Fluorescent Composite Hydrogel of Carboxymethyl Cellulose-Eu(f)/Polyvinyl Alcohol and Its Application in Functional Paper

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Research Article

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Abstract

A novel carboxymethyl cellulose-Europium(III)/polyvinyl alcohol (CMC-Eu(III)/PVA) fluorescent hydrogel was prepared by a green and facile method. The hydrogel formed a physical cross-linking network under mild reaction conditions without using volatile organic chemical reagents. A porous structure was formed by the hydrogen bonding and other interaction between the PVA chains and the free hydroxyl on CMC-Eu(III) during the composite gel transformation process. The addition of CMC-Eu(III) improved the tensile and compressive mechanical properties of PVA hydrogel. When the CMC-Eu(III) content was 15%, the maximum tensile stress of the composite hydrogel was 47.25 ± 10.35 kPa and the compressive stress was 10.14 ± 1.90 kPa. Meanwhile, the CMC-Eu(III)/PVA hydrogels exhibited a $^5D_0 \rightarrow ^7F_2$ characteristic emission peak of Eu^{3+} at 615 nm, and emitted stable red fluorescence under UV irradiation at 254 nm. Moreover, the hydrogel was applied in making fluorescent paper as an internal sizing agent. When the amount of hydrogel was 1%, the tensile strength of fluorescent paper reached 3.52 kN/m, which is promising in the application of anti-counterfeiting.

Introduction

Fluorescent hydrogels based on organic dyes (Sukul et al. 2011; Zhang et al. 2020; Zheng et al. 2014) and quantum dots (Chang et al. 2009; Wang and Zhang 2019; Zhang et al. 2020) have attracted many attentions in fluorescence applications such as anti-counterfeiting, probe detection, biosensors, and optical devices due to their flexibility, softness, and portability (Chen et al. 2019; Kang et al. 2012; Zhang et al. 2019). Rare earth metal complexes are another particularly attractive material as they emit sources in luminescent hydrogels because of their characteristics of large Stokes shift, stable fluorescence recognizability, and long fluorescence lifetime (Kumari et al. 2015; Li et al. 2019; Tan et al. 2015; Wang and Zhang 2019; Zhang et al. 2013; Zhi et al. 2018). Some rare earth metals, such as Eu^{3+} and Tb^{3+} , could form complexes with polymers to enhance their luminescence intensities via antenna effect (Gu et al. 2008; Xiao et al. 2011). Wu and coworkers reported a layered TbEuH-NO_3 complex with polyacrylamide and obtained a composite hydrogel with highly tunable photoluminescence function by *in situ* free-radical polymerization procedure (Wu et al. 2017). Zhi and coworkers synthesized an $\text{Eu}(\text{DBM})_2(\text{Phen})\text{MA}$ composite luminescence hydrogel in DMSO. The hydrogel with fluorescence showed tensile strength at 0.35 MPa and strain at the break at 422.55%, suggesting great mechanical properties (Zhi et al. 2018). Rare earth fluorescent hydrogel has become a focus of current anti-counterfeiting research. For example, Zhao and coworkers reported the application of poly(N-isopropyl acrylamide)/reduced graphene oxide hydrogel stripes as dynamic barcode labels for the anti-counterfeiting of different products (Zhao et al. 2017). Zhang and coworkers utilized the Fe^{3+} fluorescence quenching response of perylene-tetracarboxylic-acid-functionalized gelatin/polyvinyl alcohol hydrogels to demonstrate a 3D hydrogel origami anti-counterfeiting platform (Zhang et al. 2019).

All the above studies involved organic solvents, nonbiodegradable synthetic polymers, or complex processes. But with the demand for sustainable development, the concept of green chemistry and green

economy gradually interiorize. The research and application of natural polymers have become a hot topic in recent years (Chen et al. 2017; Hua et al. 2010; Zhao et al. 2016). Cellulose is a natural polymer as sustainable energy and material source. Carboxymethyl cellulose (CMC) is a cellulose water-soluble polyanion derivative. A lot of carboxyl groups in the CMC chain can be complexed with metals (Nadagouda and Varma 2007). Our previous work has proved that the CMC-Eu(III) composite possesses decent fluorescent emission (Nadagouda and Varma 2009; Ye et al. 2017; Ye et al. 2019; Ye et al. 2016). Polyvinyl alcohol (PVA) is a non-toxic, naturally degradable, and environmentally friendly material. Food and Drug Administration approved PVA as a permanent implant medical material and drug formulation component (Baron et al. 2019; Fan et al. 2016; Gonzalez et al. 2014; Kobayashi et al. 2003; Lee et al. 2005; Schmedlen et al. 2002). PVA can be combined with other water-soluble components to form a porous-wall composite physical hydrogel by freeze-thaw cycle, which is conducive to expand the multifunctionality of PVA composites (Hua et al. 2010; Huang et al. 2014).

The object of this work is to prepare a flexible and recognizable fluorescent composite hydrogel by PVA and CMC-Eu(III) using environmental-friendly method. It is expected that adding CMC-Eu(III) into the composite hydrogels enhanced the mechanical properties. Such hydrogel could use as an internal sizing agent in papermaking to prepare a fluorescent paper with excellent mechanical and fluorescent properties.

Experimental Section

Materials

PVA was purchased from Aladdin with a polymerization degree of 1799 and 98-99% (mol/mol) hydrolyzed. Food-grade CMC with a degree of substitution of 0.92 was supplied by Changshu Wealthy Science and Technology Co. Ltd. Europium oxide (Eu_2O_3) powder was purchased from Aladdin. NaOH, HCl, and AgNO_3 were purchased from Guangzhou Chemical Reagent Factory. KBr was supplied by KERMEL Chemical Reagent Company in Tianjin, dried in muffle furnace at 400°C for 2h and then cooled to room temperature. All the reagents were analytical grade and used without further purification. CTMP bamboo pulp with 36.8°SR of pulp-beating degree was provided by Guangzhou paper group Ltd.

Preparation of CMC-Eu(III) composites

0.0318 mol/L EuCl_3 solutions were made according to the reference (Ye et al. 2019). 1.0 g of CMC powder was dissolved in 100 ml of deionized water at room temperature. A 15 mL EuCl_3 solution was diluted with 40 mL of deionized water and the pH was adjusted to 7 with 1 M/L NaOH solution, followed by adding to the CMC solution dropwise (a drop rate of 1~2 drops/3s). The resulting solution was placed on a constant temperature magnetic stirrer for 30 min. The reaction mixture was then dialyzed in distillate water for 3 days until all chlorides were eliminated (texting by AgNO_3). Finally, the mixture was oven-dried at 55°C to obtain CMC-Eu(III) composite, which was ground into powder for later use.

Preparation of CMC-Eu(III)/PVA composite hydrogel

PVA with 98% ~ 99% hydrolyzed and a polymerization degree of 1799 was used in this work. PVA solution was prepared by dissolving the PVA particles in distilled water (8 wt%) at 80°C for 1.5 ~ 2 h with continuous stirring. CMC-Eu(III) suspension was prepared by dispersing the dry sample in distilled water under magnetic stirring for 1h. The two liquids were blended together to give CMC-Eu(III)/PVA precursor blend. Pure PVA hydrogel and CMC-Eu(III)/PVA (CEP) hydrogel were prepared by freezing at -20 °C for 20 h followed by exposing at room temperature for 4 h. This freeze-thaw process was repeated three times. The weight ratio of CMC-Eu(III) to PVA was 1:5, 1:10, 1:15, and the resulting hydrogels were designated as CEP-5, CEP-10, and CEP-15, respectively.

Preparation of handsheets

The diameter of handsheet was 20 cm, and the quantitative value was 90 g/m². The handsheets were prepared by RAPID-KOETHEN (RK3AKWT). The hydrogel CEP-15 was cut into a cube of about 2-5 mm in length, 1-2 mm in width, and 2 mm in thickness. The hydrogel cubes were added into the pulp and well mixed before papermaking process. The contents of CEP-15 were 0%, 1%, and 3%, respectively, named as f control, FP-1, and FP-3.

Hydrogel characterization

The surface and cross-section images were recorded with EV018 SEM (Carl Zeiss, Germany). The hydrogel samples were freeze-dried and then sprayed with gold, EHT=10.00 kV. Mesoporous were tested by WBL-820 Surface Area and Porosities Analyzer from Shanghai Instrument Co., Ltd. The FT-IR analysis was performed on a TENSOR spectrometer (Bruker, German), using KBr pellets in the spectral range of 4000-400 cm⁻¹ (1/36 resolution, baseline correction, 32 scans). Before FT-IR analysis, the samples were freeze-dried for 24 h and ground into powder. The XRD analysis was carried out by a D8 Advance X-ray diffractometer (Bruker, German). The sample was cut into a suitable size. The surface was smoothed. A back-pressurizing method was used to load the sample. Cu target, K α ray, tube pressure 40 kV, tube current 40 mA, diffraction angle range 5-60°, scanning step length 0.04°, scanning speed 0.2 s/step. The degree of crystallinity (X_c) was calculated according to the method described in the literature (Costa-Junior et al. 2009). Thermogravimetric analysis was implemented by using a German TG209F3. The samples were scanned from room temperature to 700 °C at a heating rate of 10 °C/min under an N₂ atmosphere. Crystallinity and thermal analysis process were characterized by differential scanning calorimetry in the US TA Q200 differential scanning calorimetry analyzer. Under the N₂ atmosphere, the heating rate was 10 °C/min, and the temperature scanning range was 25~300 °C. Before the differential scanning calorimetry analysis, the samples were freeze-dried for 24 hours and about 10 mg was sampled for analysis. The degree of crystallinity (X_{cr}) was calculated from the following Eq 1:

$$X_{cr} = \frac{\Delta H_m}{W_{PVA} \times \Delta H_c} \times 100\%$$

Where ΔH_m was determined by integrating the area under the melting peak over the range of 190-240 °C; W_{PVA} was the weight fraction of PVA; ΔH_c was the heat required for melting a 100 % crystalline PVA sample, 138.6 J/g. (Mallapragada and Peppas 1996)

The mechanical properties were determined using a US INSTRON 5565 analyzer with the loading rate kept at a strain rate of 50 mm/min at room temperature. The tensile specimen was a rectangle with a width of 10 mm, length of 70 mm, and thickness of 2 mm. The compressed sample was a cylindrical sample with a diameter of 32 mm and a thickness of 12 mm. The compression cycle rate was 15 mm/min with 5 cycles. Photoluminescence spectra were recorded using a Fluorolog-3 fluorescent spectrophotometer (JY, America). The excitation slit width and the emission slit width were 10 nm and 15 nm, respectively. The emission and excitation spectra were obtained at detection wavelengths of 394 nm and 615 nm, respectively.

Handsheets characterization

The surface and cross-section images of the handsheets were studied by EVO18 SEM (Carl Zeiss, Germany). The tensile strength and elongation at break of handsheet were measured by a L&W CE062 tensile tester according to GB/T 12914-2008. The tear strength of handsheet was measured by a L&W 009 tearing tester according to GB/T 455-2002. The fold resistance of handsheet was measured by a MIT/U21B folding tester according to GB/T 457-2008. The burst strength of handsheet was measured by a L&W CE180 bursting strength tester according to GB/T 1539-2007. Triplicate test were performed and the average values and standard deviations were calculated.

Results And Discussion

Morphology of CMC-Eu(III)/PVA hydrogel

Scheme 1 shows the fabrication and crosslinking structure of CEP hydrogel. The CMC-Eu(III) particles were well dispersed with good anti-sedimentation stability in the PVA solution system (Scheme 1b). The blend was able to produce hydrogel after 3 freeze-thaw cycle, which showed a stable shape and sufficient elasticity when touching with tweezers (Scheme 1c). The SEM images of the surfaces and cross-sections showed the hydrogels were highly porous (Scheme 1e and Figure 1), which was caused by the alignment of molecular chains during freeze-thaw cycle and by evaporating water during freeze-drying. The cross-section of the PVA hydrogel showed a valley shape with a few pores. The tropistic arrangement of PVA hydrogel owes to the highly regular crystalline structure of PVA (Gonzalez et al. 2014; Ma et al. 2009). The fibers loosely interweaved with many pores in CEP-5 hydrogel, while the CEP-10 had more uniform fiber interweaving and pore size. The CEP-15 hydrogel with large and small pores showed stacked lamellar

(see Figure 1). As measured by N_2 physisorption, the average mesopore diameters were around 2.67-2.78 nm for all hydrogel samples. The results indicate that the hydrogels have a network structure containing macropores and mesopores.

Chemical structural and thermal analysis

Figure 2 shows the FT-IR spectra of CMC-Eu(X) and all hydrogels. The spectra of CEP hydrogels were similar to that of PVA hydrogel. Two C-H stretching vibration peaks at $3000\sim 2800\text{ cm}^{-1}$ were observed in CEP hydrogels and PVA. And the spectra of CEP hydrogels contained a weak peak at 1715 cm^{-1} , owing to stretching C=O and C-O of CH_3COO^- from PVA residual (Mansur et al. 2008). Specifically, all hydrogels had peaks at 1145 cm^{-1} , owing to the crystallization sensitive peak of PVA (Wang and Wang 2016). And with the increased of CMC-Eu(X) content, the intensities of peaks were obviously weakened, which changed the conformation of PVA chains (Hassan and Peppas 2000; Qiao et al. 2015). These results suggest that CEP hydrogels have the crystalline structure of PVA hydrogel.

Besides, the spectra of PVA, CMC-Eu(X), and CEP also show some differences. The bands at $3600\sim 3000\text{ cm}^{-1}$ were corresponding to the stretching of -OH involved in the intramolecular and intermolecular hydrogen bonds. This peak of CEP was located at $3427\sim 3435\text{ cm}^{-1}$, which was of lower wavenumber than that of CMC-Eu(X), and higher wavenumber than that of PVA hydrogel. The -C=O vibration appeared at 1601 cm^{-1} of CEP hydrogels showed only one peak, which differed from that of PVA. The peak at 1095 cm^{-1} originated from -CO- vibration became wider after adding CMC-Eu(X). In the spectra of CEP hydrogel, the peaks at 850 cm^{-1} from C-C stretching vibration weakened slightly compared with that of PVA. These results reveal that the PVA chains in amorphous interact with the unreacted CMC segment of CMC-Eu(X) by hydrogen bonds and Van der Waals' force (Abou Taleb et al. 2009; Bi et al. 2019; Gonzalez et al. 2014; Ma et al. 2016; Mansur et al. 2008; Miyazaki et al. 2004; Zhong et al. 2020).

Figure 3 illustrates the X-ray diffraction (XRD) patterns of all samples. The PVA hydrogel exhibited the strongest diffraction peak at 19.5° , corresponding to the (101) crystal plane of PVA (Gonzalez et al. 2014; Sriupayo et al. 2005; Wang and Wang 2016). This means that some PVA chains in the hydrogel are still arranged in parallel to each other by folding chains to form crystalline regions (Qiao et al. 2015). 22.7° and 40.4° represent (200) and (111) plane, respectively (Minus et al. 2006). Besides, the diffraction peak of CEP hydrogels at 40.4° was shifted to 42.7° in the spectrum of PVA. The XRD crystallinity of PVA, CEP-5, CEP-10, and CEP-15 hydrogels were 64.96 %, 64.15 %, 61.62 %, and 64.47 % respectively. The XRD crystallinity of the CEP hydrogels had hardly changed. The crystallite sizes were calculated by the Scherrer equation (Park et al. 2009), and the results were showed as followed: PVA: 5.47 nm, CEP-5: 5.07 nm, CEP-10: 3.28 nm, CEP-15: 3.70 nm. During the formation of hydrogels, the interaction between the PVA chains and the unreacted CMC segments of CMC-Eu(X) might reduce the regularity of the PVA chains (Bercea et al. 2019; Mansur et al. 2008; Wang et al. 2010; Wang and Wang 2016), leading to the small crystallites.

The thermogravimetric and differential scanning calorimetry (DSC) curves are shown in Figure 4. The thermogravimetric curves of CEP are similar to that of PVA (see Figure 4a). The weight loss before 205

°C is because of dehydration of hydrogels. It is worth noting that the weight will not change with the increase of temperature during 205 ~ 240 °C. The DSC thermograms show a peak at 205 ~ 240 °C, which is related to the melting process with the crystallization of PVA (Yang et al. 2004). According to E_g 1 of Mallapragada's method (Mallapragada and Peppas 1996), crystallinity can be calculated and listed in Table 1. The crystallinity of hydrogels calculated from DSC curves were 47.60% (PVA), 42.78% (CEP-5), 45.20% (CEP-10), and 45.62% (CEP-15). The melting temperatures of the hydrogels crystallization zone also were obtained by Mallapragada's method (Mallapragada and Peppas 1996). The melting temperatures of CEP hydrogels were slightly lower than that of PVA. Melting temperatures is also related to the crystallinity of PVA (Abitbol et al. 2011; Butylina et al. 2016). The results of FT-IR, XRD, and DSC indicate that the PVA chains have hydrogen bonds, entanglement, and van der Waals forces with unreacted CMC segments of CMC-Eu(X).

Mechanical performance

Tensile stress-strain curves of all hydrogels are shown in Figure 5a. The curves display typical tensile behaviors, which are broken in the linear elastic region without an obvious yield phenomenon and plastic deformation. The tensile strength (σ_t) and toughness of CEP hydrogels were significantly higher than those of PVA. Specifically, the σ_t and strain of CEP-10 were 44.91 ± 2.69 kPa (Table 2) and 90%, more than quadruple and double of the results from PVA hydrogel, respectively.

After stretching, the fibers in all hydrogels were oriented in the direction of the external force and compact, as shown in Figure 5b. The results of XRD and DSC suggested that the crystallinity of all hydrogels did not change much. Even though the CMC-Eu(X) interacted with PVA chains in amorphous to form a stable gel network structure, the mechanical properties did not increase accordingly as the increased of CMC-Eu(X) content in the CEP sample. The porous network structure of the hydrogels might enhance their strength and toughness. The tensile property of the CEP hydrogel was better than that of PVA hydrogel. Moreover, the tensile properties of the CEP hydrogels are different due to their different porous sizes and fiber arrangement. The tensile strain of CEP-5 was better than the other samples because the loose network structure increased the relaxation time of fiber movement. As shown in Figure 5b, CEP-5 was stretched flat. However, the orientation of the fibers was poor, leading to lower strength. The condensed and uniform pore distribution of CEP-10 improved strength and toughness. Therefore, the strength was greater than CEP-5 and the toughness was greater than CEP-15. CEP-15 retained layered orientation after stretching, so it had a large strength, but a small strain due to uneven pore distribution.

Figure 6a shows the compressive stress-strain curves of the hydrogels. The compression properties of hydrogels exhibited nonlinear and viscoelastic behavior. The CEP hydrogel did not show significant rupture on the surface at 70 % strain and was able to return to its original shape almost immediately when releasing the pressure. The compressive strength (σ_c) of CEP hydrogel was greater than that of PVA hydrogel under the corresponding strain ratio. The σ_c of CEP-15 was up to 10.14 ± 1.90 kPa, and the compression elastic modulus (E_c) reached 47.17 ± 10.37 kPa. The results are better than the other hydrogel samples in our study, and the cellulose nanocrystal/PVA hydrogel, with σ_c at 2.1 kPa and E_c at

13.9 kPa, reported by Butylina et al (Butylina et al. 2016). In addition, the hydrogels showed decent compression fatigue resistance. The compression stress-strain curves of hydrogels at 60% strain under five loading-unloading cycles are shown in Figure 6b. The shape and strength remained intact after five cycles. The results suggest that no substantial plastic deformation or strength degradation occurred in the hydrogels, indicating an outstanding recovery behavior, as well as resistance to compressing for application in flexible materials.

The mechanical properties of CEP hydrogels are displayed through knotted stretching and close bending. In the experiment of knotted stretching of the hydrogel, no fracture was observed (Figure 7a). Additionally, the hydrogel was able to totally recovered after bending to 180° and then releasing the pressure (Figure 7b). However, the PVA hydrogel was cracked in the test. The hydroxyl group of CMC-Eu(III) and the free hydroxyl group in the PVA are linked by hydrogen bonds, which enhance the interfacial bonding strength of the network structure of the CEP hydrogel, thus improving the mechanical properties (Pan and Xiong 2009). The CEP hydrogels have deformation diversity, good compressive fatigue resistance, and toughness. And the hydroxyl groups on CMC-Eu(III) and PVA might make it possible to combine well with the cellulosic fiber, thus the CEP hydrogel can be used as an internal sizing agent, which will not affect the mechanical properties and the application of the as-prepared paper.

The fluorescence spectra of CEP hydrogels display characteristic peaks of Eu^{3+} ions (Figure 8). Under 615 nm emission, there were $^7\text{F}_0 \rightarrow ^5\text{L}_7$ at 370 nm, $^7\text{F}_0 \rightarrow ^5\text{L}_6$ at 390 nm, and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ at 460 nm transitions of Eu^{3+} (see Figure 8a). Figure 8b showed a $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition at 595 nm and a $^5\text{D}_0 \rightarrow ^7\text{F}_2$ electric dipole transition at 620 nm under 394 nm excitation (Van Opdenbosch et al. 2012). The electric dipole transition is greater than the magnetic dipole transition, which means that the coordination environment of Eu^{3+} ions is not symmetric (Wang et al. 2014). The inset of Figure 8b shows the CEP hydrogels emitted red color under UV light at 254 nm. The results indicate that the CEP hydrogel can function as a fluorescent reagent.

Fluorescent handsheets characterization

Therefore, we fabricated some fluorescent handsheets using different amounts of CEP-15 hydrogels, as it gave the strongest fluorescent intensity. As shown in Figure 9, under sunlight, it is hard to identify the hydrogel dots in FP-1 whereas the hydrogel dots in the FP-3 are bigger and more obvious. The red spots on FP-1 and FP-3 are clearly with bare eyes under UV light. The hydrogel dots of FP-1 are evenly dispersed, and they are within the size range of hydrogels cubes added, while some sizes of hydrogel dots on FP-3 are larger than the sizes of hydrogel cubes added, indicating the hydrogel cubes added aggregated in FP-3 during the paper making. It is worth to mention that the CEP hydrogel can apply to made fluorescent paper as a conventional internal sizing agent. And this utilization can take advantage of the existing process and equipment.

Figure 10 shows the SEM images of the surfaces and cross-sections of the handsheets. By adding the fluorescent hydrogels, the fibers on the surfaces of fluorescent handsheets organize directionally.

Compared with the cross-section of the control, the fibers of fluorescent handsheets were compact and order in Figure 10b. Especially, the sizes and distributions of the fibers both on the surface and cross-section of FP-1 were more even.

Figure 11 shows the fluorescent emission spectra of CEP-15 hydrogel and the handsheets. The CEP-15 hydrogel, FP-1, and FP-3 showed characteristic emission of Eu^{3+} ions. The fluorescence emission peaks at 591nm and 615nm belong to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions, respectively. The fluorescent property of CEP-15 in handsheet did not change, indicating the fluorescent is stable and this functional paper can be potentially used as anti-counterfeiting paper. However, the fluorescent intensity of electric dipole transition at 615 nm in the handsheets became weaker because of concentration quenching (Lakowicz 2006).

The mechanical properties of the handsheets are shown in Figure 12. Adding CEP-15 hydrogel enhances not only the tensile strength but also the elongation at the break of the fluorescent handsheets. Especially, FP-1 reached 3.52 kN/m of tensile strength and 1.598% of elongation at break, respectively. This might be due to the more compact and orientational of the fibers on the handsheets. Moreover, the fibers on FP-1 were organized more even (see Figure 10). However, the tear strength and fold resistance of the fluorescent handsheets were weaker, especially for the FP-3, than that of control. This might be due to the differences between fibers and pieces of the hydrogels. The regions with the hydrogels could cause phase separation on the fluorescent handsheets. The burst strength increased from 182.50 to 209.25 kPa owing to the excellent mechanical properties of CEP-15 hydrogel, compared with the control. These results demonstrate that the mechanical properties of the fluorescent handsheets are better with adding 1% of CEP hydrogel than adding 3%.

Conclusions

In summary, we have prepared a CEP hydrogel by a facile, green, and economical method that does not need organic solvents and under mild reaction conditions. The results show that CMC-Eu(Cl) and PVA chains were cross-linked by hydrogen bonding and other interactions to form a porous network structure. The composite hydrogel was similar to the PVA hydrogel crystalline form. The stretchability and flexibility of the CEP hydrogel were 44.91 ± 2.69 kPa of the tensile strength (CEP-10) and 99.08% of the tensile strain (CEP-5). Besides, the CEP hydrogel shows the characteristic red fluorescence of Eu^{3+} under UV light. We fabricated the fluorescent paper by simply blending the CEP hydrogel and bamboo pulp. The as-prepared paper showed similar fluorescent to the CEP hydrogel, therefore it is a promising material for anti-counterfeiting in labels and packaging.

Declarations

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest.

Ethical standards

This article is an original work not submitted to/published elsewhere in any form or part. Proper acknowledgment to other works is given and the results are presented clearly, honestly, and without fabrication.

Ethics approval

This article does not contain any studies involving human participants or animals performed by any of the authors.

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Tables

Table 1 The melting temperature (T_m), the heat of fusion (ΔH_m), and degree of crystallinity (X_{cr}) of CMC-Eu(III), PVA hydrogel, and CMC-Eu(III)/PVA hydrogels.

Sample	T_m (°C)	ΔH_m (J/g)	X_{cr} (%)
PVA	224.76	65.97	47.60
CEP-5	221.32	56.47	42.78
CEP-10	221.81	56.95	45.20
CEP-15	223.99	54.98	45.62

Table 2. Mechanical properties parameters of PVA and CMC-Eu(III)/PVA hydrogel with different CMC-Eu(III) content. ($P > 0.05$)

	PVA	CEP-5	CEP-10	CEP-15
E_t (kPa)	42.2 ± 23.13	33.80 ± 8.03	59.64 ± 0.16	67.87 ± 0.52
σ_t (kPa)	10.40 ± 2.48	23.30 ± 14.42	44.91 ± 2.69	47.25 ± 10.35
E_c (kPa)	33.90 ± 11.06	32.89 ± 15.21	31.18 ± 6.76	47.17 ± 10.37
σ_c (kPa)	6.77 ± 1.65	7.36 ± 2.66	6.89 ± 1.34	10.14 ± 1.90
E (kPa)	51.3	70.4	60.4	67.9

E_t : tensile elastic modules; σ_t : tensile strength; E_c : compression elastic modulus; σ_c : compressive stress; E : elastic modules of the compression cycle.

Figures

Figure 1

SEM images of the cross-section of PVA hydrogel and CMC-Eu(III)/PVA hydrogels.

Figure 2

FT-IR spectra of CMC-Eu(III), PVA hydrogel, and CMC-Eu(III)/PVA hydrogels.

Figure 3

XRD patterns of CMC-Eu(III), PVA hydrogel, and CMC-Eu(III)/PVA hydrogels.

Figure 4

(a) Thermogravimetric curves; (b) Differential scanning calorimetry thermograms of CMC-Eu(III), PVA hydrogel, and CMC-Eu(III)/PVA hydrogels.

Figure 5

(a) Tension stress-strain curves of PVA and CEP hydrogels at strains from 0% to fracture; (b) SEM images of the cross-section of PVA hydrogel and CEP hydrogels after tensile.

Figure 6

(a) Compression stress-strain curves, insert: photos of the compression process; (b) cyclic compression tests; (c) SEM images of the cross-section of PVA and CMC-Eu(III)/PVA hydrogels after compression.

Figure 7

Photographs of CEP-15 of (a) knotted stretching, (b) close bending

Figure 8

(a) Excitation spectra and (b) emission spectra of CMC-Eu(III)/PVA hydrogels (wet); the inset photo is a fluoresce dry hydrogel under UV light (CEP-5, CEP-10, CEP-15: red fluorescence).

Figure 9

Photos of all handsheets under sunlight and UV light respectively (circle: dots; rectangle: spots); the inset shows the added hydrogel (left), the hydrogel dots of FP-1(right).

Figure 10

SEM images of all handsheets (a) surface and (b) cross-section

Figure 11

Fluorescence spectra of CEP-15 hydrogel (dry) and all handsheets.

Figure 12

Mechanical properties of all handsheets : tensile strength; elongation at break; tear strength; fold resistance; burst strength.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)