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A transparent, robust, thermal Stable, and recyclable cellulose vitri- mer film with boric ester- bond exchange

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ABSTRACT: Cellulose, often considered a highly promising substitute for petroleum-based plastics, offers several compelling advantages, including abundant availability, cost-effectiveness, environmental friendliness, and biodegradability. However, its inherent highly crystalline structure and extensive hydrogen-bonded network pose challenges for processing and recycling. In this study, we introduce the concept of cellulose vitrimer (CV), wherein dynamic bonds are incorporated to reconfigure the hydrogen-bonded network, resulting in a mechanically robust, highly transparent material. CV exhibits exceptional malleability, thermal stability, and noteworthy resistance to water and solvents. Due to the dynamic bond disassociation, CV can be effectively chemically recycled using a well-established "dissolution-and-reforming" process. Moreover, CV has proven successful as flexible substrate materials for organic solar cells, outperforming traditional petroleum-based polyethylene naphthalate (PEN). Given these advantages, CV has the potential to replace conventional petroleum-based materials with recyclable and environmentally friendly

alternatives, particularly within the realm of electronic devices and displays.

simultaneously improving its processing and recycling capabilities.

1. Introduction

The global production of plastic exceeds 100 million tons annually, with a meager 2% being subjected to recycling, while the majority is incinerated, dumped in a landfill, or discarded in the ocean.^[1,2] The natural degradation of plastics in the environment extends over decades, if not centuries. This "white pollution" stemming from plastics leads to significant resource and energy wastage and jeopardizes the sustainable development of the Earth's environment. Consequently, there is a shift toward the development of naturally degradable, recyclable, and eco-friendly plastics to replace traditional petroleum-based counterparts.

Cellulose, a renewable resource obtainable inexpensively from a diverse range of sources, emerges a promising alternative to petroleum-based polymer materials. Cellulose films exhibit remarkable characteristics. They are light-weight, transparent, thermally stable, and have substantial strength, holding great potential for applications in flexible electronic devices.^[3-7] Nevertheless, cellulose poses inherent challenges, including the numerous hydrogen bonding interactions within its chemical structure, rendering it insoluble in most solvents and cannot be melted before decomposition, thereby complicating processing. The abundance of hydroxyl groups limits its utility in aqueous environments. Chemical modification of cellulose, such as etherification,^[8] esterification,^[9,10] and aldoxylation,^[11] enhances the solubility of cellulose, leading to the development of mature commercial products, like cellulose acetate and cellulose nitrate by solution processing. However, these cellulose-based plastics exhibit a high degree of hydroxyl group substitution (up to 2.0-2.5), severely compromising the original H-bonded network structure. Consequently, advantages such as mechanical strength, solvent stability, and thermal stability are greatly diminished.^[12] Therefore, a substantial challenge remains in devising an effective strategy to preserve the cellulose network's relative integrity while

Vitrimers are a category of dynamically crosslinked polymers that merge the thermal stability of thermosetting polymers with the malleability of thermoplastics.^[13] Leveraging dynamic crosslinking chemistries like transesterification,^[13-18] transamination,^[19, 20] imine amine exchange reaction,^[21, 22] transcarbamoylation,^[23-25] boronic ester exchange,^[26-28] diketoenamine amine exchange^[29], among others, the dynamic bonds within vitrimers respond to external stimuli, such as light and heat. This activation allows the crosslinking network to undergo continual breaking and reformation, bestowing plasticity upon the network while maintaining its integrity. The concept of cellulose vitrimers (CVs), wherein dynamic bonds are incorporated into the cellulose network to replace a portion of the hydrogen bonds, represents a promising avenue for expanding the applications of vitrimers while improving the performance of cellulose. Previous research primarily involved incorporating cellulose as a reinforcing component in vitrimer composites,^[30-35] with limited focus on converting cellulose into vitrimers themselves. By introducing dynamic bonds through hydroxyl group modification on the cellulose molecular chain, the H-bonded integrity of the network is disrupted, increasing the conformational entropy of the cross-linked network. This alteration benefits the solution casting of cellulose in common solvents. Simultaneously, dynamic bonding restores the disrupted network and reconstructs the H-bonded network, preserving some of the inherent advantages of cellulose. Therefore, the development of the CVs holds significant promise in addressing the challenges associated with cellulose-based material preparation. It offers an innovative approach to harness the benefits of both vitrimers and cellulose, opening new possibilities for versatile and sustainable materials.

In this study, we report a cellulose vitrimer possessing a range of exceptional characteristics, including high transparency, robust mechanical properties, thermal stability, as well as excellent resistance to both water and solvents. Notably, this CV showcases remarkable recyclability by a straightforward and effective method. Dioxaborolane metathesis, a highly efficient dynamic exchange reaction occurs, without the addition

of a catalyst at temperatures as low as 60 °C, has demonstrated success in converting olefins into vitrimers.^[26] We modify cellulose through esterification with 10-undecenoyl chloride. This modification serves to weaken the H-bonded network of cellulose, enhancing its solubility. In addition, it introduces double bonds into the cellulose structure, providing a necessary functional group for subsequent crosslinking. Cellulose vitrimers were prepared through a highly efficient thiolene click reaction, where the terminal double bonds of the cellulose chains are re-crosslinked with dioxaborolanes, as illustrated in Figure 1a. The resulting material exhibits excellent strength and toughness, as well as, a high transparency, with a transmittance exceeding 92% at a wavelength of 550 nm. (Figure 1b and Figure S1). Exploiting the unique attributes of this CV, they were successfully used as flexible solar cell substrates, outperforming traditional petroleum-based PEN polymer. (Figure 1c) The CV excels in terms of chemical recyclability. Waste CVs can be readily dissolved in solvents and reformed through solvent evaporation, akin to thermoplastics. This recyclability enables the incorporation of novel functionalities, such as Aggregation-Induced Emission (AIE) molecules, leading to transparent patterned films. (Figure 1d) As a consequence of these remarkable properties and capabilities, CVs have emerged as a promising candidate for replacing conventional petroleum-based polymers. Its potential for flexible electronic devices and displays is evident, but extends also into domains that demand sustainable and high-performance materials.

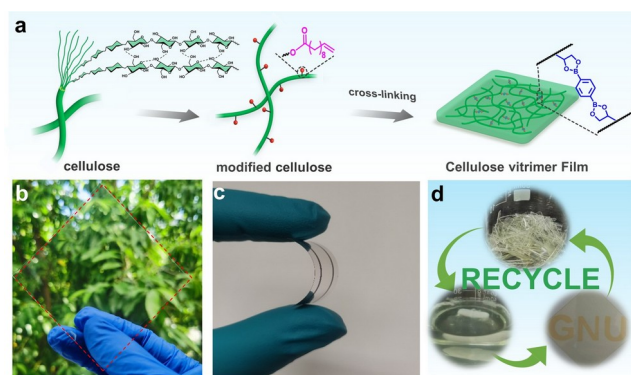


Figure 1. Design strategy and some advantages of CV. a) Schematic illustration of the synthesis of CV film. b) Photograph of the transparent CV film. c) Photo to show good flexibility of CV as applied in organic solar cells substrate. d) Image to show the closed-loop recycling of CV.

2. Results and Discussion

2.1 Preparation and mechanical properties of CV

The synthesis of CV was conducted in two steps. Initially, microcrystalline cellulose (MCC), the raw material, was dissolved in an ionic liquid for a homogeneous esterification reaction with 10-undecenoyl chloride.^[36] (Figure 2a) This process yielded modified cellulose (m-Cell, featuring a hydroxyl substitution fraction of 0.75 (as detailed in the Supporting Information). This modification led to the transformation of the highly crystalline cellulose into an amorphous, disordered material, as evidenced by x-ray diffraction (XRD,

(Figure S2), further enhancing its solubility. Subsequently, the m-Cell underwent a thiol-ene click reaction with (1,4-phenylenebis(1,3,2-dioxaborolane-2,4-diyl))dimethanethiol (BDB) under UV illumination. (Figure 2a) By carefully controlling the ratio of the BDB to the modified cellulose, we prepared three CVs (CV-10, CV-20, and CV-30) with varying BDB ratios. (Table S1) The chemical structures of the synthesized m-Cell and CVs were examined by FTIR. (Figure 1b) The FTIR spectra of m-Cell shows the characteristic absorption peaks at 3074, 908, and 1733 cm^{-1} , corresponding to C=CH, C=C, and C=O, respectively, confirming the successful preparation of m-Cell. In the FTIR spectra of CV, new peaks associated with B-O and C-S bonds emerged at 1312 and 652 cm^{-1} , respectively, affirming the successful preparation of CV. ^{13}C solid-state NMR (ssNMR) provided further evidence of the successful introduction of dynamic bonds into the cellulose network, as shown in Figure 2c. For m-Cell, the chemical shifts at 115 ppm and 138 ppm correspond to the distal double bond, and the chemical shift at 173 ppm represents the carbonyl group, confirming the successful modification of cellulose.^[37] As for CV, the signal from the benzene ring of the cross-linker appears at 133 ppm in the NMR spectrum, indicating dynamic bonds, associated with the crosslinker, were effectively introduced into the cellulose network, further validating the presence of dynamic bonds in the CV.

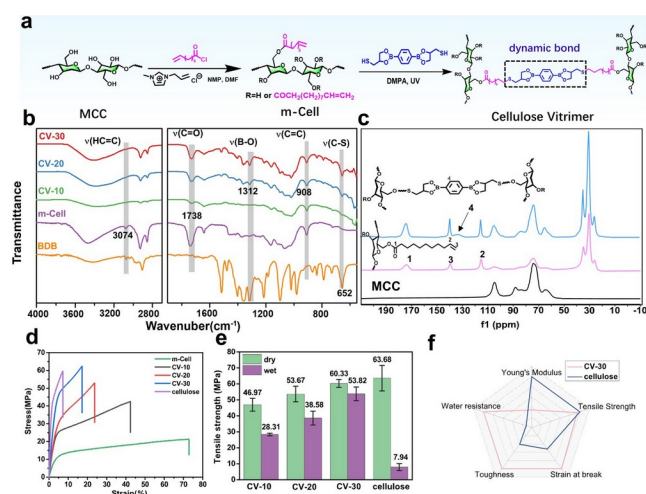


Figure 2. Synthesis and mechanical properties of CVs. a) synthesis route of m-Cell and CVs. b) FT-IR spectra of BDB, m-Cell and CVs. c) Solid state ^{13}C NMR spectra of MCC, m-Cell and CV-20.

d) The tensile stress-strain curves of pure cellulose, m-Cell and CVs. e) The dry and wet (30 min infiltration in water) tensile strength of CVs and pure cellulose film. f) Radar chart to compare CV-30 with pure cellulose.

Mechanical properties of cellulose vitrimers were investigated by tensile testing. An obvious reduction in the tensile strength and modulus of cellulose after modification is evident, primarily attributed to the disruption of its crystalline and H-bonded structure. (Figure 2d, Table S2) Cross-linking plays a pivotal role in gradually establishing the cellulose network, resulting in a subsequent increase in mechanical strength. As the content of the BDB increases from 10%, 20% to 30%, corresponding to CV-10, CV-20 to CV-30, the tensile strength progressively rises from 46.97, 53.67 to 60.33 MPa. It is interesting to note that despite achieving the same tensile strength as pure cellulose,

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elongation at break for CV-30 is twice that of pure cellulose, indicating better flexibility to the material compared to pure cellulose.

Pure cellulose shows a rapid deterioration in mechanical strength when exposed to water, significantly limiting its practical use. We compared the stability of CV to pure cellulose after immersion in water for 30 minutes. In stark contrast to pure cellulose, which shows an 8-fold decrease in strength, the wet and dry strength of CV remains relatively stable. (Figure 2e, Table S3) Contact angle measurements further underscore this contrast. After 10-minutes the contact angle of pure cellulose decreased from 59.3 to 32.2 degrees, while that of CV showed a much smaller decrease, remaining at 50 degrees, indicating the superior stability of CV in water (Figure S3). It is noteworthy that the water resistance of CV improves with increasing cross-link density, due to the denser crosslinking that hinders the penetration of water. CVs also show outstanding stability in a variety of organic solvents. (Figure S4 and Table S4) A comprehensive comparison between the properties of CV-30 and pure cellulose materials is shown in Figure 2f. Remarkably, aside from a slight decrease in modulus, CV-30 outperforms pure cellulose in tensile strength, elongation at break, toughness, and water resistance. This superior performance paves the way for a diverse range of future applications for CV.

2.2 dynamic and thermal properties

The mobility of cellulose segments is inherently restricted by the molecular structure due to the presence of a dense H-bonded network. However, when hydroxyl groups are partially substituted, this disrupts the integrity of the H-bonded network and enhances the mobility of the cellulose segments. We performed dynamic thermo-mechanical analysis (DMA) to investigate the viscoelastic properties of CV. As shown in Figure 3a, the storage modulus gradually decreases with increasing temperature but does not exhibit the typical rubbery plateau observed in conventional polymers. The loss modulus, which represents viscosity, remains relatively constant. This is attributed to the low degree of substitution in our CV, which maintain a relatively rigid network structure with limited chain segments mobility. The $\tan\delta$ curve reveals a terrific glass transition temperature (T_g) of 239.7°C for CV-20, ensuring material stability during high-temperature annealing. A weak transition peak is observed at 88.4 °C, which we attribute to the motion of 10-undecenoyl chain. However, the absent a glass transition in both m-Cell and CV up to 200 °C range, as evidenced by DSC, (Figure 3b) which is similar to pure cellulose, further validating the existence of strong hydrogen bonding interactions in CV. This corroborates the idea that low-substituted cellulose can maintain a more robust crosslinking network density that constrains the full mobility of chain segments and ensuring thermal stability. Furthermore, TGA data indicate that CV has a decomposition temperature of 300 °C (Figure S5). The dimension change was char-

acterized thermal mechanical analysis (TMA). As shown in Figure 3c, CV-20 shows a rapid dimension decrease at temperatures exceeding 180 °C, which is distinct from the typical response seen in conventional thermoset polymers, that show a continuous dimension increase.^[38] This unique behavior in CV is attributed to the ability of the dynamic bond exchange reactions within the network to eliminate internal stresses that may exist between the chains. As a result, the material undergoes a macroscopic dimension decrease as it adjusts its conformation.

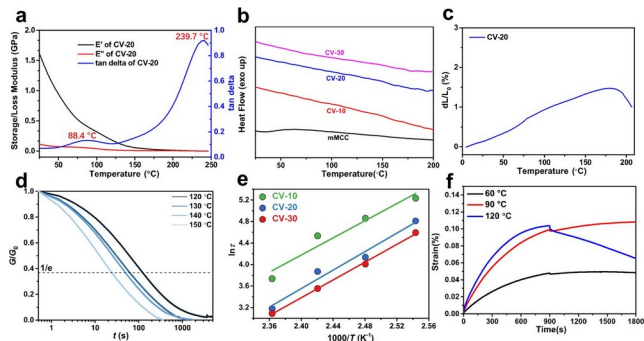


Figure 3. Dynamic and thermal properties of CV. a) Temperature-Dependent storage modulus (E'), loss modulus (E'') and $\tan\delta$ for CV-20. b) DSC curves of m-Cell and CV. c) TMA curves of CV-20. d) Normalized stress-relaxation curves at different temperatures for CV-20. Dashed lines indicate 37% of G_0 . e) Arrhenius analysis and the activation energy of CVs. f) Tensile creep and recovery of CV-20 with an applied stress of 0.01 MPa at different temperature.

To further investigate the dynamic behavior of CVs, stress relaxation experiments were performed using DMA. In the linear viscoelastic region, stress decay was monitored as a function of time while maintaining a fixed strain of 1%. Despite the extensive cross-linking of CV, complete relaxation was observed after the application of strain over the entire temperature range, signifying the highly malleability of CV. (Figure 3d Figure S6 and S7) The relaxation time τ^* , defined as the time when stress decrease to 1/e of the initial stress, was examined. As shown in Figure 2d, when the temperature gradually increased from 120 °C to 150 °C, the corresponding relaxation time decreased from 120 seconds to 24 seconds due to the increased rate of bond exchange reactions at high temperatures. Notably, at the same temperature, the relaxation time resulted shorter as BDB content increased. For instance, at 120°C, the τ^* decreased from 187 seconds to 98 seconds as BDB content increased from 10% to 30%. (Figure S8) It's essential to note that our CV exhibit two types of cross-linking: H-bonded and dynamic bond facilitated by BDB. When BDB content is low, both types contribute to stress relaxation. However, as the BDB content increases, the dynamic bonds gradually become the dominant factor in stress relaxation. The relaxation time and temperature data can be well fit to, an Arrhenius behavior of CV. From the slopes of the fit lines, we calculated the activation energies of the dynamic exchange reaction to be 66.3 kJ/mol, 71.4 kJ/mol, and 68.7 kJ/mol for CV-10, CV-20, and CV-30, respectively. (Figure 3e) Additionally, creep-recovery tests were conducted on CV-20. As shown in Figure 3f, at lower temperatures (60 and 90 °C), creep was minimal, and the deformation recovery upon withdrawal of the external force was limited. However, as the temperature increased to 120 °C, although the creep

remained relatively small, a gradual recovery of deformation upon the withdrawal of the external force was observed. This behavior is attributed to the activation of dynamic exchange reaction, allowing CV segments to adjust their conformation, resulting in a gradual recovery. These results indicate that the dynamic exchange reaction of bis-dioxaborolane in the CV imparts excellent flow ability, malleability and deformation recovery at high temperatures, positioning it as a compelling alternative to plastics intended for high-temperature applications.

2.3 Chemical recycling of CVs

The recovery of thermoset materials often involves complex processes such as acid degradation to break them down into monomers, followed by the separation and purification of these monomers for closed-loop polymer-to-monomer recovery.^[29] In contrast, the recovery of CV is remarkably simpler, requiring only common solvents, and it can be repeatedly dissolved and reformed, similar to thermoplastic materials. Taking CV-20 as an example, in the presence of water, it degrades into linear cellulose molecular chains (C1 and C2) and 1,4-phenylenediboric acid, as shown in Figure 4a. This structure was verified by ¹³C NMR. (Figure 12) Degradation rate tests were conducted at different temperatures, and the results indicated that higher temperatures led to faster degradation rates, with complete degradation achievable at 80°C in ~ 30 minutes. (Figure 4b) C1, C2, and 1,4-phenylenediboric acid can be dissolved in solution without requiring separation. After solvent evaporation and dehydration, they can be restored to the network structure of CV-20. ¹³C ssNMR and FTIR confirmed that the chemical structure of the recycled material is identical to that of the original. (Figure 4c and Figure S10) Mechanical property tests were conducted after four cycles of “dissolving-reforming”, showing that the tensile strength and elongation at break were not significantly changed, (Figure 2d and Table S5) demonstrating that this recycling method preserves the chemical stability of the network structure. It is noteworthy that the storage moduli and *T_g*’s of the recovered CV are higher than those of the initial ones. (Figure S11) This observation suggests that the internal defect structure of CV undergoes reconfiguration, resulting in a denser crosslinked network structure following the recovery process. This straightforward and effective recycling method enables the addition of functional molecules, such as tetraphenylethylene (TPE), thereby imparting new functionalities to the material. Figure 4e illustrates a case where CV-20 was dissolved in a DMF/H₂O (V/V=10/1) solution, to which TPE was added, resulting in a transparent film. The film can be subjected to UV illumination under a photomask with “GNU” letters to create a patterned transparent film. These experiments highlight the capability of CVs to be chemically recycled in a closed loop using simple solvents while also being modified to possess new functions.

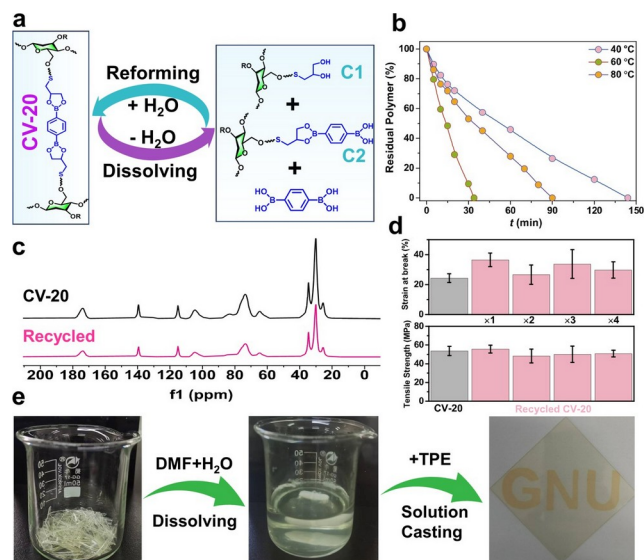


Figure 4. Closed-loop of chemical recycling CVs. a) Schematic illustration to show the chemical structure change during dissolving-reforming process. b) Temperature-dependent degradation kinetic curves of CV-20 in DMF/H₂O solution. c) Solid state ¹³C NMR spectra of CV-20 and recycled one. d) Tensile properties of CV-20 and recycled CV-20. f) Image to show closed-loop recycling of CV-20, resulting a transparent patterned film.

2.4 Application for organic solar cells substrate

Considering the remarkable attributes of CVs, which include high transmittance in the visible range, mechanical robustness, thermal stability, as well as resistance to both water and solvents, one promising application is its use as a flexible substrate for organic solar cells (OSCs). To assess the performance of CV as a substrate for OSCs, we conducted a comparative analysis with commercial polyethylene naphthalate (PEN). When processed into films, the surface roughness and modulus of CV-20 are very similar to PEN (Figure. 5a). As shown in Figure. 5b, the transmittance CV-20 in visible range is comparable to that of PEN and the haze of the CV-20 and PEN films are 2.6% and 1.9%. Using CV-20 the OSC is fabricated with structure of CV-20/ITO/interfacial layer/bulk heterojunction (BHJ)/interfacial layer/silver and the device performance is characterized by current density-voltage (J-V) curves (Figure 5e, 5f, 5g). Corresponding device parameters are listed in Table S6. ITO is fabricated by sputtering. The molecular structures of BHJ materials (PM6 and BTP-eC9) are shown in Figure. 5d. In conventional OSCs, the interfacial layer coated on substrates are PEDOT:PSS. As for PEDOT:PSS, despite strong acidity, 160 °C annealing is necessary during device fabrication. As shown in Figure. 5e, the higher fill factor (FF) of CV-20-based OSC indicates the stability of substrate under strong acidic conditions with 160 °C annealing. In the inverted devices, the interfacial material zinc oxide (ZnO) can be obtained by on-substrate heating the coated precursor. The abundance of ZnO in the heated film is directly proportional to annealing temperature in range from 100 to 200 °C. Thus, we compared the performance of devices based on CV-20 and PEN at three temperatures (100, 150 and 200 °C) in Figure. 5f and 5g. The power conversion efficiency (PCE) of PEN-based devices decrease as the temperature increases, while the PCEs of CV-20-based devices are maintained

even at 200 °C. This is a clear indication that the higher T_g and

excellent thermal stability makes CV-20 more suitable as a substrate for OSCs. Based on the data presented in Figure 5, CV, along with the design strategy used, offers valuable insights and guidance for the design of reliable OSC substrates.

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Author Contributions

All authors contributed to the writing of the manuscript.

Notes

The authors declare no competing financial interests.

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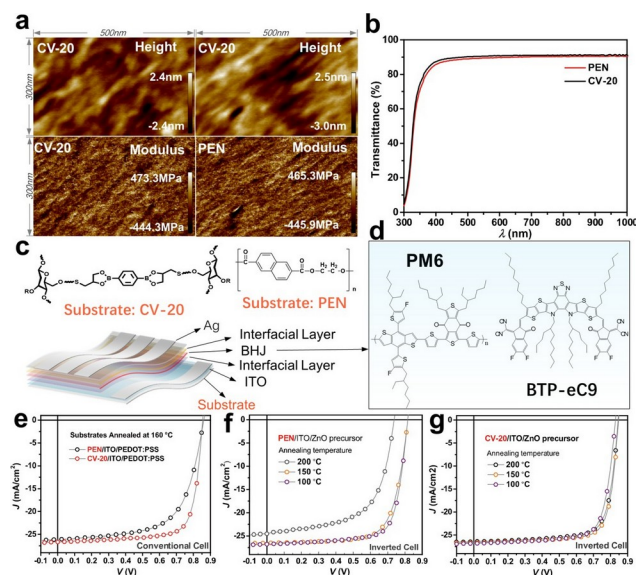


Figure 5. CV-20 applied as organic solar cells substrate. a) AFM images of CV-20 and PEN films. b) The transmittance of CV-20 and PEN films. λ refers to wavelength. c) The molecular structures of CV-20, PEN, PM6 and BTP-eC9. d) The device structure of OSC e) The J-V curves of CV-20- and PEN-based conventional OSCs. e) The J-V curves of CV-20-based inverted OSCs. f) The J-V curves of PEN-based inverted OSCs.

3. Conclusion

In summary, cellulose vitrimers (CVs) were prepared using a well-established strategy and introduced dynamic crosslinking bonds into the cellulose network to replace some of the hydrogen bonds and reconfigure the cellulose network. The presence of dynamic bonds disrupted the integrity of the H-bonded network, making cellulose molding and reprocessing much easier. The resulting CV films showed nearly an equal tensile strength and about twice the elongation at break compared to pure cellulose materials, along with better water resistance. Furthermore, CV displayed excellent thermal stability and malleability which can be reprocessed by thermal pressing, coupled with a T_g . Importantly, CVs can be recycled like thermoplastics by solution processing and endowed with new functions after their service life. CVs were successfully used as flexible solar cell substrates, outperforming the traditional petroleum-based polymer PEN. CV, as a sustainable and recyclable material, holds significant promise as a substitute for traditional petroleum-based materials especially in the field of electronic devices and displays.

ASSOCIATED CONTENT

Supporting Information: Experimental details and characterization data can be found in supporting information

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