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Tough, resilient and pH-sensitive interpenetrating polyacrylamide/alginate/montmorillonite nanocomposite hydrogels

Xing Su^a, Biqiong Chen^{b*}

^a*Department of Materials Science and Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom.*

^b*School of Mechanical and Aerospace Engineering, Queen's University Belfast, Stranmillis Road, Belfast BT9 5AH, United Kingdom.*

*Corresponding author. *E-mail address:* b.chen@qub.ac.uk.

ABSTRACT

Alginate, a naturally abundant and environmentally friendly carbohydrate polymer, can form ionically crosslinked hydrogels with Ca^{2+} . Therefore, a novel design of interpenetrating nanocomposite hydrogels (PMACa) is proposed, which is synthesized by *in situ* polymerization of acrylamide in the presence of montmorillonite platelets and sodium alginate at an elevated temperature, followed by secondary crosslinking of the hydrogel using a CaCl_2 solution. PMACa displays superior tensile strength and strain at break under the fully swollen state, as well as rapid shape recovery and insignificant residual strain upon the release of an external load. Furthermore, PMACa also shows remarkable reversible pH-dependent swelling/deswelling behaviors due to the pH-sensitivities of alginate network and montmorillonite platelets. These new high-performance interpenetrating alginate-containing nanocomposite hydrogels may find potential applications as aquatic load-bearing materials for artificial tissues, actuators, agriculture, etc.

Keywords: interpenetrating nanocomposite hydrogel; alginate; mechanical properties; shape recovery; pH-sensitivity; fully swollen state

1. Introduction

Hydrogels have been studied for decades because of their ability of absorbing and keeping water in the crosslinked network. They are widely used in the applications of tissue engineering (Zhu, 2010), wound dressing (Zhang, Xia, & Zhao, 2012), drug delivery (Hoare & Kohane, 2008), food industry (Chen et al., 1995), agriculture (Saxena, 2010), wastewater treatment (Wu et al., 2016) and sensors (Ju, Kim, & Lee, 2001). Besides, their unique stimuli response and swelling behaviors are promising to mimic the nature of biological soft tissues for potential tissue reconstruction (Yu & Ding, 2008; Zhu, 2010). However, the poor mechanical properties limit the application of hydrogels (Gong, Katsuyama, Kurokawa, & Osada, 2003). One popular way of making tough hydrogels is to synthesize double-network (DN) systems, which often combine a rigid highly crosslinked polyelectrolyte with a ductile loosely crosslinked neutral polymer (Gong, 2010; Gong et al., 2003). This unique structure gives rise to high tensile strength (up to 10 MPa) and fracture toughness (up to 9000 MJ m⁻³) of DN hydrogels (Gong, 2010; Sun et al., 2012). Yet, there are two main limitations for DN hydrogels. On one hand, the tensile hysteresis is relatively high (≥ 0.5) and increases with increasing strain, and the hydrogels could not recover quickly from a large deformation (strain $\geq 100\%$) (Gong, 2010). On the other hand, the fatigue threshold energy is usually significantly lower than the fracture energy (e.g., for a PAM/alginate DN hydrogel: 55 J m⁻² for fatigue fracture and 10000 J m⁻² for tensile fracture (Bai et al., 2017)), making DN hydrogels easy to fail under cyclic strain (Bai et al., 2017; Gong, 2010). Some of the chemical bonds break irreversibly during deformation, and the internal damage accumulates as the hydrogel experiences more cycles of deformation (Webber, Creton, Brown, & Gong, 2007).

Alginate (A), a natural carbohydrate polymer consisting of mannuronic acid (M unit) and guluronic acid (G unit), is widely used for making hydrogels, because of its biocompatibility (Baumberger & Ronsin, 2010) and biodegradability. Alginate can be degraded under mild conditions (ambient temperature and neutral pH) by different methods such as alginate lyase enzyme (Kim, Lee, & Lee, 2011) and marine fungi (Schaumann & Weide, 1990). G blocks from different alginate polymer chains can be readily crosslinked *via* ionic bonding by divalent or multivalent cations such as calcium cations (Ca^{2+}) (George & Abraham, 2006), and become long-term insoluble and stable in water (Rhim, 2004). Ca^{2+} -crosslinked alginate has recently been shown to toughen chemically crosslinked polyacrylamide (PAM) hydrogels because of its excellent capability of energy absorption by unzipping the ionic crosslinks during deformation (Sun et al., 2012). This double-network hydrogel (denoted as PACa) with a water content of 86 wt% displayed a high tensile strength up to 160 kPa, a large strain at break of 20 and a high fracture energy up to 2 MJ m^{-3} , which are higher than those of the conventional chemically crosslinked PAM hydrogel (Sun et al., 2012). Like most DN hydrogels, there are limitations of PACa. For instance, they showed pronounced hysteresis upon unloading. Apart from mechanical properties, alginate-based hydrogels were frequently reported as pH-sensitive (Abd El-Ghaffar, Hashem, El-Awady, & Rabie, 2012; Ju et al., 2001; Obara, Yamauchi, & Tsubokawa, 2010). The Ca-alginate hydrogels tend to shrink in the acidic solution and swell in the basic solution.

Clay and acrylamide (AM) can form physically crosslinked nanocomposite hydrogels by *in situ* polymerization without a chemical crosslinker, achieving excellent extensibility and water stability due to the high aspect ratio, as well as multiple physical bonding between the nanoscale clay platelets and *in situ*

polymerized PAM chains (Gao, Du, Sun, & Fu, 2015; Haraguchi, 2007; Haraguchi & Takehisa, 2002). With synthetic hectorite containing abundant hydroxide groups, poly(N-isopropyl acrylamide) (PNIPAM)/clay nanocomposite hydrogels could be stretched by 10 times without failure and recover 98% of its original length in one minute (Haraguchi & Takehisa, 2002), unlike conventional chemically crosslinked PNIPAM hydrogels which are usually brittle and weak. Montmorillonite (MMT) is selected in this study instead of other nanoparticles such as hydroxyapatite nanoparticles, layered double hydroxides and graphene oxide for making nanocomposite hydrogels because of its natural abundancy, high hydrophilicity and negatively charged surface for easy exfoliation into single nanoplatelets, high cation exchange capacity and ability to form multiple interactions with many organic substances (Chen & Evans, 2004; Gao et al., 2015; Su et al., 2017). It has been used as a reinforcement and a complementary physical crosslinker of PAM chemically crosslinked hydrogels (Guilherme et al., 2010). Physically crosslinked, ultrastretchable and self-healable PAM-MMT hydrogels were also synthesized (Gao et al., 2015). An incredibly high strain at break of 12000% was obtained by a MMT content of 5 wt%. However, a residual strain of 500% was observed in the first cycle during cyclic tests to a maximum strain of 2000%. This was attributed to the polymer chains detached from the clay platelets. A full shape recovery could only be achieved after 5 days at 25 °C. However, tensile tests have rarely been conducted for fully swollen polymer-clay nanocomposite hydrogels. One of the main reasons could be that they swelled significantly in water, over 20 times (Haraguchi, Li, Song, & Murata, 2007; Ren, Zhu, & Haraguchi, 2011), and might be too weak to test (Chen et al., 2016; Wang et al., 2012). Most of the tensile data reported so far in the literature for PAM-clay hydrogels were as-prepared hydrogels containing 80~90 wt% water. A

polyacrylamide/chitosan/MMT nanocomposite hydrogel (PM5CHI) with a clay content of 4.6 wt% in the dry nanocomposite was recently reported by us (Su et al., 2017). It was found that PAM chain branching and PAM-chitosan covalent bonding, brought in by elevated temperature (60 °C) polymerization gave rise to an enhanced crosslinking density and thus better mechanical properties at the fully swollen state than the conventional PAM-MMT nanocomposite hydrogels synthesized at ambient temperature with a catalyst. PM5CHI contained 99.4 wt% water at its equilibrium swollen state, displaying a Young's modulus of 1.2 kPa, a tensile strength of 8.6 kPa and a strain at break of 11.1. The deformed nanocomposite hydrogel could quickly recover its original shape within one minute when the external load was removed. In contrast, the fully swollen conventional PAM-MMT nanocomposite hydrogels became too weak to be tensile tested. Nanocomposite hydrogels based on PAM, sodium alginate (SA) and MMT were also studied. Superabsorbent PAM/SA/MMT hydrogels were recently synthesized by the polymerization of AM in the presence of a chemical crosslinker (N,N'-Methylenebisacrylamide), SA and MMT. With the incorporation of SA, it displayed a fairly high equilibrium swelling ratio (up to 863) and absorption capacity (2639 mg g⁻¹) for methylene blue (Qiu, Qiu, Wang, Zhang, & Zheng, 2014). PAM/SA/MMT hydrogels could also be effective in the absorption of microcystin-LR (Wang et al., 2015). However, the mechanical properties of these hydrogels were not investigated.

In this study, we aimed to synthesize a strong, tough and resilient hydrogel even at its fully swollen state, based on a double network consisting of PAM, alginate, MMT and Ca²⁺, denoted as PMACa. The primary network was formed by *in situ* free-radical polymerization of acrylamide in the presence of MMT nanoplatelets and alginate at an elevated temperature of 80 °C, and the second network was formed by Ca²⁺-

crosslinked alginate chains. PMACa was different from the previously reported PAM/SA/MMT hydrogels (Qiu et al., 2014; Wang et al., 2015) in that no chemical crosslinker was used and a second network of Ca^{2+} ionically crosslinked SA was formed in this new hydrogel. This temperature was selected for polymerization to bring in PAM-chain branching and PAM-alginate covalent bonding which would help ensure the high resilience of the hydrogels. As previously described, DN hydrogels hold big promise for achieving high strength and high toughness, but often display large hysteresis and progressively increased residual strain under cyclic loading. Nanocomposite hydrogels are effective in reaching large extension and good resilience in some cases; however, they are usually very weak when fully swollen. It was hypothesized in this study that the newly designed interpenetrating DN in this hydrogel would provide high strength and high toughness at the fully swollen state like other DN hydrogels, while the resilient and stretchable first network and the effective energy-dissipating second network would provide high resilience, extensibility and toughness as well as added-value pH-sensitivity from alginate. Hopefully, the resulting new hydrogels could serve in aquatic, load-bearing and pH-sensitive applications.

2. Materials and methods

2.1. Materials

Acrylamide, potassium persulfate (KPS) (purity $\geq 99.0\%$), N,N,N',N'-tetramethylethylenediamine (TEMED) (purity $\geq 99.0\%$), calcium chloride anhydrous (purity $\geq 93\%$), hydrochloride acid (HCl, 37%), and sodium alginate (SA), with a purity of 99%, molecular weight of 12000~40000, and mannuronic/guluronic ratio of 1.6, from brown algae were purchased from Sigma Aldrich. Sodium hydroxide

(NaOH) (assay $\geq 98.9\%$) was purchased from VWR International. MMT, which has a cation exchange capability of 90 meq (100 g)⁻¹, was provided by Southern Clay Products (for the exfoliated single platelets, thickness: 0.98 nm and aspect ratio: 40~180 nm; the lateral size distribution was shown in the Supplementary Information) (Chen & Evans, 2004, 2006). All chemicals were used as received.

2.2. Preparation of hydrogels

Following the same procedure from our previous research (Su et al., 2017), 15 g MMT was added into 1 L distilled water, and its fine dispersion was achieved after 24 hours' rotation on a table roller. The derived MMT suspension was then treated with 30 minutes' sonication by Fisherbrand™ FB15051 ultrasonic cleaner and another 24 hours' standing settling. At last, the supernatant, which was an exfoliated MMT suspension, was separated for future use. The content of MMT in the suspension was calculated to be 0.012 g mL⁻¹ by subtracting the weight of the dry un-exfoliated clay precipitate.

The typical synthetic routine of PMACa hydrogel was shown below. MMT suspension (21.5 mL) which contained 0.25 g MMT was sonicated for 30 min. 0.801 g of Na alginate was added into MMT suspension and stirred for 3 hours. Then 4.827 g of AM monomer was added and stirred for another 22 hours. Finally, 0.075 g KPS initiator in 3.44 mL water was added and stirred for 30 min. The precursor solution was transferred into plastic tubes and submerged in a water bath at 60 °C for 10 min for initiation (Fanood, 1998; Su et al., 2017). Reaction temperature for *in situ* polymerization was elevated from 60 °C to 80 °C gradually within 1 hour and then held at 80 °C for 1 hour for steady polymerization which could still be completed within a few hours. After the reaction, the hydrogels were washed with distilled water

for 3 times which removed uncrosslinked polymers as well as water-soluble oligomers and monomers. The hydrogels were then submerged in 0.3 M CaCl_2 solution allowing 2 days' absorption for crosslinking. They were weighed every 8 hours and after 40 hours of absorption, their weight became constant. The fully swollen hydrogels were collected and the surface was washed by distilled water for 3 times to remove the excess Ca^{2+} cations. The weight ratio of alginate/AM was set to be 1/6, which was found to be the optimal ratio among 1/4, 1/6 and 1/8 for PAM/alginate hydrogels to achieve the highest tensile strength and fracture energy (Sun et al., 2012) (See the Supplementary Information). Separately, the hydrogels were also submerged in distilled water instead of the CaCl_2 solution for 2 days (denoted as PMAW) for comparison.

Polyacrylamide MMT nanocomposite hydrogel (PM) was also synthesized for comparison. Typically, MMT suspension (21.5 mL) was sonicated for 30 min at first. 5.616 g AM was added under stirring for 22 hours. Afterwards, KPS solution (0.087 g KPS in 3.44 mL water) was added and stirred for 30 min. Reaction started from 60 °C rising to 80 °C within 1 hour, and was held at 80 °C for 1 hour. Similarly, samples were washed and submerged in 0.3 M CaCl_2 solution (PMCa) or water (PMW) allowing 2 days' absorption. Then the surface of the fully swollen hydrogels was washed by distilled water for 3 times. The MMT content and the overall solid content in all the hydrogels before absorption were fixed at 0.008 and 0.238, respectively (Gao et al., 2015; Sun et al., 2012), giving a fix MMT content of 4.2 wt.% in the solid of the hydrogel.

In addition, some control samples were prepared for comparison. PAM was polymerized following the same method without using MMT and post-treatment. AM was also polymerized in the presence of alginate with a weight ratio of alginate/AM of

1/6 following the same method without using MMT and post-treatment, generating covalently bonded polyacrylamide and alginate, denoted as PAMALG. PAM-MMT nanocomposite hydrogel was also synthesized by using the method of Gao et al (2015) at 25 °C with the catalyst of N,N,N',N'-tetramethylethylenediamine, denoted as PMcata.

2.3. Characterization

X-ray diffraction was conducted on a STOE STADI P (Cu K α) diffractometer in the transmission mode, with an incident X-ray wavelength of 0.154 nm and a scan rate of 1.0 ° min⁻¹. Fourier transform infrared spectroscopy was carried out on a Spectrum 100 spectrophotometer (PerkinElmer). The spectra were collected within the wavenumber region from 4000 to 600 cm⁻¹. Each sample was scanned for 8 times with a resolution of 1 cm⁻¹. Dynamic scanning calorimetry was performed on a PerkinElmer DSC 6 with the temperature ranging from 25 to 380 °C. The scan rate and the nitrogen flow were set to be 50 °C min⁻¹ and 20 mL min⁻¹, respectively. A scan rate of 20 °C min⁻¹ was also used but it did not show a clear T_g peak, therefore 50 °C min⁻¹ was adopted. The analysis was based on the second heating curve. Thermogravimetric analysis was done by using a Pyris 1 TGA instrument (PerkinElmer) by heating the sample from 25 °C to 650 °C at a rate of 30 °C min⁻¹ under a nitrogen flow of 20 mL min⁻¹, and then held at 650 °C for 10 min. Dried hydrogel samples were ground into powder for XRD, FTIR, DSC and TGA. Inductively coupled plasma mass spectrometry was conducted on a Spectro-Ciros-Vision ICP-Optical Emission Spectrometer. Residues of PMACa, PMAW and PMCa from TGA tests were used because the extraction of Ca²⁺ from the ashes from TGA tests was easier than that from the dry nanocomposite hydrogels. The ashes were

treated by aqua regia at 150 °C for 30 min so that Ca^{2+} in the ashes was extracted and the derived suspensions were tested. The Ca content in the suspensions was measured at the 430.253 nm emission line following calibration using standards of known Ca contents.

Tensile tests were performed on a Hounsfield test equipment LTD. The rod-like PMACa, PMAW, PMCa and PMW samples had a full length of 15 mm and a gauge length of 5 mm, with diameters of 5~8 mm. They were tested at a crosshead speed of 100 mm min⁻¹ with a 10 N load cell. Ten samples were measured for each hydrogel. For cyclic tests, 8-cycle tensile tests to the maximum strains of 100% and 500% were investigated on PMACa with the same sample dimensions and testing parameters as stated earlier. The cyclic hysteresis ratio h was defined by the equation: $h = 1 - A_2/A_1$, where A_1 and A_2 are the integral areas of the tensile and the return curve, respectively (Kinloch, 1983). For the shape-recovery tests of PMACa, the sample experienced one tensile cycle to a strain of 300%, then the tensile load was removed and the samples were allowed to recover for 15 minutes. This process was repeated 10 times.

The cylindrical samples were freeze-dried by a Freezone Triad Benchtop Freeze Dry System from LABCONCO for swelling tests, which were conducted at ambient temperature by placing those pre-weighed freeze-dried hydrogel discs in excess distilled water for 350 hours to achieve equilibrium swelling. The equilibrium swelling ratio by weight ϕ_w was defined as, $\phi_w = (W_e - W_d)/W_d \times 100\%$, where W_e and W_d were measured using an analytical balance, representing the weights of the fully swollen sample and the freeze-dried sample before swelling tests, respectively.

Rheological tests were carried out on an AR2000 Advanced Rheometer (TA Instruments). The storage moduli G' and loss moduli G'' of the nanocomposite hydrogels were obtained by the dynamic frequency sweeps with the angular frequency

ranging from 0.1 to 100 rad s⁻¹ under 25 °C. A constant strain of 1%, which was confirmed by strain sweep tests, was chosen because it was in the linear viscoelastic region. All samples were tested using a parallel plate geometry (diameter: 20 mm; gap between two parallel plates: 1.0 mm) with a solvent trap to prevent from water loss.

pH-sensitivity of PMACa was studied by submerging the dehydrated PMACa samples in HCl solution (pH = 1), distilled water (pH = 7) and NaOH solution (pH = 14), respectively. PMACa samples were cut off from a cylindrical block with a thickness of 5 mm and a diameter of 14 mm, and then dried in the oven at 50 °C for 72 hours. The weight and volume of the samples were measured by an analytical scale and a densitometer before and after swelling in different environments for two weeks to reach equilibrium. The determination of the equilibrium swelling ratio ϕ_v by volume was similar to ϕ_w , expressed as $\phi_v = (V_e - V_d)/V_d \times 100\%$, where V_e and V_d represented the volumes of the fully swollen samples and the dried samples, respectively.

Scanning electron microscopy (SEM) was conducted on an Inspect F FEG SEM (acceleration voltage: 5 kV). Images were taken on the fractured surface of the samples with carbon coating. To prepare SEM samples, the fully swollen hydrogel samples were freeze-dried and then fractured in liquid nitrogen. The characteristic elements of O, Si and Ca were detected by energy dispersive X-ray analysis (EDX).

3. Results and discussion

3.1. Formation of nanocomposite hydrogels

The novel PMACa hydrogel (Scheme 1) was synthesized by a two-step method by which AM was polymerized in the presence of MMT platelets partially covered by

sodium alginate chains (Wu et al., 2016), and then immersed in a Ca^{2+} solution to reach equilibrium. The unique chemical structure of PMACa was depicted in Scheme 1 (a). Shown in XRD traces (Figure 1 a), a distinct (001) peak at $2\theta = 7.1^\circ$ was displayed for the neat MMT, which suggested a basal plane spacing of 1.23 nm (Chen & Evans, 2004; Su et al., 2017). However, this peak was absent in the traces of PMACa, PMAW, PMCa and PMW, indicating a high degree of exfoliation of the MMT platelets in the four dry nanocomposite hydrogels with a relatively high clay loading (4.2 wt %) (Gao et al., 2015; Su et al., 2017).

When alginate chains were introduced into the MMT suspension, hydrogen bonding formed between carbonyl groups of alginate and hydroxyl groups of MMT platelets, as well as between hydroxyl groups of alginate and SiO_4 geometry of MMT (Scheme 1 b) (Abdollahi, Alboofetileh, Rezaei, & Behrooz, 2013). However, alginate only covered part of the surface of MMT platelets despite of its high content because of the electrorepulsion between negatively charged MMT platelets and negatively charged alginate (Wu et al., 2016). So, PAM was still expected to form hydrogen

Scheme 1. Schematic illustration of (a) the chemical structure and (b) the key interactions in PMACa hydrogel; and photos of different shapes of PMACa: (c) thin thread and thick cylindrical block, (d) knotted, and (e) largely extended.

Fig. 1. (a) XRD traces of the neat MMT (Su et al., 2017), and PMACa, PMAW, PMCa and PMW samples; (b) FTIR spectra of alginate and the nanocomposite hydrogels, as well as PMcata.

bonding with the hydroxyl groups of MMT platelets via its amine groups (Scheme 1 b), like in other PAM clay nanocomposite hydrogels which were initiated by KPS that formed ionic complex with MMT platelets (Gao et al., 2015; Haraguchi, Li, Matsuda, Takehisa, & Elliott, 2005; Haraguchi & Takehisa, 2002). As seen from FTIR spectra (Figure 1 b), the two absorption peaks of N-H stretching at around 3190 cm^{-1} and 3333 cm^{-1} were characteristic for PAM. In comparison, a shift toward a lower wavenumber was observed in these two peaks for all MMT-containing nanocomposite hydrogels, confirming the formation of hydrogen bonding between PAM and MMT (Gao et al., 2015). The amine groups of acrylamide or other acrylic monomers were known to be able to form dense hydrogel bonding, though the surface of MMT platelets had already been partially covered by alginate chains (Liang et al., 2016; Wu et al., 2016). However, unlike the PAM-MMT nanocomposite hydrogels synthesized by a low temperature method (Gao et al., 2015), PAM synthesized at a temperature higher than 50°C introduced branching (Su et al., 2017), as evidenced by the two peaks at 2852 cm^{-1} and 2932 cm^{-1} . The former corresponded to secondary CH_2 and tertiary CH groups, while the latter represented primary CH_3 groups (Yu & Ding, 2008; Zhang et

al., 2012). When comparing the relative intensity of those two peaks, the relative intensity of CH₂ and CH groups in respect to that of CH₃ of PAM, PAMALG, PMW, PMCa, PMAW and PMACa declined compared to that of PMcata synthesized at 25 °C following a previous study (Gao et al., 2015), being 0.182, 0.183, 0.178, 0.203, 0.301 and 0.310 versus 0.406. It was known that CH₂ was stable during polymerization (Fanood, 1998; Gleason, Miller, & Sheats, 1959). This indicated that the amount of tertiary CH decreased, which is strong evidence of chain transfer reaction and branching (Gough, Zelinski, Wiens, Rak, & Dixon, 2003; Su et al., 2017). When polymerization occurred at a higher temperature (≥ 50 °C), the tertiary hydrogen atoms were replaced by free radicals to form polymer radicals, onto which AM was polymerized, leading to PAM chains with branches (Fanood, 1998; Su et al., 2017).

Besides, there were covalent bonds between alginate chains and PAM through amidation by amine groups of PAM and carboxyl groups of alginate (Sun et al., 2012) as described in Figure 2 a and Scheme 1 b. This was evidenced by the fact that the relative intensity of C-N (1020 cm^{-1}) to C-O (1044 cm^{-1}) of PAMALG, PMAW and PMACa was higher than that of PMcata, PMW and PMCa (Mushtaq, Mukhtar, & Shariff, 2014; Sun et al., 2012; Tripathi & Mishra, 2012), being 1.078, 1.067 and 1.036 versus 0.954, 0.931 and 0.945. The PAM-alginate covalent bonds might lead to effective load transfer and thus good mechanical properties. When alginate chains contacted with Ca²⁺ ions, the alginate chains were crosslinked and formed the second interpenetrated ionic network. Furthermore, positively charged Ca²⁺ ions might also interact with the negatively charged MMT platelets by electrostatic attraction (Rytwo, Banin, & Nir, 1996).

DSC curves (Figure 2 b) were also indicative of PAM branching, PAM-alginate covalent bonds, polymer-clay interfacial interaction and Ca²⁺-MMT electrostatic

interaction. Branched PAM polymerized at 80 °C displayed a glass transition temperature (T_g) of 211 °C, which was higher than the branched PAM synthesized at 60 °C (198 °C) (Su et al., 2017). The T_g values were affected by the macromolecular entanglement (Mi, Xue, & Lu, 2003), branched degree (Su et al., 2017) and scanning rate. A higher T_g (231 °C) was presented by PAMALG because the PAM-alginate covalent bonds reduced the mobility of PAM chains (Tripathi & Mishra, 2012). The T_g of PMW (214 °C) was slightly higher than that of neat PAM due to interactions between PAM and MMT. The incorporation of MMT also increased the T_g of PAMALG to 257 °C (PMAW) owing to the PAM-MMT and/or alginate-MMT hydrogen bonding. Moreover, with the incorporation of Ca^{2+} , PMCa showed a significantly higher T_g (302 °C) than that of PMW. This indicated the strong electrostatic interaction between Ca^{2+} and the negatively charged MMT platelets (Scheme 1 b) (Brevik & Burgess, 2012; Rytwo et al., 1996). PMACa displayed a much higher T_g (313 °C) than that of PMAW because of Ca^{2+} -alginate ionic crosslinking and Ca^{2+} -MMT electrostatic interactions (Brevik & Burgess, 2012; Liang et al., 2016; Rytwo et al., 1996). Furthermore, PMcata containing linear PAM chains showed a T_g of 203 °C, which was lower than that of PMW, which contained branched PAM chains. In the consideration of their similar chemical composition, the higher T_g of PMW might be due to the higher crosslinking density brought by branched PAM chains (Fanood, 1998; Su et al., 2017). It is worth noting that these values are for qualitative analysis only due to the high scanning rate.

The presence of Ca^{2+} in PMACa and PMCa was confirmed by EDX, TGA and ICP-MS. In Figure 2 (c-f), as the characteristic element for both PAM and MMT, O was detected in all the samples. Similarly, Si, which was characteristic for MMT platelets, was also presented in all the samples. Characteristic dots appeared on the Ca

mapping graphs of PMACa and PMCa, while there were no characteristic dots shown on the Ca mapping graphs of PMAW and PMW. This result suggested that Ca^{2+} cations were successfully incorporated into PMACa and PMCa after the hydrogels had been immersed in CaCl_2 solution. According to ICP-MS, the weight fraction of Ca^{2+} was 0.110 for the dry PMACa, 0.131 for the dry PMCa and 0.001 for the dry PMAW (Table 1), which is supported by the TGA results (Figure 2 g and Supplementary Information). These results confirmed the significant absorption of Ca^{2+} in PMACa

Fig. 2. (a) Formation of covalent bonding between PAM and alginate; (b) DSC traces of PMACa, PMAW, PMCa and PMW dry samples and their control samples, PAM and PAMALG and PMcata; EDX graphs taken from the cross-sectional surface of freeze-dried (c) PMACa, (d) PMAW, (e) PMCa, and (f) PMW hydrogels, (Scale bar: 10 μm); (g) TGA traces of PMACa, PMAW, PMCa and PMW.

and PMCa by MMT platelets and/or alginate. PMCa had a higher Ca^{2+} content than PMACa because the former had a higher equilibrium swelling ratio, and thus adsorbed more CaCl_2 solution after fully swelling. The small amount of Ca^{2+} in PMAW was probably brought by MMT (Hillier & Lumsdon, 2008).

3.2. Mechanical properties of fully swollen nanocomposite hydrogels

The tensile properties of the fully swollen nanocomposite hydrogels were depicted in Figure 3 (a) and Table 1, and their swelling behaviors were shown in Figure 3 (b).

Fig. 3. (a) Typical tensile stress-strain curves of the fully swollen nanocomposite hydrogels, and (b) swelling ratio in respect to water immersion time of the dry nanocomposites.

Table 1. Tensile properties of fully swollen hydrogels

Sample	Young's modulus / kPa	Tensile strength / kPa	Strain at break	Energy at break / MJ m^{-3}	Swelling ratio, ϕ_w	Ca^{2+} wt content
PMACa	8.0 ± 0.2	106.2 ± 7.6	10.1 ± 0.4	523.3 ± 41.4	9.8	0.110
PMAW	0.5 ± 0.1	1.6 ± 0.1	5.7 ± 0.6	4.9 ± 1.3	47.7	0.001
PMCa	2.4 ± 0.1	3.8 ± 0.3	2.5 ± 0.2	5.8 ± 1.1	11.7	0.131
PMW	2.2 ± 0.1	2.4 ± 0.1	1.5 ± 0.1	2.2 ± 0.3	37.6	-

When fully swollen, PMACa displayed significantly higher tensile strength, strain at break and energy at break than the other three control hydrogels. The mechanical properties of a hydrogel are closely related to its water content and crosslinking network. Comparing PMACa with PMAW at the same contents of polymer and clay,

the incorporation of Ca^{2+} led to apparent differences in the structure and properties of PMACa. First, Ca^{2+} crosslinked alginate chains during the diffusion of CaCl_2 solution into the polyacrylamide/sodium alginate hydrogel and the replacement of sodium cations with calcium cations (Scheme 1 b) (Yang et al., 2013). It was noticed that the swelling ratio of PMAW began to drop slightly after 100 hours (Figure 3 b) probably because of partial dissolution of the nanocomposite hydrogel, which might be a small amount of residual low molecular weight PAM oligomers and/or K_2SO_4 . The swelling of alginate was, however, significantly restricted by Ca^{2+} , leading to a lower water content of 90.7 wt% for PMACa versus 97.9% for PMAW. This made PMACa stiffer and stronger than PMAW.

Secondly, in the PMACa the Ca^{2+} crosslinked alginate network formed an interpenetrating double network with the PAM-MMT network. The latter, with entangled and branched PAM chains, crosslinked by PAM-MMT multiple hydrogen bonding (Scheme 1 b), was elastic and highly stretchable (Gao et al., 2015; Haraguchi, 2007; Haraguchi & Takehisa, 2002; Su et al., 2017). Meanwhile, the Ca^{2+} crosslinked alginate was brittle but adequate in dissipating energy by unzipping the Ca^{2+} -alginate ionic crosslinks during tensile deformation, bringing in fairly high energy at break (Sun et al., 2012). Moreover, there were covalent bonds between PAM and alginate as discussed previously, ensuring the efficient load transfer between the two networks, making PMACa strong and tough (Sun et al., 2012).

Thirdly, it was possible that Ca^{2+} also interacted with MMT platelet surface and thus restricted the swelling process further. During the water swelling process of Na-MMT (Segad, Jonsson, Akesson, & Cabane, 2010), the divalent Ca^{2+} could interact with both negatively charged alginate chains and MMT platelets (Scheme 1 b) (Huang et al., 2015). Because of the higher cation charge number carried by Ca^{2+} than Na^+ ,

Ca^{2+} displayed stronger electrostatic attraction with MMT than Na^+ (Segad et al., 2010), potentially causing higher tensile energy required to deform PMACa compared to the case with PMAW at the same strain. This could be evidenced by the fact that PMCa showed only one third swelling ratio of that of PMW, and nearly one-fold higher tensile strength and strain at break than PMW. While for PMAW, without the restriction of crosslinking, hydrophilic alginate absorbed a large amount of water which made PMAW weaker than PMACa. Besides, the MMT platelet surface was partially covered by alginate chains, which was likely to decrease the number of PAM-MMT hydrogen bonding. Despite the alginate-MMT hydrogen bonding and the covalent bonds between PAM and alginate, the overall crosslinking degree of PMAW reduced in respect to PMACa. Furthermore, most of the tensile load in PMAW was carried by PAM-MMT network instead of alginate chains because alginate chains were not crosslinked by Ca^{2+} in this hydrogel and the hydrogen bonding between alginate and MMT was weak in the aqueous environment (Wu et al., 2016). In consequence, lower Young's modulus, tensile strength and energy at break were obtained by PMAW than PMACa.

Comparing PMACa with PMCa or PMW, the former showed significantly higher tensile strength, strain at break and energy at break, but lower equilibrium swelling ratio. The superior tensile strength, strain at break and energy at break of PMACa confirmed the synergistic effect of the elastic and stretchable PAM network and the stiff Ca^{2+} -alginate network as expected from the previous study (Sun et al., 2012) and the Ca^{2+} -induced restriction on the swelling of PMACa. Comparing PMAW with PMW or PMCa, the former displayed lower Young's modulus and tensile strength, but higher strain at break and equilibrium swelling ratio. This confirmed that the MMT platelet surface was partially covered by highly swellable alginate chains, which

formed relatively weak hydrogen bonding with MMT and reduced the crosslinking degree (Gao et al., 2015; Wu et al., 2016).

Comparing the swelling ratio of all the hydrogels in this study to that of polyacrylamide/MMT nanocomposite hydrogel with a similar clay content in the literature (Gao et al., 2015), ϕ_w for the former was significantly lower. The reduced equilibrium swelling ratio was probably due to branching and a higher crosslinking degree. The branching of PAM gave rise to an enhanced crosslinking degree, which was significantly different from that synthesized at a low temperature with a catalyst, where a linear chain of PAM was obtained (Fanood, 1998; Gao et al., 2015; Gleason et al., 1959; Su et al., 2017).

In summary, PMACa, even after full swelling and with a water content of 90.7 wt%, still presented an excellent strain at break of 10.1, a high strength of 106.2 kPa, a Young's modulus of 8.0 kPa and an energy at break of 523.3 kJ m⁻³ whereas the other three control hydrogels showed drastically lower values (Table 1). These values of PMACa are also much higher than those reported for fully swollen PNIPAM/synthetic hectorite nanocomposite hydrogels containing a much higher clay content (0.281 versus 0.043 based on the mass of the dry polymer) from a previous study (Wang et al., 2012), with a tensile strength of 13.9 kPa and a strain at break of 3.6. In comparison with a recent polyacrylamide/chitosan/MMT nanocomposite hydrogel (PM5CHI) with a similar clay content (0.046 versus 0.043 based on the mass of the dry polymer) (Su et al., 2017), fully swollen PM5CHI showed a much lower Young's modulus (1.2 kPa) and tensile strength (8.6 kPa) although with a slightly higher strain at break (11.1).

The crosslinking density, as an important parameter for the interpretation of the mechanical properties of hydrogels, could be calculated by the classic kinetic theory of

rubber (Haraguchi, Farnworth, Ohbayashi, & Takehisa, 2003), with Equation (1) (Gao et al., 2015; Haraguchi, 2007; Su et al., 2017):

$$F = N^*RT(\alpha - \alpha^{-2}) \quad (1)$$

where F , N^* , R , T and α are the force per unit original cross-sectional area of the hydrogels, effective crosslinking density, gas constant, absolute temperature and the extension ratio, respectively. Here α was 2 corresponding to a strain of 100% and T was set to be 298.15 K. From Table 1, N^* was calculated to be 1.8 mol m⁻³, 0.076 mol m⁻³, 0.5 mol m⁻³ and 0.48 mol m⁻³ for PMACa, PMAW, PMCa and PMW, respectively. PMACa displayed a much higher N^* than the others because of the dense ionic crosslinking of alginate by Ca²⁺. PMCa and PMW presented similar N^* values, indicating Ca²⁺ did not significantly participate in crosslinking due to the lack of alginate. PMAW displayed considerably low crosslinking density probably because some part of MMT platelets was covered by alginate chains which decreased the density of PAM-MMT hydrogen bonding. Though alginate could form hydrogen bonding with MMT platelets, it was much weaker than that between PAM and MMT platelets and could be easily destroyed during swelling process. The main reason was that both MMT platelets and alginate chains were negatively charged which were easier to swell in the aqueous environment due to electrostatic repulsion (Liang et al., 2016; Wu et al., 2016). Besides, amine groups of AM could be more strongly adsorbed onto the MMT platelets (Kinter, 1961) than hydroxyl groups of alginate.

The crosslinking state of the nanocomposite hydrogels could also be depicted by rheological data. The rheological behaviors were shown in Figure 4. PMACa displayed much higher storage modulus than the other hydrogels, over 10 times of the storage modulus of PMAW, confirming the formation of strong ionic crosslinks between alginate chains by Ca²⁺. By comparing the storage moduli of the four fully

swollen nanocomposite hydrogels, it was obvious that the rheological data were in accordance with the sequence of the crosslinking density (Piao & Chen, 2016) as discussed earlier, *i.e.*, PMACa $\gg$ PMCa $\geq$ PMW $\gg$ PMAW.

Fig. 4. Storage modulus G' and loss modulus G'' of PMACa, PMAW, PMCa and PMW hydrogels.

The results obtained by the rubber theory and rheology tests could be further proved by SEM as shown in Figure 5. PMAW, PMW and PMCa, with the water contents of 97.9 wt%, 97.4 wt% and 92.1 wt% respectively, and free from the ionic crosslinking between Ca^{2+} and alginate, showed interconnected porous structure with pore sizes of $112.4 \pm 11.7 \mu\text{m}$, $76.1 \pm 18.5 \mu\text{m}$ and $71.3 \pm 13.3 \mu\text{m}$, respectively. The pore size was in the order of $\text{PMAW} > \text{PMW} \geq \text{PMCa}$. It indicated that when fully swollen, the significantly lower crosslinking density of PMAW than those of PMW and PMCa allowed PMAW to absorb more water and thus a larger pore size was obtained. However, there was no obvious porous structure observed in PMACa. These results confirmed that polymer chains in PMACa were much more restricted than those of the other three (Zhang, Pang, & Qi, 2015). The high restriction over the

polymer chains in PMACa resulting from the dense and interpenetrating crosslinking gave rise to a lower water content and fewer and smaller ice crystals during freezing process, thus contributing to the significantly better mechanical properties.

Fig. 5. SEM images of cross-sectional surface of freeze-dried (a) PMACa, (b) PMAW, (c) PMCa, and (d) PMW hydrogels.

In order to measure the elasticity and hysteresis of the hydrogels, cyclic tests were conducted on PMACa. The results were shown in Figure 6. PMACa displayed high resilience under a tensile deformation of 100% with an extremely low hysteresis ratio of 0.01 (Figure 6 a). After 8 cycles, PMACa still showed similar tensile curves to those of the first cycle, indicating that the resilience of PMACa within this strain was

excellent. This implied that during cyclic tension to a strain of 100%, some PAM-MMT hydrogen bonds dissociated upon the stretching process and recovered fully instantly upon the return process. The dissociation of Ca^{2+} -alginate electrostatic bonds was considered negligible under this strain (Su et al., 2017). The unique and superior

Fig. 6. Representative cyclic tensile testing curves of PMACa hydrogel: cyclic tensile to (a) 100% and (b) 500%.

resilience of PMACa reported here originated from the strong ionic interaction between Ca^{2+} ions and negatively charged MMT platelets or alginate, the ample hydrogen bonding between the MMT platelets and the PAM chains, PAM branching, as well as strong PAM-alginate covalent bonds. First, some of the Ca^{2+} ions were adsorbed onto the surface of MMT platelets, serving as extra crosslinking sites for alginate in addition to the free Ca^{2+} ions in the hydrogels. Secondly, the branched PAM chains and MMT platelets provided multiple reversible hydrogen bonds between PAM and MMT, making it possible for PMACa to recover from a relatively large deformation. Thirdly, PAM branching also brought in additional chemical crosslinks with alginate which increased the crosslinking density and the strength of PMACa (Su et al., 2017). Finally, the strong PAM-alginate covalent bonds could effectively transfer stress between PAM and alginate chains in PMACa, promoting a fast recovery

of both polymer networks upon removal of the external load. So when a tensile load was removed, both PAM and alginate networks could bounce back fast and the dissociated PAM-MMT hydrogen bonding could recover quickly.

When the cyclic strain reached 500% (Figure 6 b), a much higher 1st-cycle hysteresis ratio of 0.44 was received. Most of PAM-MMT hydrogen bonds (Okay & Oppermann, 2007) and Ca²⁺-alginate electrostatic bonds broke when stretched. Unlike the case of cyclic tension to a strain of 100%, the broken PAM-MMT hydrogen bonds could not recover fully instantly under a large cyclic strain of 500%, which contributed to the high 1st-cycle hysteresis (Su et al., 2017). More importantly, Ca²⁺-alginate electrostatic bonds were known to be effective in dissipating energy and they could not recover quickly after being unzipped, which inevitably also resulted in the large 1st-cycle hysteresis (Sun et al., 2012; Yang et al., 2013). Besides, the MMT platelets and polymer macromolecular chains were stretched and oriented (Haraguchi & Li, 2006) to a greater extent compared to the case with 100% strain. The steric effect and friction force made it difficult for the oriented MMT platelets and stretched polymer chains to rotate back to their original orientation during the returning cycle, again contributing to the large 1st-cycle hysteresis (Su et al., 2017; Zhu et al., 2006). As more cycles were experienced, a drastically reduced hysteresis of 0.04 was obtained by the 8th cycle, compared to that of the 1st cycle. This could be partially attributed to the more oriented MMT platelets and/or polymer chains with increasing testing cycle (Su et al., 2017; Zhu et al., 2006). Besides, fewer Ca²⁺-alginate electrostatic bonds dissociated as more tensile cycles were performed, due to the slow recovery of the unzipped Ca²⁺-alginate electrostatic bonds (Sun et al., 2012; Yang et al., 2013).

Shape-recovery capability of PMACa was also investigated at a tensile strain of 300% (Figure 7) for a direct comparison with a previous study on PAM/alginate DN hydrogel

without clay (Sun et al., 2012). The hysteresis ratio of the 1st cycle to a strain of 300% for PMACa was 0.38. At ambient temperature, PMACa could accomplish $88\% \pm 0.5\%$ of recovery within 15 minutes after being stretched to a strain of 300% for the first time. When subjected to more cycles to a strain of 300%, the sample was still able to recover 88% of its original shape within 15 minutes each time after the load had been removed (Figure 7 b-d), as seen from the nearly overlapped hysteresis loops for different cycles (Figure 7 a).

Fig. 7. (a) Cyclic tensile curves of PMACa hydrogel with the 15 minutes' recovery interval, and (b-d) demonstration of shape-recovery capability of PMACa hydrogel from a tensile strain of 300%: (b) before stretching, (c) under stretching, and (d) 15 min after being unloaded.

These results are better than the previous results from the PAM/alginate DN hydrogel with a water content of 86 wt% and the same alginate/AM weight ratio of 1/6 as PMACa (Sun et al., 2012; Yang et al., 2013). In the work of Sun et al. (2012), the first-cycle hysteresis at a strain of 300% was 0.76, and the hydrogel recovered 74% of its original length in about 24 hours at 80 °C. However, regardless of experiencing how many tensile cycles (up to 11 cycles), PMACa prepared in this work always exhibited a shape recovery to 88% of its original state much faster and at a much lower temperature, without increasing residual strain with increasing tensile cycle. In the

PAM/alginate DN hydrogels (Sun et al., 2012), the loosely and chemically crosslinked PAM network was responsible for the stretchability and shape recovery capability. On one hand, the crosslinking density of the PAM network was low, giving rise to good stretchability (Gong, 2010). On the other hand, the low crosslinking density indicated a small amount of memory sites, making it difficult for the PAM/alginate DN hydrogel to recover its original shape quickly from a high tensile deformation (strain $\geq 100\%$) (Webber et al., 2007). However, for PMACa, the introduction of the multifunctional MMT platelets and high temperature reaction brought in much more crosslinks and hence memory sites, enabling a much faster shape recovery at a lower temperature. As discussed earlier, the ionic interaction between Ca^{2+} ions and anionic MMT or alginate, the reversible PAM/MMT hydrogen bonding, PAM branching and PAM-alginate covalent bonds contributed to the fast shape recovery. While PMACa displayed a residual strain for the 1st cycle, it did not show additional residual strain with the increasing tensile cycle from the 2nd cycle demonstrating good stability.

It was noted, though, that the tensile stress at a strain of 300% for the 2nd cycle (onwards) of PMACa was lower than that of the 1st cycle. The slow recovery of the broken Ca^{2+} -alginate electrostatic bonds, as discussed before, was responsible for this reduction. Similarly, lower tensile stresses and residual strains were also observed in the PAM/alginate DN hydrogel (Sun et al., 2012). Increasing the recovery period of time, temperature and humidity (Gao et al., 2015; Sun et al., 2012; Wu & Chen, 2016) may speed up the recovery process and reduce the residual strain. For instance, if the stretched PMACa sample was left for 6 months in water at ambient temperature, the ratio of shape recovery could reach $95\% \pm 1.5\%$.

3.3. pH-sensitivity of PMACa hydrogel

The structure of alginate chains ionically crosslinked by Ca^{2+} was shown in Scheme 1 b and Figure 8 (a) (Sun et al., 2012). Apart from the remarkable mechanical properties, PMACa also displayed notable pH-sensitivity as the equilibrium swelling states were significantly different, as shown in Figure 8. PMACa, fully swollen in distilled water further swelled in base (Figure 8 d, e). When pH value was enhanced from 7 to 14, the equilibrium swelling ratio by weight (ϕ_w) increased from 9.8 to 24.2, and the equilibrium swelling ratio by volume

Fig. 8. (a) The chemical structure of crosslinked Ca-alginate blocks; (b) reversible reactions of carboxyl groups in M blocks; dry PMACa samples immersed in (c) strong acid (BA-PMACa), (d) distilled water (PMACa), and (e) strong base (B-PMACa); the mechanisms of pH-dependent swelling/shrinking behaviors of PMACa between the pH value of (f) 7 to 14, and (g) 1 to 14; (h) Equilibrium swelling ratios of BA-PMACa, PMACa, and B-PMACa.

(ϕ_v) increased from 1.5 to 15.7 (Figure 8 h); the hydrogel became base-treated PMACa (denoted as B-PMACa). When B-PMACa was placed back to distilled water (pH = 7), it shrank and reached equilibrium within two weeks. Similar phenomena were also observed from pH = 7 to pH = 10. This reversible weight/volume change was due to the pH-sensitive nature of Ca^{2+} -crosslinked alginate hydrogels (Abd El-Ghaffar et al., 2012). Alginate is a kind of block copolymer composed of mannuronic acid (M unit) and guluronic acid (G unit), and only G-blocks were able to form ionic crosslinking by divalent cations such as Ca^{2+} (Figure 8 a) (George & Abraham, 2006; Sun et al., 2012).

In neutral pH environment (pH = 7), Ca^{2+} crosslinked the adjacent carboxyl groups of the G blocks, while for the M blocks, COO^- ions were surrounded by the dissociated H^+ ions (George & Abraham, 2006; Obara et al., 2010). When altering the external environment from neutral (pH = 7) to basic (pH = 14), COOH groups of the M blocks in PMACa were dissociated and the dissociated H^+ ions were surrounded by abundant OH^- ions donated by NaOH (Obara et al., 2010). So the nanocomposite hydrogel further swelled from pH = 7 to pH = 14 due to the diffusion of H^+ and the enhanced electrostatic repulsion by COO^- ions and OH^- ions (Figure 8 b & f) (Obara et al., 2010).

While PMACa fully swollen in distilled water did not change its shape when the environmental pH value was changed from 7 to 1, a remarkable shape change was received when the environmental pH value turned from 14 suddenly to 1, with ϕ_w decreasing from 24.2 to 1.2 and ϕ_v decreasing from 15.7 to 0.3, in the period of two weeks (Figure 8 h). The derived material was denoted as BA-PMACa. BA-PMACa could swell remarkably only if the external environment was altered directly from strongly acidic to strongly basic. Similar behavior was also observed for PMW. The main reason could be attributed to the dissolution of quartz impurities (SiO_2) (Hillier & Lumsdon, 2008) and/or tetrahedral Si-O layers in MMT by NaOH (Carroll & Starkey, 1971), and the formation of SiO_2 from Si-O by HCl (Figure 8 g) (Wells, 2012). At a high pH (~ 14), NaOH reacted with SiO_n by turning it to SiO_3^{2-} (Carroll & Starkey, 1971; Wells, 2012). Once the pH value was altered from 14 to 1, SiO_3^{2-} reacted with HCl and turned into SiO_2 precipitate (Wells, 2012), increasing the opacity (Figure 8 c). The low hydrophilicity and low solubility of SiO_2 resulted in the significantly reduced equilibrium swelling ratio. The shrunken hydrogel could not further swell in distilled water (Wiberg, Holleman, & Wiberg), but could swell in strong base. Besides, the shrinkage of PMACa at a low pH environment ($\text{pH} \leq 5$)

could also be due to the significantly enhanced positive edge charge of MMT platelets under acidic environment (Cashen, 1966). At a low pH environment, the edges of MMT platelets are protonated because of their hydroxyl groups and the edge charge changes from negative to positive (Furukawa, Watkins, Kim, Curry, & Bennett, 2009; Permien & Lagaly, 1994). The attractive interaction between the negatively charged MMT surface and the positively charged MMT edges induced the shrinkage (Frenkel, Goertzen, & Rhoades, 1978; Permien & Lagaly, 1994). This interaction facilitated some MMT surfaces and MMT edges to stick to each other, forming face-to-edge aggregates which were difficult to be separated in water (Frenkel et al., 1978; Furukawa et al., 2009; Permien & Lagaly, 1994). As a result, the network structure of PMACa became more compact. The pH-sensitivity of PMACa means that this nanocomposite hydrogel could also be used in pH-sensitive drug delivery and agricultural applications.

4. Conclusions

Based on a biocompatible and naturally abundant carbohydrate polymer, alginate, we developed a novel polyacrylamide/alginate/montmorillonite interpenetrating nanocomposite hydrogel (PMACa). PMACa displayed a significantly lower equilibrium swelling ratio and much higher tensile strength, strain at break and energy at break under the fully swollen state, reaching 106 kPa, 1000% and 0.5 MJ m⁻³, respectively, compared to its control samples (PMAW, PMW and PMCa), as well as existing conventional nanocomposite hydrogels. The hysteresis during cyclic tensile tests to a strain of 100% was minimal, with an extremely low value of 0.01. When subject to a tensile strain of 300% PMACa could repeatedly quickly recover 88% of its original shape within 15 min under ambient temperature.

The hydrogel also showed strong and reversible pH-dependent swelling behaviors which swelled by 9 times in basic medium compared to the volume in distilled water with neutral pH. PMACa pre-swollen in a strong base shrank by 36 times in a strong acidic medium. This process was also reversible when the external environment changed between acidic and basic directly. However, there was no reversible shape change between pH of 1~7.

The remarkable properties of PMACa were attributed to its unique chemical structure and intermolecular bonding including chain interpenetrating, chain branching, multiple hydrogen bonding, covalent bonding, and electrostatic interactions which were confirmed by XRD, FTIR, SEM, DSC, EDX, TGA and ICP-MS, and the high crosslinking density of PMACa which was based on the classic kinetic theory of rubber and confirmed by rheology tests. The unique properties, along with the use of green materials (alginate, montmorillonite nanoplatelets and CaCl_2) and the fabrication versatility, made it possible for PMACa to serve in a diverse field of applications in bioengineering, drug delivery, actuation and agriculture such as high performance artificial tissues, pH-sensitive drug carriers and heavy metal ion uptake, in the aquatic load-bearing environment. This study also provides a new scope of developing carbohydrate polymers-based multifunctional interpenetrating nanocomposite hydrogels.

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