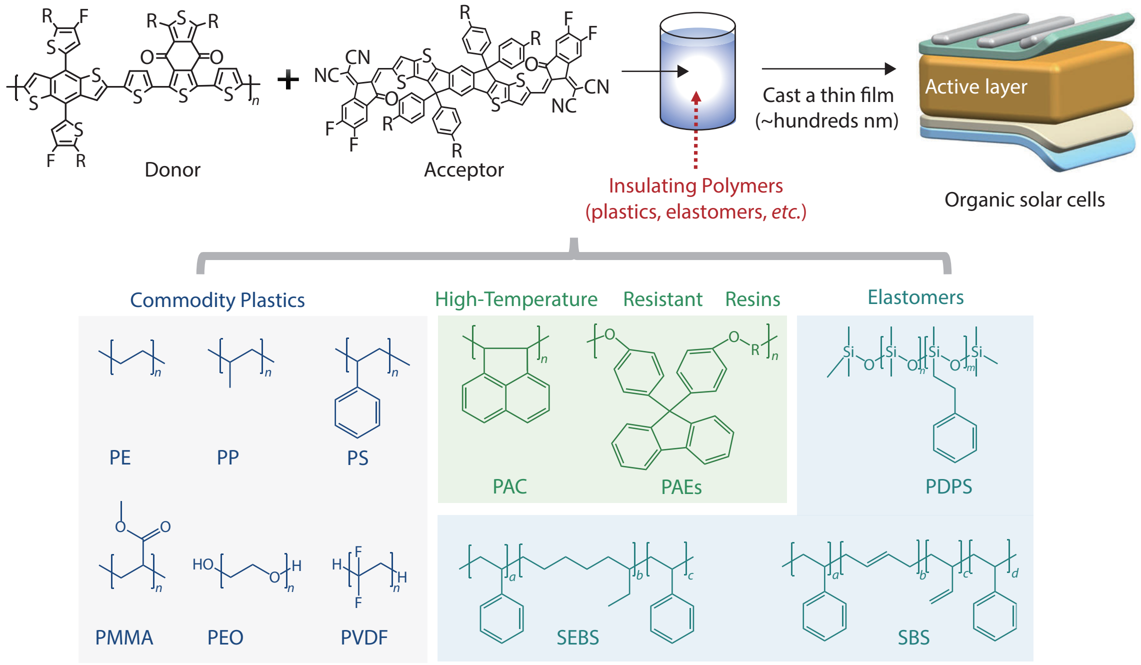

Fig. 1 Schematic of OPVs featuring insulating polymers and chemical structures of insulating polymers used in the OPV community.

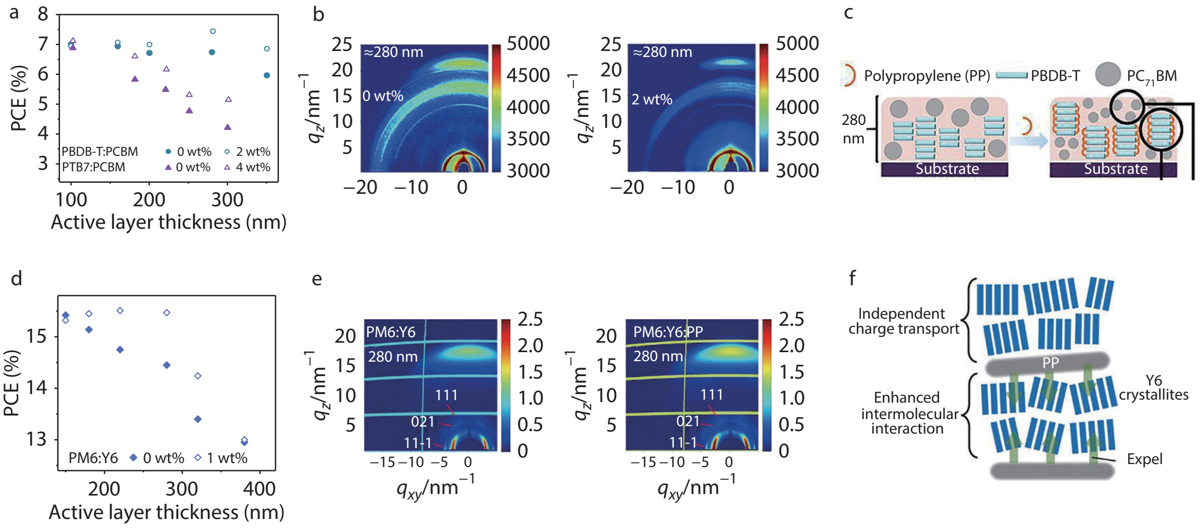

Fig. 2 (a) Graphical representation Influence of doping of insulating polymer on thickness. (b) Working principle of insulating polymer in PBDB-T:PC$_{71}$BM:PP (2 wt%) films. (c) 2D GIWAXS patterns of 280 nm PBDB-T:PC$_{71}$BM and PBDB-T:PC$_{71}$BM:PP (2 wt%) films. (d) PCE of active layer processed with PM6:Y6 with/without 1 wt% PP based on different thicknesses. (e) Working principle of insulating polymer in PM6:Y6:PP (1 wt%) films. (f) 2D GIWAXS patterns of 280 nm PM6:Y6 and PM6:Y6:PP (1 wt%) films. (Reproduced with permission from Refs. [33, 34]; Copyright (2019, 2021) Wiley, American Chemical Society).

explain the different trends of efficiency change caused by the film thickness between the two systems. As to non-fullerene OPVs, Hao *et al.*[34] further incorporated PP to PM6:Y6 system and observed the same phenomenon of thickness-insensitive PCE in the thickness range of 150-300 nm by reducing the trap state density (Fig. 2d). The comparison of images in Fig. 2(e) shows that, for 280 nm blend films, the addition of PP can improve the proportion of face-on crystallinites. They concluded that PP can repel small Y6 molecules to enhance their intermolecular interaction and packing order as illustrated in Fig. 2(f), which are more favorable for charge transport. Consequently, the short-circuit current density (J_{sc}) of the device was significantly improved in different thicknesses with 1 wt% PP.

There are many other common plastics such as poly(ethylene glycol) (PEG),[35] polymethylmethacrylate (PMMA),[36–38] and poly(vinylidene difluoride) (PVDF)[39] that can be used as third insulation additives for OPVs. For example, Yan *et al.*[40] introduced PS and a series of widely accessible nonconjugated insulting polymers as additives into the fullerene-free active layer PBDB-T:ITIC. Incorporating 5 wt% PS into the photovoltaic layer greatly improved the device efficiency by 16%. Other polymer insulators also led to efficiency enhancements at optimum amounts. The significant performance improvements can be attributed to the enhanced crystallinity of PBDB-T, carrier mobility, and lifetime induced by the insulators. They found that the glass transition temperature (T_g) and side chain size are two crucial factors to optimize the optoelectronic properties of OPVs. Insulating polymer can exhibit positive effect on device performance when the annealing temperature higher than T_g. Larger side chain size helps fill in the interspace and optimize the molecular packing to lower traps and defects in active layers. Different from the above examples, Yang *et al.*[41,42] introduced the block copolymers of PS and other polymers into polymer:non-fullerene systems, and also achieved the regulation of the morphology and the efficiency of the correspondng OPV devices.

In a word, the incorporation of commodity plastics can not only greatly reduce the cost of the active layer materials, but also adjust the morphology of the film and improve its crystallization, which is conducive to realize comparable charge transport and PCE in a thicker film. However, the addition of various commodity plastics may have different effects on diverse blends, as many factors, such as T_g and molecular structure, can affect the role of commodity plastics as additives.

HIGH-TEMPERATURE RESISTANT RESINS

The commercialization of organic solar cells requires excellent environmental stability, except for high efficiency. High-temperature resistant resins are proved to be effective for the stable operation of organic thin-film transistors.[43] They possess high T_g, which are expected to boost device stability under heat stress.[44] Recently, our group reported the introduction of such insulating polymer, for instance, polyacenaphthylene (PAC) with high T_g over 200 °C and excellent transparency to PTB7-Th:EH-IDTBR system,[45] and a high lifetime of up to 800 h were realized. It was found that PAC and EH-IDTBR have great compatibility that can form networks to largely maintain EH-IDTBR morphology as the temperature increases, which does not result in a negative impact on charge transport (Fig. 3a). The average efficiency of the blend with 10 wt% PAC was slightly lower than that of the reference system without additive, while the value was much more stable after long-time annealing up to >800 h, as illustrated in Fig. 3(b). This high lifetime was among the best values reported for OPVs operating at 150 °C.

Microscopic images of the ternary blend incorporating 10 wt% PAC system were similar to that of the binary system even upon annealing at 150 °C for 24 h. The endothermic and exothermic peaks gradually weakened and even disappeared

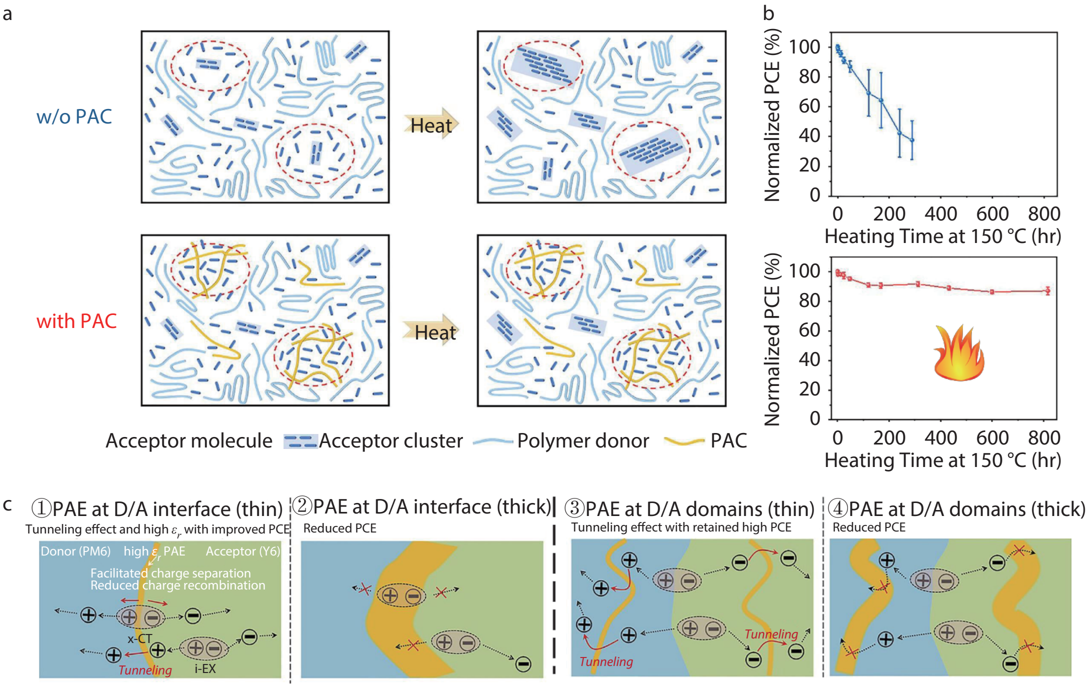

Fig. 3 (a) Schematic illustration of the morphology evolution of the blend films without and with PAC under thermal stress. (b) Normalized PCE of PTB7-Th:EH-IDTBR without (blue line) and with (red line) PAC annealed at 150 °C with annealing time. (c) Tunneling effect under four circumstances: thin (1) and thick (2) PAE region at the D/A interface, thin (3) and thick (4) PAE region at D/A domains. (Reproduced with permission from Refs. [45, 46]; Copyright (2021, 2021) Wiley, Cell Press).

in differential scanning calorimetric curves with the increase of the PAC content. Further time-depenent GIWAXS characterizations also demonstrated that the presence of PAC can suppress the degree of crystallization of EH-IDTBR. Moreover, PAC also enabled the stability improvement of the star donor:acceptor system PM6:Y6 under heating.

Alternatively, Bao and Yang *et al.*[22] proposed the use of an insulating polymer matrix based on high-temperature resistant resins. As shown in Fig. 1, poly(aryl ether) (PAE) resin has an aromatic backbone similar to some organic photovoltaic materials but without any side chains, resulting in excellent tolerance to heat. Incorporating PAEF with high T_g not only enhanced the thermal stability of the PM6:Y6 system but also improved the flexibility to 4.4-fold elongation at a break of ~25%. In this ternary mixed system, tunneling effect was observed which can suppress the recombination of free carriers and not damage the charge transfer largely to the maintained initial efficiency. In addition, adding PAEF as supporting matrices can effectively restrain the movement of the chain of donor and acceptor to maintain the microstructure, leading to the improvement of flexibility.

On the basis of this study, they further investigated a series of high-temperature resistant PAEs,[46] giving an in-depth insight into how charges tunnel through the resins. OPVs with five different T_g of PAEs all exhibited tunneling effects compared to PMMA, which sufficiently blocked charge transfer in the active layers. To further understand this phenomenon, they fabricated the layer-by-layer OPVs based on an architecture of PM6/PAEs/Y6, and found that the PAEs between PM6 and Y6 layers with thin thickness can facilitate charge transport and inhibit charge recombination. However, if the thickness increases to a certain extent, it will have the opposite effect (Fig. 3c). Furthermore, they added the PAEs to the PM6 or Y6 domains with similar architecture and found the same phenomenon. Thus, PAEs mixed matrices must keep thin to act as tunneling effect in blends.

This section mainly introduced polyester containing aromatic ring and ether bond in the backbone that have high temperature resistance and can withstand continuous thermal treatment at high temperature. As an additive, the resin can greatly improve the thermal stability of the OPVs. Moreover, the introduction of these well-known high temperature resistance resins can form tunneling effect in the blends to promote charge transfer and inhibit charge recombination. Therefore, these insulating components can improve the thermal stability of the OPV device without sacrificing its performance, and simultaneously maintain high PCE after many hours of heating at 150 °C.

ELASTOMERS

An elastomer is a polymer with viscoelasticity and with weak intermolecular forces, generally low Young's modulus and high fracture strain compared with other polymers. Thermoplastic elastomers are a diverse family of rubber-like materials that can be readily processed like thermoplastic polymers. Considering that the present high-performance conjugated polymers and small molecule acceptors are very brittle,[47–50] thermoplastic elastomers may serve as elastic aids to OPVs. Very recently, our group put forward a facile strategy to introduce a commercially available thermoplastic elastomer (*i.e.*, polystyrene-block-

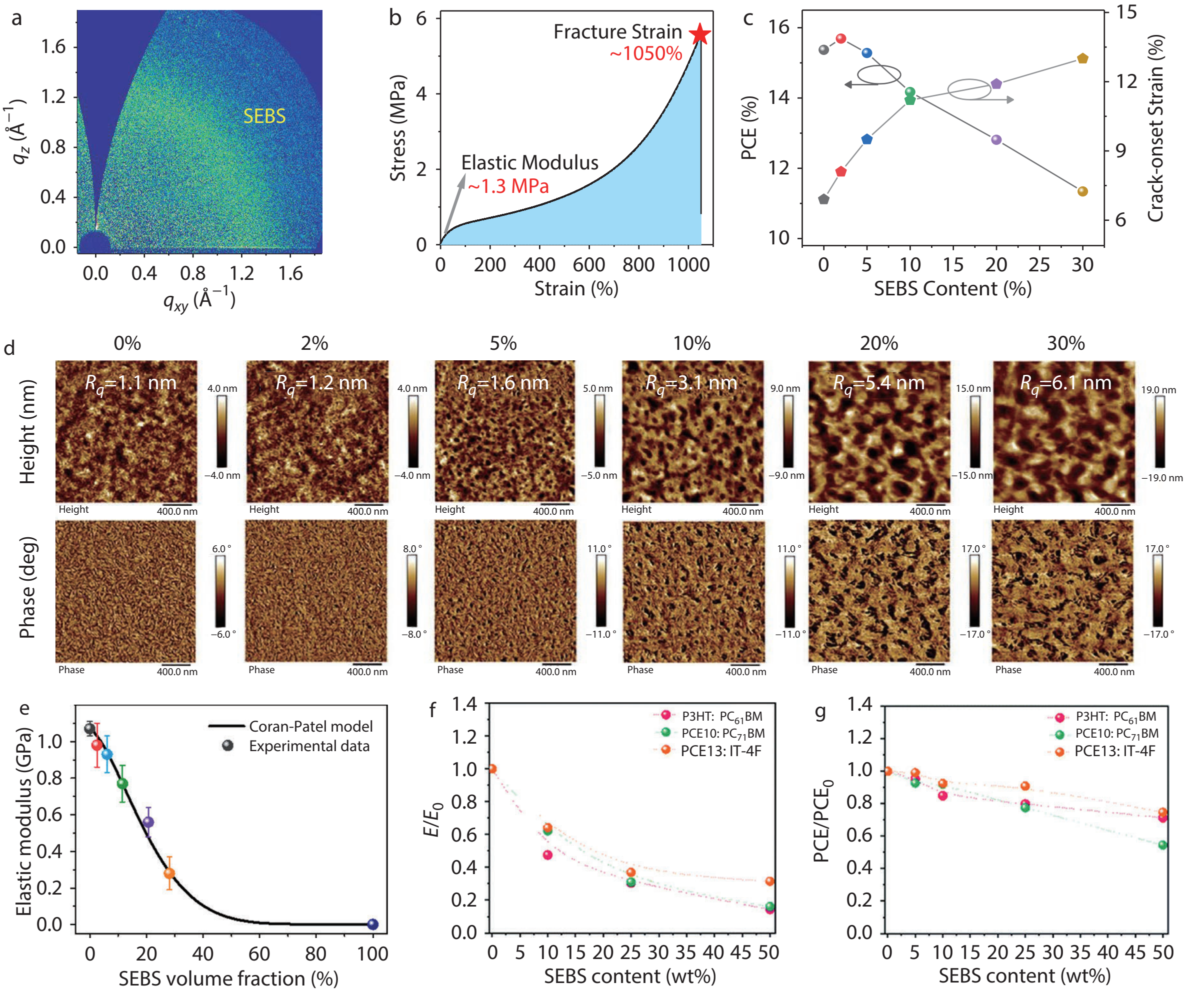

Fig. 4 (a) 2D GIWAXS pattern and chemical structure of the thermoplastic elastomer SEBS. (b) Stress-strain curve of bulk SEBS, the elastic modulus and elongation at break are noted. (c) The PCE and COS plots as a function of the SEBS content based on PM6:N3:SEBS blends. (d) The AFM images of the PM6:N3:SEBS blend films with varied SEBS contents. (e) Theoretical prediction with Coran-Patel model and experimental data obtained by the FOE method. Comparative effect of the SEBS content on the original elastic modulus (f) and power conversion efficiency (g). (Reproduced with permission from Refs. [51, 52]; Copyright (2021, 2022) Wiley, The Royal Society of Chemistry).

poly(ethylene-*ran*-butylene)-block-polystyrene, SEBS) into multiple cases of high-efficiency polymer:small molecule blends.[51] Based on GIWAXS characterizations (Fig. 4a) and mechanical tests (Fig. 4b), SEBS is amorphous in thin film and shows a high fracture strain of >1000%. As shown in Fig. 4(c), the device efficiency of PM6:N3 first increased and then declined with the increase of SEBS weight fraction, but the crack onset strain (COS) increased all along. As observed in microscopic images, there are larger aggregations and higher film roughness when the amount of SEBS is increased (Fig. 4d). The incorporation of 10 wt% of SEBS resulted in higher efficiency and stretchability in a benchmark polymer: nonfullerene small molecule blend PM6:N3, because SEBS possesses great stretchability. They further tested the utility of SEBS in other two well-known blend systems(PBQ*x*-TF:eC9-2Cl and PBDB-T:ITIC) and confirmed the broad applicability. The crack onset strain is greatly improved in both systems. Interestingly, the elastic modulus of the ternary system (polymer:small molecule:SEBS) can be nicely predicted with a classcial polymer composite model, *i.e.*, Coran-Patel model (Fig. 4e).

Shortly afterwards, the Anthopoulos' group also applied SEBS to two fullerene-based systems (P3HT:PC$_{61}$BM and PCE10:PC$_{71}$BM) and a non-fullerene system (PM6:IT-4F), respectively.[52] Atomic force microscopy (AFM) test shows that the addition of SEBS can promote the phase separation. As shown in Fig. 4(f), the elastic modulus decreases to less than 40% of the initial value when the amount of SEBS is below 25% for all blends and the PCE of the device remains within 70% of the original value (Fig. 4g). In 2022, Li *et al.*[53] introduced another elastomer styrene-butadiene-styrene (SBS) to a high-efficiency polymer:nonfullerene small molecule blend PM6:BTP-BO-4Cl. Due to the poor miscibility of the additive and the photovoltaic system, PS and SBS form self-aggregation, resulting in defects. As a result, charge recombination is enhanced and electron transport is hindered with the addition of SBS. PS shows better compatibility with PM6:BTP-BO-4Cl compared to SBS and they speculated that PS has a larger proportion of hard part to achieve better miscibility with π-conjugated polymers, which provides ideas for selecting suitable insulating polymer additives.

All-polymer systems can also benefit from this facile elastomer strategy. Silicone rubber is also an elastomer. The backbone is composed of silicon atoms and oxygen atoms alternately (—Si—O—Si—) and highly saturated. Si—O bond has good flexibility, and the intramolecular and intermolecular forces are weak, which rends it low elastic modulus and elongation at break. For instance, Yang *et al*.[47] grafted PS onto poly(dimethylsiloxane) (PDMS) and synthesized poly(dimethylsiloxane-*co*-methyl phenethylsiloxane) (PDPS) with high viscosity as an additive into the TQ-F:N2200 all-polymer system. AFM and transmission electron microscope (TEM) showed that the blends with 10 wt% PDPS had the appropriate phase separation to form the polymer networks, which not only enhance the mechanical strength but also facilitate the charge transport. With the increase of PDPS content in the blends, the geminate recombination loss increased and the J_{sc} value decreased gradually, while the value of the open-circuit voltage (V_{oc}) is barely changed. It is worth noting that the addition of 10% PDPS provided a decent fill factor (FF) of ~66%, while the J_{sc} just decreased slightly, compared with that of 0% PDPS. A high PCE of 6.87% was generated and 90% of the initial PCE was even maintained after 100 bending cycles with a bending radius of 3 mm.

Double-cable conjugated polymers can be used as an active layer alone and are of particular interest to OPV researchers.[54−56] Recently, Li *et al*.[57] respectively incorporated SBS and PDMS to the double-cable conjugated polymer JP02, in which conjugated backbones as electron donor and naphthalene diimides as electron acceptor to investigate the impact of miscibility on the optoelectronic performance of the OPVs. PS was used for comparison. The addition of the insulating polymers reduced the charge transport ability but improved the flexibility of JP02 which has a relatively planar backbone. They concluded that miscibility is the key factor to balance flexibility and photovoltaic performance. GIWAXS results illustrated that JP02:PS and JP02:SBS blends exhibited similar mixed orientation in films to neat JP02. However, JP02:PS has smaller interaction parameters (χ), indicating that JP02:PS has the best miscibility to avoid large self-aggregation and would form interpenetrating networks, which are beneficial to charge transport. The PCE (6.71%) of single component OPVs based on JP02:PS was just slightly lower than 7.51% of the control cell based on JP02. Noteworthy, the COS was increased to 4.69%, which is approximately two-fold of neat JP02 with 2.48%.

The facile elastomer strategy suggests that the elastomers with good mechanical properties can be simply added into the blend system to endow devices with good flexibility, proposing a new simple strategy to ameliorate the performance and the processing of the OPVs. When the elastomer is added into the blend system as an additive, the surface morphology of the film is greatly affected. Good compatibility and appropriate amount are two very important prerequisite.

CONCLUSIONS AND PERSPECTIVES

To summarize, we highlighted the synchronous use of cost-effective insulating polymers and conjugated polymers in constructing high-performance OPVs, in particular those featuring nonfullerene small molecule acceptors. The efficiency, stability, and stretchability can be in part or fully optimized. The surface energies of the individual components need to be well manipulated to achieve the desired phase structure and function.

Moving forward, the molecular weight dependence of these insulating polymers needs to be systematically examined. As the insulating polymers reported in the literature might not be the best match with organic photovoltaic materials, many new kinds of emerging resins and elastomeric materials can be further explored. We anticipate that the continually developed polymer:small molecule systems and the emerging all-polymer solar cells[58−61] based on polymerized small molecular acceptors[62−64] and other polymer acceptors[65,66] can also benefit greatly from this smart approach. The idea of incorporating insulating polymers could be further expounded to the organic photodetectors[67,68] and organic/quantum dot hybrid electronics.[69,70] However, the mutual interactions[71] between different components have not yet been fully understood. Thus, more efforts should be concentrated on this problem to precisely control the insulator distribution in the functional blends and *in situ* studies of molecular aggregation and phase separation in conjugated polymer/insulator blends for functioal electronics.[72,73]

BIOGRAPHY

Long Ye received his Ph.D. degree from the Institute of Chemistry, Chinese Academy of Sciences (ICCAS) in 2015. From 2015 to 2019, he was a postdoctoral researcher and was later promoted as a research assistant professor at North Carolina State University. He joined the School of Materials Science and Engineering of Tianjin University as a professor in October 2019. His current research interests focus on the fundamental physical properties (thermal/mechanical properties), condensed structure and multi-scale structure-performance relationships of organic/polymer optoelectronic functional materials.

NOTES

The authors declare no competing financial interest.

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