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Multi-Scale Mechanical Properties of Bulk-Heterojunction Films in Polymer Solar Cells

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Abstract

The mechanical properties of bulk-heterojunction (BHJ) films play critical roles in the operational stability of flexible polymer solar cells (PSCs). However, research on the mechanical properties of BHJ films is far behind the studies on their optoelectronic properties. Herein, investigations are conducted to systematically evaluate the multi-scale mechanical properties of the BHJ films. The fullerene derivative PC₇₁BM, the fused ring non-fullerene electron acceptor Y6, and the polymer acceptor PRi-C39 are selected as the acceptor materials of the BHJ films for comparative analysis. Interestingly, the tensile moduli of the films based on PC₇₁BM, Y6, and PRi-C39 measured by using the “film-on-water” (FOW) method decrease sequentially, and their fracture strain and toughness show an increasing trend. Moreover, the nanoindentation moduli of the BHJ films based on different electron acceptors vary in accordance with the results of FOW characterizations, and their moduli and hardness distributions are uniform in these films. Time-dependent creep analyses from both macroscopic tensile measurements and microscopic indentation characterizations illustrate that the occurrence of creep deformation in the PC₇₁BM, Y6 and PRi-C39 based films decrease sequentially. Contact angle tests demonstrate that the main reason for the different mechanical properties in these films is the varied interactions between the donor and the acceptors. All results above demonstrate the effects of acceptor type on the multi-scale mechanical properties of the BHJ films, which are of great importance for the designing of novel electron acceptor materials and manufacturing of reliable flexible PSCs.

Introduction

In the past decades, the interest from both academia and industry toward flexible polymer solar cells (PSCs) has risen enormously due to their unique advantages of being conformable, mechanically flexible, and not easily breakable [1-3]. One of the basic requirements for these flexible devices is that the bulk-heterojunction (BHJ) films used as light-harvesting layers must retain flexibility and portability to function in complex deformation conditions. For this consideration, the BHJ films should possess both good optoelectronic and mechanical properties. Over years, research efforts have been mainly focused on the optoelectronic performance of the BHJ layers [4-7]. However, few attempts have been made to understand the mechanical behaviors of these BHJ layers. In fact, mechanical properties like elasticity, plasticity, and viscoelasticity of the BHJ layers are of critical importance in practical applications since they may affect the long-term stability of flexible devices. The main reason for the lack of mechanical-related research is that the thickness of the BHJ layer is only about 100 nm, and it is difficult to accurately measure the mechanical properties of such thin films experimentally using conventional methods. This situation has been greatly improved after several metrological techniques, including the water-based pull test [8] and nanoindentation [9], were proposed.

The water-based pull test is often referred to as the “film-on-water” (FOW) method, except that the thin film floats on the water surface, this test is very similar to the traditional tensile test. Using the FOW approach, many meticulous studies on the mechanical properties of BHJs were conducted. For example, Kim *et al.* studied the effect of the ratio of polymer donor to fullerene acceptor on the modulus and toughness of BHJ films, and found that increasing the content of PCBM raises the modulus of BHJ films but decreases their toughness [10]. Ye and co-workers unraveled the variation of molecular mixing on the mechanical properties of all-polymer BHJs [11]. Wang *et al.* explored the impact of flexible conjugation-break spacers (FCBS) of non-conjugated polymer acceptors on the mechanical properties of the BHJ layers, and they concluded that introducing appropriate FCBS with short length can simultaneously enhance the

photovoltaic performance and mechanical robustness of the devices ^[12].

Since the FOW method measures the mechanical properties of relatively large-area (usually on the millimeter scale or even larger) films, the local mechanical responses within the films cannot be studied at a more microscopic scale with this method. Nanoindentation is an advanced technique developed for quantitatively probing the mechanical properties of materials at a very small scale (from micron to nanoscale) or at the surface or sub-surface regions ^[13]. Using this approach, Logothetidis *et al.* studied the effect of the fullerene presence and the annealing on the P3HT:PCBM nanomechanical behaviors ^[14]. Jeng and coworkers determined the hardness and modulus of the P3HT:PCBM blend films, and attempted to correlate the mechanical properties to the power conversion efficiency of devices ^[15]. The above studies have deepened the understanding of the mechanical properties of BHJ thin films. However, considering the complex scenarios in flexible solar cells, there is still a lot of work to be done. For example, previous studies have not considered the change of mechanical properties of the BHJs over time, which is not in line with the real working conditions of flexible PSCs. In addition, the response of the nanoscale BHJ to periodic external forces is also poorly understood. To clarify these issues, it is necessary to study the mechanical properties of the BHJs at multiple scales.

In this work, multi-scale mechanical properties of the BHJ films with three representative acceptors: the classical fullerene derivative PC₇₁BM ^[16], the fused ring non-fullerene electron acceptor Y6 ^[17], and the polymer acceptor PRi-C39 ^[18] are reported. Specifically, the FOW method was employed to measure the macroscopic tensile properties (tensile modulus, fracture strain, and toughness) of the BHJ films, and nanoindentation was adopted to study the micro-to-nanoscale mechanical characteristics (distribution of modulus and hardness, elastic and plastic deformation under local compressive stress, etc.) of these films. Especially, the time-dependent mechanical issues, such as creep deformation, are the focus of this research effort. To the best of our knowledge, this is the first work reporting the creep characteristics of the photoactive layer of PSCs. In addition, nano-dynamic mechanical tests, which are useful for evaluating the response of the film to periodic external forces with different

frequencies, were performed to investigate the effect of the interaction between the electron donor and electron acceptor on the mechanical properties of the films. Finally, the relative strength of the interaction between the donor and the acceptor was studied experimentally by using contact angle measurements. The implications of the results are also discussed for the potential application of flexible PSCs.

Results and Discussion

Tensile mechanical properties

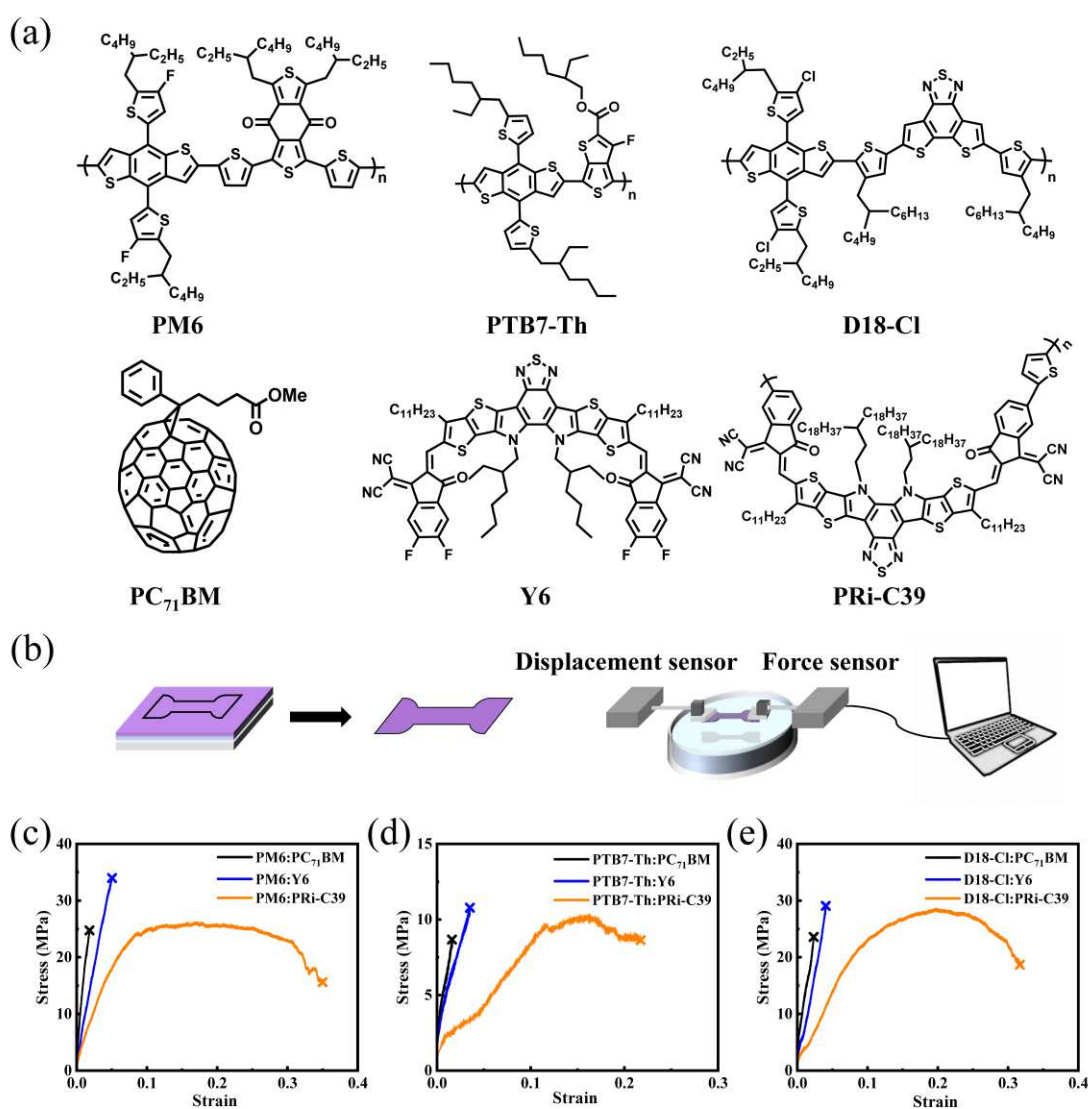


Fig. 1 (a) Molecular structures of the photovoltaic materials used in the study. (b) Schematic illustration of the tensile test of films on water. The film is firstly spin-coated on the substrate, then etched into a dog-bone shape by laser etching, and finally, a high-

precision force sensor and a linear displacement stage are used for data acquisition. The stress-strain curves of (c) PM6, (d) PTB7-Th, and (e) D18-CI-based blend layers.

To explore the mechanical properties of the BHJ films, three typical acceptors, namely the fullerene derivative PC₇₁BM, the non-fullerene electron acceptor Y6, and the polymer acceptor PRi-C39, were selected as the research objects. For donor materials, high-efficiency donor polymers PM6^[19], PTB7-Th^[20], and D18-CI^[21] were chosen (Fig. 1a). The FOW technique was firstly employed to investigate the tensile mechanical properties of the BHJ blend films^[8,11], and a schematic illustration of the test process is shown in Fig. 1b. Through this test, the intrinsic mechanical properties of the nanofilms, including tensile modulus, fracture strain, and toughness can be directly measured without any approximations or assumptions. Stress-strain curves for PM6, PTB7-Th, and D18-CI-based photoactive layers with different acceptors are presented in Figs. 1(c)–1(e), respectively. Regardless of the donor material used, when PC₇₁BM and Y6 were employed as acceptors, the stress of the blend film increased substantially and linearly with increasing strain until the films break. However, the all-polymer films based on PRi-C39 displayed distinct characteristics. As the strain increased, the stress-strain curves firstly rose linearly, and when the strain reached a certain critical value, the growth rate of the curves slowed down. With a further increase in strain, the stress of the film slowly decreased, and eventually the fracture occurred. In addition, the slopes of the curves based on PC₇₁BM, Y6 and PRi-C39 films decreased sequentially in the linear growth stage, indicating that their tensile moduli decrease accordingly. **Table 1** summarizes the statistical results of the thin film mechanical parameters extracted from the stress-strain curves. Taking PM6-based BHJ films as an example, the average values of tensile modulus were measured to be 1224.79±202.02, 609.09±194.62, and 325.51±40.52 MPa when PC₇₁BM, Y6 and PRi-C39 were selected as the acceptors, respectively, indicating that the rigidity of the active layer film can be adjusted in a wide range by using different kinds of acceptors. Specifically, the films with PC₇₁BM as the acceptor had the highest rigidity, followed by the Y6 films, and the PRi-C39 films with the lowest rigidity. In addition, the fracture strain values of these

films were also significantly different. The fracture strains of PC₇₁BM films were generally small, ranging from 0.01 to 0.03, indicating that these films are very brittle. After replacing PC₇₁BM with small molecule Y6, the brittleness of the films was reduced to a certain extent, and their fracture strains were improved to be 0.03–0.06. Surprisingly, the fracture strain of PRi-C39 based films was generally above 0.2, and the average value of PM6:PRi-C39 film was even as high as 0.351. It is worth noting that such high fracture strains in the all-polymer systems can meet the requirements (tensile strain over 20%) needed for the applications in the field of wearable electronics [22,23]. In other words, the small fracture strains of PC₇₁BM- and Y6-based films will limit their applications in flexible devices. The mechanical properties of the blend films were also checked by comparison of the toughness. A remarkable contrast in the toughness values of the all-polymer films with the PC₇₁BM and Y6 films was observed. For the PM6 systems, the toughness of the PRi-C39 films (5.440±0.873 MJ m⁻³) was ~16 times greater than that of the PC₇₁BM films (0.335±0.097 MJ m⁻³) and ~6-fold higher compared to that of the Y6 thin films (0.896±0.183 MJ m⁻³). It should be noted that similar results also appeared in the PTB7-Th and D18-C1 systems. Since the toughness is indicative of a material's resistance to fracture, it is believed that the all-polymer films have an excellent ability to absorb energy and plastically deform without fracturing when a crack is present.

Table 1. Summary of the mechanical parameters from the stress-strain characterizations.

Donor	Acceptor	Modulus ^a (MPa)	Fracture strain ^b	Toughness ^c (MJ m ⁻³)
PM6	PC ₇₁ BM	1224.79±202.02	0.027±0.008	0.335±0.097
	Y6	609.09±194.62	0.055±0.009	0.896±0.183
	PRi-C39	325.51±40.52	0.351±0.069	5.440±0.873
PTB7-Th	PC ₇₁ BM	437.82±73.90	0.017±0.001	0.094±0.028
	Y6	210.31±62.05	0.030±0.004	0.127±0.057
	PRi-C39	95.06±16.97	0.243±0.063	1.853±0.510
D18-C1	PC ₇₁ BM	1059.09±198.69	0.020±0.002	0.281±0.019
	Y6	833.54±109.34	0.046±0.008	0.588±0.086

^aDerived from the linear regime of the stress-strain curves using the Hooke's law.

^bObtained from the stress at failure. ^cCalculated by integrating the area under the stress-strain curve.

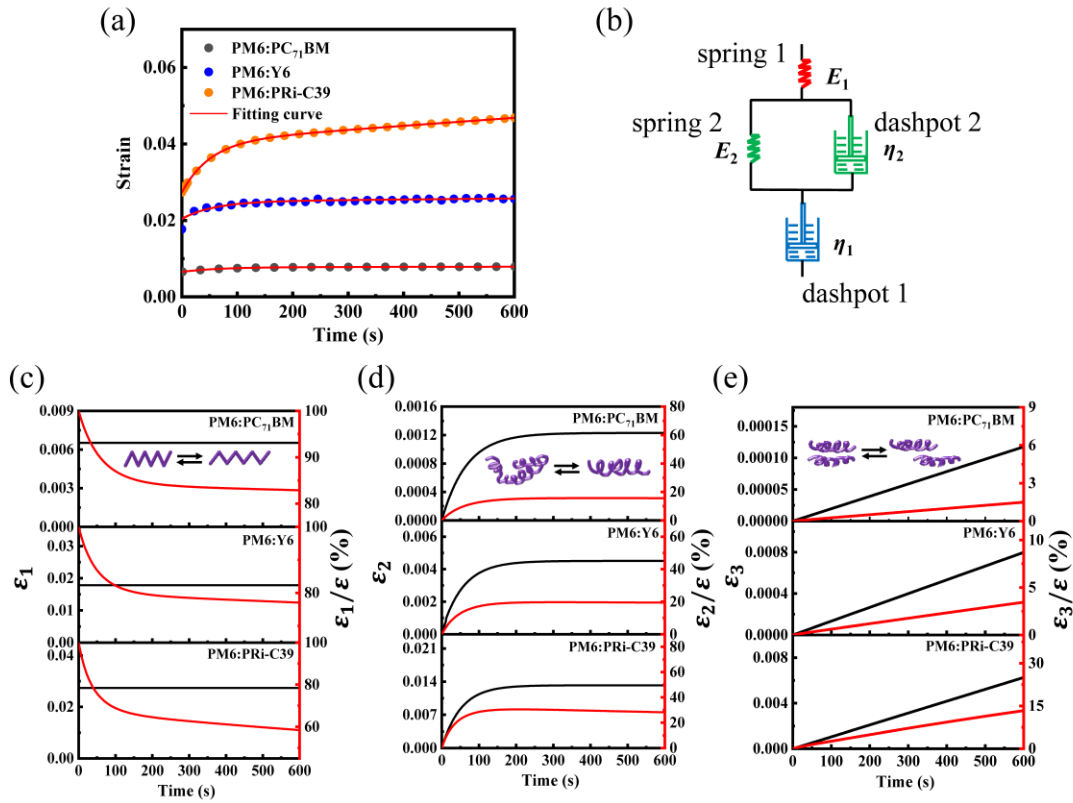


Fig. 2 (a) Creep curves of the PM6-based blend films with different acceptors under the same constant force. (b) Four-element viscoelastic model used to fit the creep deformation. (c) ϵ_1 , (d) ϵ_2 and (e) ϵ_3 and their proportions in the total creep deformations versus creep time. Insets in (c)–(e): Schematic diagram of the molecular movements.

Creep deformation is a time-dependent mechanical issue often encountered when polymer-based materials are used [24-26]. The reliability of the flexible PSCs may be affected by the creep deformation during devices being on service under long-term stress conditions. To the best of our knowledge, no previous studies have been conducted on the creep properties of active layer thin films in PSCs. In this context, we performed an in-depth study on the creep properties of PM6-based active layers using the FOW method. The creep curves of the PM6-based blend films with different

acceptors are presented in **Fig. 2a**. In all creep curves, an instantaneous increase in strain occurred and was followed by a time-dependent rise. Within the test range, the strain values of the all-polymer film were always the largest, indicating that its creep is the most obvious. In contrast, under the same condition, the strain and its time dependence of PM6:Y6 films were moderate. Unlike the PRi-C39 and Y6 films, the creep curve of the fullerene film was very stable, and the strain values were always the smallest. These results suggest that the all-polymer system is prone to creeping under constant external force, while the fullerene film has a better creep resistance.

To understand how the acceptor affects the creep behavior of the film, a four-element viscoelastic model (Fig. 2b) was employed to analyze the creep deformation of the BHJ films [27]. In this model, the total strain ε is composed of three independent components ε_1 , ε_2 and ε_3 . The ε_1 is the general elastic deformation caused by the change of bond length and bond angle inside the molecule. When the material is subjected to external force, the bond length and bond angle in its molecular chain will change immediately. Since the chemical bond is rigid, this deformation has the characteristics of ideal elasticity, and is completed instantaneously when the external force is applied. Therefore, this deformation can be calculated using Hooke's law (Equation 1):

$$\varepsilon_1 = \frac{\sigma}{E_1} \quad (1)$$

where σ is the applied strain and E_1 is the coefficient of elasticity of the spring 1. As the polymer chain is usually in a coiled state, hence, its molecular chain gradually stretches upon external force, resulting in the generation of high elastic deformation ε_2 . Theoretically, the ε_2 can be described by a parallel combination of an ideal spring (spring 2) and an ideal dashpot (dashpot 2) and expressed by Equations 2 and 3 as follows:

$$\varepsilon_2 = \frac{\sigma}{E_2} \left(1 - e^{-\frac{t}{\tau}} \right) \quad (2)$$

$$\tau = \frac{\eta_2}{E_2} \quad (3)$$

where E_2 and η_2 are the coefficient of elasticity of the spring 2 and the coefficient of

viscosity of the dashpot 2. In the absence of chemical crosslinking of the molecular chains of the polymer, a relative slippage between the polymer chains will also occur during the creep process, that is, viscous flow. This deformation cannot be recovered after the external force is removed, and thus, it is an irreversible deformation, which is represented by ε_3 . The ε_3 can be described by an ideal dashpot (dashpot 1) and expressed by Equations 4 as follows:

$$\varepsilon_3 = \frac{\sigma}{\eta_1} t \quad (4)$$

where η_1 is the coefficient of viscosity of the dashpot 1. Therefore, the total creep deformation ε is the sum of the above three parts, namely:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{\sigma}{E_1} + \frac{\sigma}{E_2} \left(1 - e^{-\frac{t}{\tau}}\right) + \frac{\sigma}{\eta_1} t \quad (5)$$

The experimentally obtained creep curves were fitted by using Equation 5, the fitting results are displayed as the solid lines in Fig. 2a, and the parameters used for fitting are summarized in **Table S1**. As a result, the experimental data could be well described by using this theoretical model, indicating the high accuracy of this model. Figs. 2c–2e present the relationships of ε_1 , ε_2 and ε_3 with creep time, respectively, and the insets describe the schematic diagrams of the creep deformations at the molecular level. As seen in Fig. 2c, the general elastic deformation occurred instantaneously at the moment the external strain was applied, and thereafter, the values of ε_1 remained unchanged. However, as the high elastic deformation and viscous flow deformation continued to occur, the proportion of ε_1 in the total creep ($\varepsilon_1/\varepsilon$) gradually decreased. After 600 s of creep, the proportion of ε_1 in the total ε of the PC₇₁BM, Y6 and PRi-C39 films decreased from the initial 100% to 82.9%, 77.1% and 58.5%, respectively. Such high proportions indicate that in all these films the creep is dominated by the general elastic deformation throughout the test time range. In addition, the values of $\varepsilon_1/\varepsilon$ in the PC₇₁BM-based film were always the largest at each specific time, indicating that the general elastic deformation in the PC₇₁BM film is more obvious than that in the Y6 and PRi-C39 films. The variation trend of ε_2 with time was obviously different from ε_1 . As shown in Fig. 2d, in the initial stage, ε_2 rose rapidly, then the growth rate gradually

slowed down until ε_2 was no longer increasing. Finally, the values of $\varepsilon_2/\varepsilon$ in PC₇₁BM, Y6 and PRi-C39 films were approximately 15.6 %, 19.5 % and 28.2 % at the creep time of 600 s, respectively. As mentioned earlier, ε_3 is an irreversible deformation caused by mutual slippage between polymers, and increases linearly with creep time. As depicted in Fig. 2e, the experimental results were constant with the theoretical model as all the ε_3 rose linearly. Moreover, at the same creep time, the PC₇₁BM-based films had the smallest $\varepsilon_3/\varepsilon$ (1.5% at 600 s), indicating that PC₇₁BM can effectively “lock” the blend networks. Comparatively, the $\varepsilon_3/\varepsilon$ value of the Y6 film was 3.4%, while that of PRi-C39 was as high as 13.3%. We speculate that in the all-polymer film, both the donor and the acceptor will undergo irreversible intermolecular slip under external force, resulting in much higher $\varepsilon_3/\varepsilon$ values than those in the other two films.

Nanoindentation test

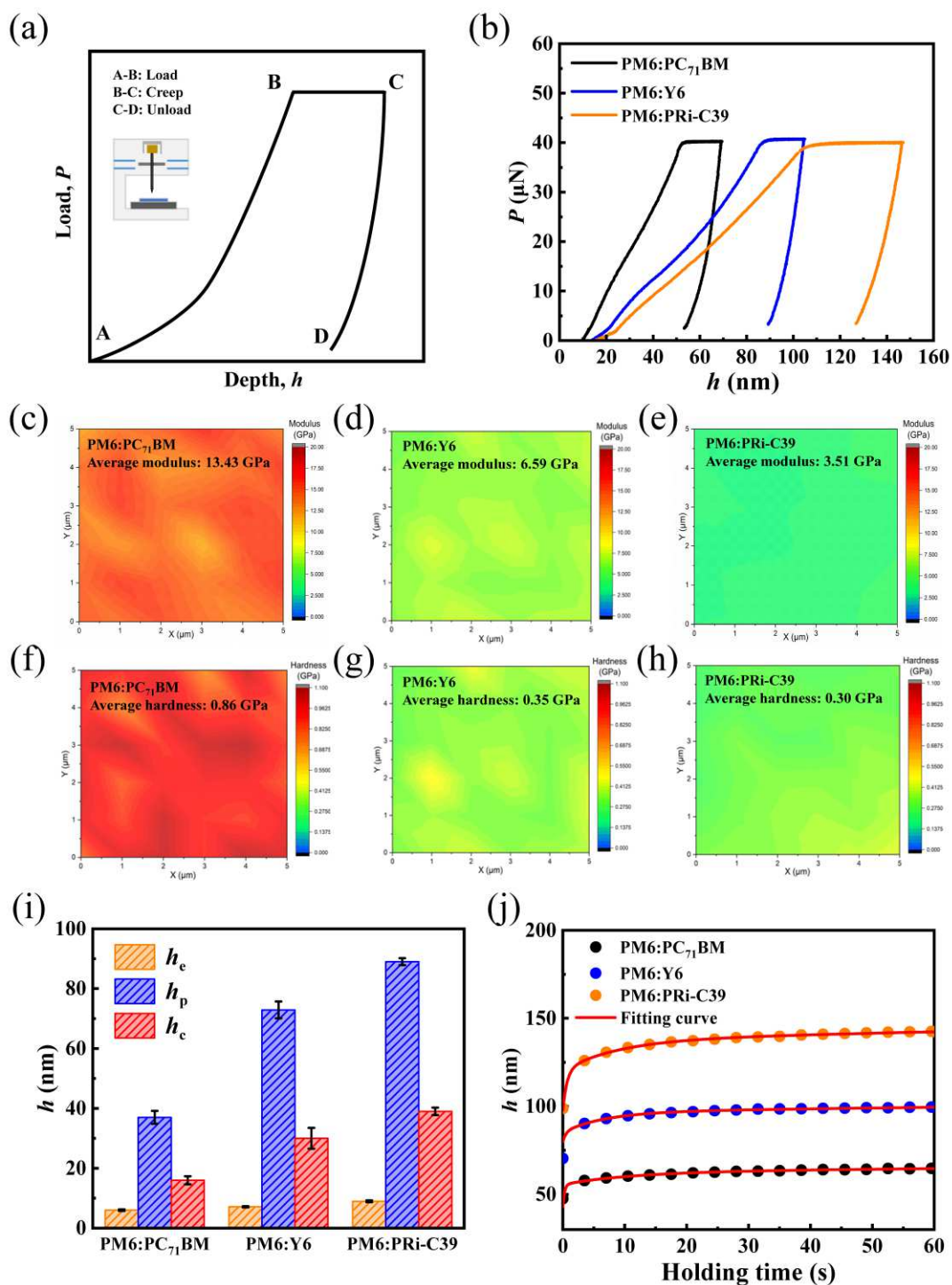


Fig. 3 (a) The schematic diagram of the nanoindentation test together with a typical load versus displacement ($P-h$) curve. (b) The representative $P-h$ curves of active layer films based on different electron acceptors. The modulus distributions of (c) PM6:PC₇₁BM, (d) PM6:Y6, and (e) PM6:PRi-C39 films. The hardness distributions of (f) PM6:PC₇₁BM, (g) PM6:Y6, and (h) PM6:PRi-C39 films. (i) The extracted statistical values of h_e , h_p , and h_c from the $P-h$ curves. (j) Changes of indentation displacement

with time during holding.

The above analyses are based on the macroscale uniaxial tensile tests. However, considering the complexity of the donor: acceptor blend, this experimental approach alone cannot fully reveal the mechanical properties of the films. To further study the mechanical properties of the photoactive layers, the nanoindentation test, an advanced technology that can provide quantitative results at a more microscopic level, was employed to characterize the corresponding films. The schematic diagram of the nanoindentation test together with a typical load versus displacement ($P-h$) curve are exhibited in **Fig. 3a**. A typical nanoindentation experiment involves applying a load to force an indenter into the sample surface (A–B), then holding the load over a period (B–C), and finally unloading the force (C–D). In a specific study, the force loading, holding, and unloading processes should be set reasonably according to the research purpose. By analyzing the loading/holding/unloading curves, many important mechanical parameters of the film, such as indentation modulus, elastic deformation (h_e), plastic deformation (h_p), and creep depth (h_c) can be accurately determined [28]. To ensure the reliability of the results, 50 sets of nanoindentation experiments were performed on each BHJ film on an area of $5\ \mu\text{m} \times 5\ \mu\text{m}$. The representative $P-h$ curves and the modulus distributions of BHJ films based on different electron acceptors are displayed in Fig. 3b and Figs. 3c–3e, respectively. It is seen that the indentation responses of the three acceptors-based films were highly misaligned, indicating their microscopic mechanical properties are quite different. Figs. 3c–3e show that the average indentation moduli of the films based on PC₇₁BM, Y6 and PRi-C39 decreased sequentially, which were 13.43 GPa, 6.59 GPa and 3.51 GPa, respectively. This trend is the same as that of the tensile elastic modulus results, which verifies the FOW tensile test. Nonetheless, it should be noted that the moduli measured by nanoindentation were generally about an order of magnitude higher than those obtained by the FOW method. There are two possible reasons for this discrepancy: first, the tensile measurement measures the mechanical properties of the film as a whole, while the results obtained by the nanoindentation measurement are only related to the molecules near the indenter

probe; second, when the nanoindentation test is performed, the tested material is in a compressed state, which is obviously different from the tensile test, possibly causing the difference between the two measurement results as well. In fact, relatively high modulus values for conjugated polymer-based films measured by nanoindentation have been reported in previous literature [15,29].

Figs. 3f–3h depict, respectively, the maps of the hardness of the PC₇₁BM, Y6, and PRi-C39 based photoactive layers in the same area as those of the modulus images. The indentation hardness (H) can be calculated using Equation 6 as follows [30]:

$$H = \frac{P_{max}}{A_c} \quad (6)$$

where P_{max} is the peak indentation load, and A_c is the projected contact area, which is readily calculated from the contact depth (h_c) using $A_c = 24.5h_c^2$. As a result, the BHJ appeared uniform in all the three blend films, and this indicates that the acceptors are mixed very uniformly with the polymer donor at the microscopic level, which is also demonstrated by the atomic force microscope test results shown in **Fig. S1**. Moreover, in the tested area, the PC₇₁BM-based BHJ film had the largest average hardness with a value of 0.86 GPa, followed by the Y6 film with a hardness lower than half of the former (0.35 GPa). In contrast, the average hardness in the all-polymer BHJ film (0.30 GPa) was slightly lower than that of the Y6 film. According to Equation 6, since the peak indentation load applied to measure the hardness was the same (40 μ N), the reason for the difference in the hardness of these films is that the values of h_c are different, that is, the films deformed differently when subjected to an external load. Therefore, the deformation in the films needs to be further investigated. The extracted statistical values of h_e , h_p , and h_c from the P - h curves are depicted in Fig. 3i, and the corresponding data are shown in **Table S2**. The average h_e for PM6:PC₇₁BM, PM6:Y6 and PM6:PRi-C39 BHJ films were measured to be 6.02, 7.13, and 9.04 nm, respectively. It is seen that the h_e in the all-polymer film was much larger than those in the PC₇₁BM and the Y6 based films, which is consistent with the variation tendency of the general elastic deformation in the tensile creep test. Due to the use of a sharp indenter tip, large values of h_p were observed in all films. Specifically, the h_p values of PC₇₁BM, Y6 and PRi-C39 films

were 37.13, 72.88, and 89.11 nm, respectively. Since the h_p of the PC₇₁BM film in the indentation experiment was much lower than those of the Y6 and PRi-C39 films, we can reasonably infer that the fullerene electron acceptor can prevent the movement of the donor molecules at the microscopic scale. In fact, this speculation can be further supported by the nanoindentation creep results as the PC₇₁BM, Y6 and PRi-C39 based films underwent creep with depths of 16.01, 30.10 and 39.05 nm within the same time period of load holding, respectively. Fig. 3j shows the changes in indentation displacement with time during holding (nanoindentation creep) at the maximum indentation load for the BHJ films. It is clear that the indentation depth curves can be divided into two regions, i.e., a primary stage and a steady state stage. In the primary stage, the indentation depth increased with holding time, but the rate of ascent decreased gradually. In the second stage, the indentation displacement changed little and remained basically stable. It should be noted that although the displacement-hold time curves shown in Fig. 3j are similar to the strain-time curves shown in Fig. 2a, the two should not be confused because their physical meanings are quite different. During the tensile creep tests, the large-sized films are subjected to the uniaxial tensile stress and the results reflect the behavior of a large number of molecules under stretching. However, indentation creep is under a localized stress field, and only molecules near the tip of the indenter are involved in the creep process. In addition, the variations of indentation displacement with holding time can be well fitted by the method proposed by Zeng *et al.* through Equation 7^[31].

$$h = h_0 + h_1[1 - \exp(-t/\tau_1)] + h_2[1 - \exp(-t/\tau_2)] + mt \quad (7)$$

where h_0 is the indentation displacement at the beginning of the creep, (h_1+h_2) describes the limit of the primary creep at a long enough time, τ_1 characterizes the initial creep rate, τ_2 describes the transition from the primary stage to the steady state stage, and m is the steady-state creep rate which is related to the viscosity of the materials. The solid lines in Fig. 3j are the fitting results obtained according to Equation 7 and the fitting parameters are summarized in **Table S3**. The τ_1 showed an increasing trend in the PM6:PC₇₁BM, PM6:Y6 and PM6: PRi-C39 films, with values of 0.26, 0.50, and 0.66 s, respectively, illustrating that the creep in the PC₇₁BM film occurs very slowly at the

primary stage and the PRi-C39 film creeps much faster after force loading. Moreover, the steady-state creep rate m in the PRi-C39 film was the largest (0.079 nm s^{-1}), followed by the Y6 film (0.045 nm s^{-1}), and the smallest appeared in the PC₇₁BM film (0.035 nm s^{-1}). These results show that even when a relatively stable steady state stage is reached, the creep rate of the all-polymer film is still the fastest.

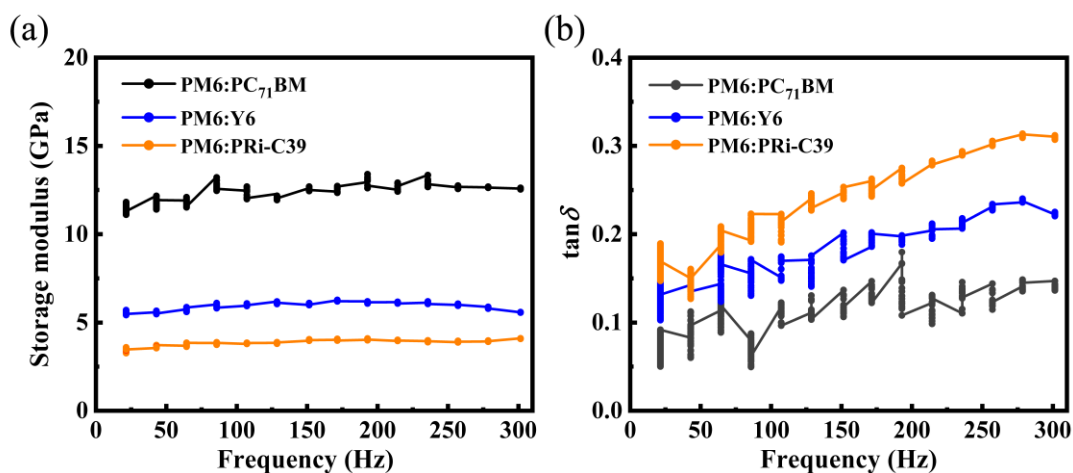


Fig. 4 The behavior of (a) storage modulus and (b) $\tan\delta$ as a function of loading frequency for various blend films.

Considering that organic solar cells, especially flexible organic solar cells, may encounter dynamic loads during practical use, it is necessary to study the mechanical properties of the photoactive layers at various strain rates. Typically, storage modulus and loss tangent ($\tan\delta$) are parameters often used to describe the dynamic mechanical properties of materials. Since these parameters are sensitive to different kinds of molecular motions, relaxation processes, transitions, and other structural heterogeneities^[32], interpreting the parameters could provide information at the molecular level to understand the mechanical behavior of the photoactive layers. Limited by the thickness of the active layers (usually around 100 nm), traditional experimental methods cannot be effectively used to determine the dynamic mechanical properties of the photoactive layers. Herein, the nano-dynamic mechanical analyzer (nano-DMA) technique was employed to study the dynamic mechanical behaviors of these films. In this method, a small periodic load is applied to the nanoscale indentation tip during the loading cycle and by monitoring the phase lag in the load-displacement

curve, the frequency-dependent mechanical properties of the material can be evaluated. This technique has been successfully applied in measuring the dynamic mechanical properties of many polymer composites [33-35]. **Fig. 4** illustrates the behavior of storage modulus and $\tan\delta$ as a function of loading frequency for various blend films. It is seen from Fig. 4a that the storage moduli of all tested samples remained stable over the test frequency range. Since the storage modulus is a measure of the elasticity of materials, this observation indicates that films based on these three acceptors are capable of withstanding alternating stresses over a wide frequency range. Unlike the storage modulus, the $\tan\delta$ showed an increasing trend with growing frequency in all films (Fig. 4b). The reason for this growth trend is not clear, we speculate that it may be attributed to an increase in internal friction between the acceptors and PM6 polymer matrix during dynamic loading, which can be understood as follows: as the loading frequency increases, more energy will be dissipated on the donor-acceptor interpenetrating networks near the tip of the indenter, which enhances chain mobility and consequently results in additional viscous response. In fact, the phenomenon that internal friction-induced $\tan\delta$ increases with frequency has been reported in other polymer composites [36]. In addition, as seen in Fig. 4b, all the loss tangent values in the test range were less than 1, indicating that the storage modulus is larger than the loss modulus (shown in **Fig. S2**), which confirms that the mechanical properties of these films are dominated by elasticity rather than plasticity. Moreover, this result is consistent with the small ϵ_3/ϵ values in the tensile creep experiment (Fig. 2e), which proves the correctness of the tensile creep fitting model (Equation 5).

Another striking feature in Figs. 4a and 4b is that the type of electron acceptor had a significant effect on the storage modulus and $\tan\delta$ of the blend films, and this is another direct evidence that the mechanical properties of the blend films are closely related to the acceptors. Taking the storage modulus as an example, the average storage modulus of the PC₇₁BM-based blend film was 12.06 GPa in the test range, while those of the Y6 and PRi-C39 films were 5.78 GPa and 3.69 GPa, respectively. This variation trend was the same as that of the elastic modulus obtained from the previous FOW tensile test. As the blend films have the same donor material (PM6), the difference in

modulus can reasonably be assumed to be the variations in the strength of the donor-acceptor interactions. That is to say, the larger storage modulus in the PC₇₁BM film is due to the strong interaction between PC₇₁BM molecules and PM6 molecules, while the lowest storage modulus in the PRi-C39 film is because of the weakest interaction between PRi-C39 and PM6.

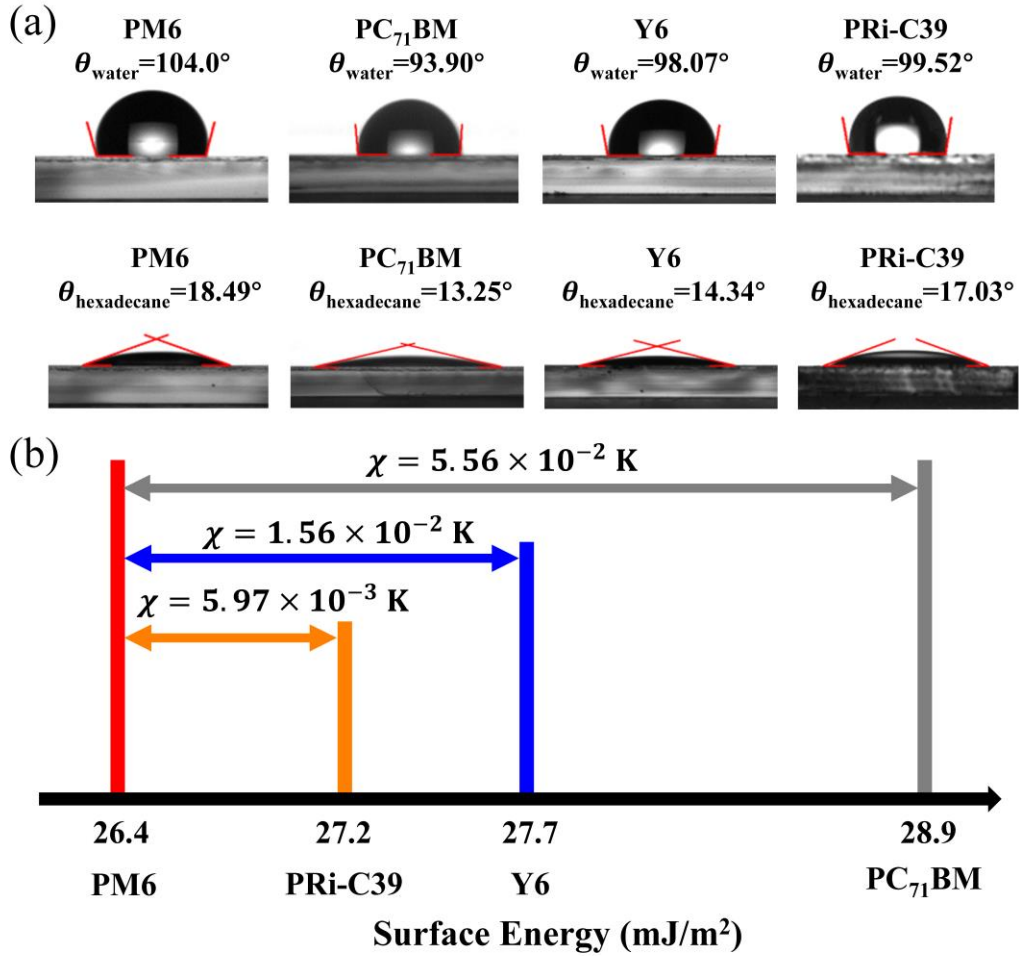


Fig. 5 (a) Droplet contact angle images of the pure films of PM6, PC₇₁BM, Y6, and PRi-C39. (b) Illustration of calculated surface energy γ and Flory-Huggins interaction parameter χ from the contact angle measurements.

To experimentally verify that the difference in the interaction between the donor and the acceptor is the reason for the variation in the mechanical properties of the active layer films, the contact angle measurement, by which the Flory-Huggins interaction parameter χ can be calculated from the surface energy γ ^[37], was conducted. The images of the droplet contact angles (θ) of water and hexadecane on the pure films of PM6,

PC₇₁BM, Y6, and PRi-C39 are shown in **Fig. 5a**, and the γ and χ are depicted in Fig. 5b. The values of γ for the PM6, PC₇₁BM, Y6, and PRi-C39 pure films were 26.4, 27.2, 27.7, and 28.9 mJ/m², respectively. Accordingly, the PM6:PC₇₁BM, PM6:Y6 and PM6:PRi-C39 pairs exhibited χ values of 5.97×10^{-3} K, 1.56×10^{-2} K, and 5.56×10^{-2} K, respectively. The smallest χ value for the PM6:PC₇₁BM film indicates strong PC₇₁BM–PM6 interactions, and this strong donor-acceptor interaction can make the film maintain a stable interpenetrating network structure when subjected to external force, which is the essential reason for the high modulus of PM6:PC₇₁BM film. While the higher χ value of the PM6:Y6 indicates relatively weaker interactions between the small molecule Y6 and PM6, thus leading to moderate elastic and storage moduli. When the polymer PRi-C39 was used as the electron acceptor, the interaction between PRi-C39 and PM6 was the weakest, and a relative slippage between molecules is easy to occur. This reduces the stiffness of the blend film, but also means that the all-polymer film possesses better stretchability.

Conclusions

In conclusion, the multi-scale mechanical properties of three representative electron acceptors based BHJ films were studied. The tensile modulus of films based on PC₇₁BM, Y6, and PRi-C39 measured by using the FOW method decreased sequentially, but their fracture strain and toughness showed an increasing trend. The nanoindentation test results indicated that the modulus and hardness in all of the three different acceptors-based films were uniformly distributed on the nanometer scale. Furthermore, the fullerene acceptor system had the largest average modulus and hardness, while the all-polymer system exhibited the best flexibility. The mechanical properties of small-molecule acceptor-contained films were intermediate between the fullerene systems and the polymer acceptor systems. Time-dependent creep analyses from both macroscopic tensile measurements and microscopic indentation characterizations illustrated that PC₇₁BM could effectively immobilize the BHJ interpenetrating networks and alleviate the occurrence of creep deformation. In contrast, BHJ films based on Y6 and PRi-C39 were more prone to creep, and this was more

serious in the PRi-C39 system. Contact angle test results demonstrated that the reason for the dissimilar mechanical properties in these films was the different interactions between PM6 and the acceptors. These experimental results showed that the mechanical properties of the BHJ films are multifaceted and complex. In addition to the "flexibility" and "rigidity" in the conventional sense, the time-dependent creep and dynamic mechanical behavior of the BHJ films are also very important for practical applications. Therefore, this work provides novel insights into the mechanical properties of the BHJs in PSCs from the macroscale to the microscale, which is beneficial to the materials design and device fabrication of flexible PSCs, thereby promoting the development of flexible PSCs and even flexible electronics.

Experimental Section

Materials: The electron donor materials PM6, PTB7-Th and D18-Cl and the electron acceptor materials PC₇₁BM and Y6 were purchased from Solarmer Materials Inc., Beijing. The polymer acceptor material PRi-C39 was synthesized according to prior literature ^[18].

BHJ Film Preparations: Glass substrates were firstly cleaned using consecutive ultrasonic baths in acetone, detergent, deionized water, and isopropyl alcohol, respectively, and then dried in an oven. For the FOW samples, substrates were treated with oxygen plasma for 5 min, and then a 40 nm-thick poly(styrene sulfonate)-doped poly(ethylenedioxythiophene) (PEDOT:PSS, Clevios AI 4083) film was obtained by spin-coating on the glass. The substrates were subsequently dried at 150 °C. After that, the mixture solutions of donor and acceptor (1:1.2 w/w, chlorobenzene as the solvent) were spin-casted in an N₂-glovebox and baked at 120 °C for 10 min. The thickness of the BHJ films was kept around 100 nm. For the nanoindentation sample preparation, the BHJ films of about 1 μm were directly spin-coated on glass substrates which were treated with plasma for 5 minutes, then the films were annealed at 120 °C for 10 min.

Characterizations: In the FOW measurements, the BHJ films were cut into a dog-bone shape by laser etching and transferred onto the water surface. The sample was then fixed with the PDMS on the fixture through Van der Waals interaction. The load values

were measured by a load cell with high resolution (LTS–10GA, KYOWA, Japan), and the strain values were recorded through a micro mechanical testing system (IBTC–300, CARE, China). During the tensile creep test, the constant stress applied to the sample was 13.25 MPa. The nanoindentation tests (including nano-DMA characterizations) were conducted with a nanoindenter (TI980, Bruker, USA) equipped with a Berkovich diamond indenter with a radius of ≈ 120 nm. To get the values of h_e , h_p , and h_c , a loading rate of 40 $\mu\text{N/s}$, a load of 40 μN that held for 100 s, and an unloading rate of 40 $\mu\text{N/s}$ were preset. Modulus and hardness profiles were recorded in an automatic measurement mode, in which the loading, holding, and unloading durations were all 0.1 s. The sample preparation conditions of nano-DMA were the same as those of the nanoindentation test. Experiments were performed at room temperature over the frequency range from 25 to 300 Hz. During the test, a small oscillation (1 μN) was superimposed on a constant quasi-static force of 40 μN . The contact angles were estimated with a goniometer equipped with a CCD camera (Model JY–82, China).

DATA AVAILABILITY

The experimental data that support the findings of this study are available from the corresponding author upon reasonable request.

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COMPETING INTERESTS

The authors declare no competing interests.

AUTHOR CONTRIBUTIONS

T. Z. and F. G. contribute equally to this work. B. X. and R. Y. directed this work. T. Z. and F. G. conducted experiments, fabricated devices, and analyzed data. S. L., Q. L. and X. W. helped to analyze the data. T. J. provided the materials. All authors contributed to the manuscript revisions.

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