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Hydrothermal effect and mechanical stress properties of carboxymethylcellulose based hydrogel food packaging

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ABSTRACT

The PVP–CMC hydrogel film is biodegradable, transparent, flexible, hygroscopic and breathable material which can be used as a food packaging material. The hygroscopic character of CMC and PVP plays a big role in the changing of their mechanical properties where load carrying capacity is one of important criteria for packaging materials. This paper reports about the hydrothermal effect on the mechanical and viscoelastic properties of neat CMC, and PVP–CMC (20:80) hydrogel films under the conditions of combined multiple stress factors such as temperature, time, load, frequency and humidity. The dry films were studied by transient and dynamic oscillatory experiments using dynamic mechanical analyser combined with relative humidity chamber (DMA-RH). The mechanical properties of PVP–CMC hydrogel film at room temperature (25 °C), in the range of 0–30%RH remain steady. The 20 wt% of PVP in PVP–CMC hydrogel increases the stiffness of CMC from 2940 to 3260 MPa at 25 °C and 10%RH.

1. Introduction

Packaging material for food industry is very authoritative because it needs to fulfil several objectives: physical protection, barrier protection, information transmission, marketing communication and so on (Sorka, 2009). Beside this, food packaging material should fulfil at least three functional properties such as mechanical protection of food product during transport and storage, air and moisture barrier and protection against contamination by microorganisms. Thus, researchers are giving emphasis for the development of film which would be biodegradable but also offer better oxygen barrier and water barrier properties. Though the concept of *hydrogel food packaging* is relatively new like green packaging or sustainable packaging, it does not yet come into the forefront for its use in practicality. Hydrogels can offer new opportunities for the design of efficient packaging materials with desirable properties (i.e. durability, biodegradability mechanical properties etc.) when prepared with carboxymethylcellulose and polyvinylpyrrolidone (Roy, Saha, & Saha, 2011a; Roy, Saha, Kitano, & Saha, 2011b, Roy, Saha, Kitano, & Saha, 2012) as base polymers.

Carboxymethylcellulose (CMC) is a hydrophilic, water soluble cellulose derivate (Sjostrom, 1993) and biodegradable polymer wide-used in paper, textile, food and beverages, pharmaceutical and cosmetic industry (Anita, Thatheyus, & Ramya, 2013; Heydarzadeh, Najafpour, & Nazari-Moghaddam, 2009; Paunonen, 2013). The forecast for the global market of CMC is estimated to reach about 892 million pounds by 2017 (Jose, 2012) which could be served as food packaging material and other purposes. The range of applications of neat CMC film in packaging area can be enlarged by its modification with other bio- or synthetic polymers while mainly charge interactions rather than hydrogen bonding are expected (De Azeredo, 2009; Mensitieri et al., 2011; Mu, Guo, Xinying, Wie, & Defu, 2012; Roy, Saha, Kitano, & Saha, 2012; Russo et al., 2009). Other works have shown the improvement of some physical properties (density, mechanical properties, thermal stability, water solubility and permeability) of the final CMC films by its mixing with other polymers or additives such as hydroxyethylcellulose, starch, glycerol, chitosan nanoparticles, gelatin, sunflower oil, polyvinlypyrrolidone and polyvinylalcohol (Ghanbarzadeh, Almasi, & Entezami, 2010; Juliyarsi, Melia, & Sukma, 2011; Moura, Lorevice, Mattoso, & Zcolotto, 2011; Paunonen, 2013; Prusov & Prusova, 2007). It is also reported that the mechanical properties of CMC films can be improved by its self-crosslinking or by crosslinking initiated with the addition of other crosslinking agents (Anbergen & Oppermann, 1990; Wach, Mitomo, Nagasawa, & Yoshii, 2003).

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Polyvinylpyrrolidone (PVP) as a hydrophilic synthetic polymer has been discovered already in 1939 (Fischer & Bauer, 2009). It has been used in cosmetic, pharmaceutical and food industry as a binding agent or even stabiliser (Keipert & Voigt, 1979). PVP is known as a water soluble polymer accessible for hydrogel dressings with good biomedical properties, however, recognised with poor mechanical properties (Alcantara, Taqueda, & Lugao, 2009; Rosiak, 1991). Due to water solubility and film forming ability PVP can be mixed with CMC and create wet or dry films with new mechanical properties (Wang et al., 2007).

In our previous studies, we have prepared and characterized the biocompatible hydrogels based on CMC and PVP (Roy, Saha, Kitano, & Saha, 2010; Roy, Saha, Kitano, & Saha, 2010; Roy, Saha, Humpolicek, & Saha, 2010). In addition to wound dressing, we have reported about the importance of PVP–CMC hydrogels as food packaging materials (Roy, Saha, & Saha, 2011a; Roy, Saha, Kitano, et al., 2011b, Roy et al., 2012) to keep the fruits and vegetables long time fresh and protect from spoilage. The dry PVP–CMC hydrogel films were prepared by solution casting method, without addition of any chemical crosslinking agent but applying physical stimulating agents: heat and temperature. The PVP–CMC hydrogel films are biodegradable, transparent, flexible, hygroscopic and breathable having transient junction with it (i.e. cross linking junction of PVP and CMC base polymer and others). We have shown that PVP–CMC hydrogel film with the concentration of 20:80 is easy process-able and possesses the reasonable mechanical strength (Roy, Saha, & Saha, 2011a; Roy, Saha, Kitano, et al., 2011b; Roy et al., 2012). Based on these results, it could be suggested that PVP–CMC film at the ratio of 20:80 may be suitable for food packaging of materials releasing moisture such as fresh fruits, vegetables and other food stuffs (Roy et al. 2011; Roy et al., 2012). It is known that hygroscopic character of CMC and PVP play a big role in the changing of their mechanical properties depending on the water content. The swelling capacity of PVP–CMC films partially depends on their mixture concentration (Roy et al., 2010a; Roy et al., 2010b; Roy, Saha, Humpolicek, et al., 2010; Wang, 2007; Zhao, Xu, Mitomo, & Yoshii, 2006).

The objective of this work is to assess the hydrothermal effect on mechanical and viscoelastic properties of hydrogels under the conditions of combined multiple stress factors such as temperature, time, load, frequency and humidity. It can be presumed from the report of Gregorova, Lahti, Schennach, and Stelzer (2013) that moisture/humidity has some influence on original mechanical properties of PVP–CMC and CMC hydrogels which may alternate depending on the temperature profile. Also, we hypothesize that the application of these stress factors allows estimating the behaviour of dry hydrogels under moisture atmosphere similar to service life. The effect of hydrothermal degradation on mechanical properties of neat CMC and PVP–CMC (20:80) was studied by transient and dynamic oscillatory experiments using dynamic mechanical analyser combined with relative humidity chamber (DMA-RH). Furthermore, chemical structure, morphology (surface and internal structure), swelling and de-swelling nature of neat PVP, neat CMC, and PVP–CMC (20:80) hydrogels were studied to compare their physico-chemical behaviour and their firmness as biodegradable polymeric material for food packaging. Our main goal to perform this investigation is to recognise the modified viscoelastic properties of PVP–CMC (20:80) hydrogel in dry atmosphere and at atmosphere with relative humidity as it is acclaimed as hydroscopic food packaging material. In addition, since the water uptake capacity is more or less analogous to neat CMC and PVP–CMC (20:80) hydrogel compared to neat PVP hydrogel, only these two hydrogels (CMC and PVP–CMC) were considered for the assessment of hydrothermal effect and mechanical stress properties.

2. Experimental

2.1. Materials

Sodium carboxymethyl cellulose (CMC: viscosity (20 g/L, 25 °C) 800–1200 mPa s, Degree of substitution (DS) 0.59–0.85) was purchased from Sinopharm Chem. Reagent Co., Ltd, China; polyvinylpyrrolidone K 30 (PVP: molecular weight 40,000); polyethylene glycol 3000 (PEG: average molecular weight 3015–3685) and agar were supplied by Fluka, Switzerland; glycerin was obtained from Lachema Ltd, Czech Republic.

2.2. Preparation of PVP, CMC and PVP–CMC hydrogel films

The hydrogel films of PVP, CMC and PVP–CMC were prepared by solution casting method using individual aqueous polymer solutions, where the polymer solution was prepared under controlled moist heat treatment (Roy et al., 2010a, 2010b; Roy, Saha, Humpolicek, et al., 2010;Roy, Saha, & Saha, 2011a; Roy, Saha, Kitano, et al., 2011b; Roy et al., 2012; Saha, Benlikaya, Slobodian, & Saha, 2014). 1.0% PVP for PVP hydrogel, 1.0% CMC for CMC hydrogel, and 0.2% PVP and 0.8% CMC for PVP–CMC hydrogel were used as base polymers and other ingredients like PEG (1.0%), agar (2.0%), and glycerine (1.0%) were remained constant in all the hydrogels. To prepare these PVP, CMC and PVP–CMC hydrogel films, at first polymer solutions were prepared individually following the above mentioned constituents and treated under physical stimulations (15 lbs pressure and 120 °C temperature for 20 min.) Then, each polymer solution (pH 6.5) was casted in solvent casting plate and allowed for cooling and drying at room temperature (22–25 °C), respectively. Finally, in each case, hydrophilic dry films were achieved having thickness 0.3–0.05 mm for PVP, 0.05–0.07 mm for CMC and 0.09–0.1 mm for PVP–CMC hydrogel. These hydrogel films were used for their general characterization like: chemical structure, surface morphology, internal morphology, swelling and de-swelling properties and to evaluate the modified viscoelastic properties by DMA and DMA–RH analysis in dynamic and static mode.

2.3. Method of characterization

The chemical structures of PVP, CMC and PVP–CMC hydrogel film were characterized using a Fourier transform infrared spectrophotometer (Thermo Scientific, NicoLETis5, USA) with attenuated total reflectance (ATR) accessory and operating in the range of 4000–400 cm^{-1}, resolution of 4 cm^{-1}. The attenuated total reflectance (ATR-FTIR) spectra were analysed using "Omnic" software. The morphology of the hydrogels (PVP, CMC and PVP–CMC) were evaluated through scanning electron microscope (SEM, Vega//TESCAN, Czech Republic), and in order to perceive the internal structure, surface topography and roughness of these three hydrogels (PVP, CMC and PVP–CMC) were investigated under Atomic Force microscope (FastScann with BRUKER AFM probe), and X-Ray diffraction pattern of same three hydrogel samples were recorded in the range of 5°–50° on a Phillips X-ray diffractrometer equipped with a scintillation counter.

2.4. Swelling and de-swelling studies

The gravimetric method was employed to measure the swelling behaviour of the hydrogel sample, (PVP, CMC and PVP–CMC) in distilled water. For swelling kinetics, pre-weighted dried samples (25 mm × 25 mm) were immersed in excessive distilled water at room temperature (20–22 °C) to reach the swelling equilibrium. At pre-determined time intervals (i.e.15 min), the hydrogel samples were taken out from the aqueous solution and weighed after

removing the excess water on the surface with wet filter paper. The equilibrium water uptake was calculated by the following equation:

$$Q_{eq} = (W_s - W_d)/W_d \quad (1)$$

where, Q_{eq} (g/g) is the water absorbency per gram of dried sample, W_d (g) and W_s (g) are the mass of dried and swollen samples, respectively.

For de-swelling kinetic, the pre-weighted swollen hydrogel samples equilibrated in distilled water and then the swollen samples were placed at room temperature (20–22 °C) for dry. The samples were weighted every 30 min interval and then the percentage of water retention (WR) was defined as follows:

$$WR\% = (W_i - W_d)/(W_s - W_d)_x 100 \quad (2)$$

Where, W_i is the weight of wet samples at time t. The other symbols are the same as defined above.

2.5. Dynamic mechanical analysis (DMA)

The DMA measurements were carried out under tensile geometry in transient (DMA creep and controlled force experiments) and in dynamic oscillatory (DMA frequency/strain experiments) mode using the instrument of DMA Q800-RH (TA Instruments, USA). Strips with a width of 3 mm were cut from dry hydrogel sheets and mounted in the DMA with a gauge length of 10 mm. The thickness of dry hydrogels was 50 and 90 μm for CMC and PVP–CMC, respectively.

2.5.1. Transient (static) experiments

The E-Modulus, tensile strength and tensile strain at break of hydrogels were measured using DMA Q800-RH at the temperature of 25, 35 and 45 °C and at the relative humidity of 0, 10, 30, 50, 70 and 90%RH. Before force loading every sample were conditioned in DMA oven for 5, 15, 35, 55, 75 or 95 min depending on the applied moisture. Hydrogel strips were stressed at a tensile mode with a force ramp of 3 N/min until a fracture. Totally five measurements for each hydrogel specimen were made.

Creep experiments were performed on hydrogels strips at tensile mode by applying a constant stress of 10 MPa for 5 min and 5 min recovery time. Hydrothermal aging under stress conditions was simulated with the change of temperature (25, 35 and 45 °C) and relative humidity (0, 10, 30, 50, 90% RH). Before stress loading every samples were conditioned in DMA oven for 5, 15, 35, 55, or 95 min depending on the applied moisture. The received deformation under stress was expressed as a change of a strain, and creep compliance. Creep compliance (J) expresses the sample's willingness to yield [2]:

$$J = \frac{d\varepsilon}{d\sigma} \quad (3)$$

where, ε is a strain and σ is a stress at a specific time.

The sample relaxation was determined as a value of recoverable compliance. Two measurements for each sample were performed.

2.5.2. Dynamic oscillatory experiments

The storage modulus (E′) and loss tangent ($\tan\delta = E''/E'$) of hydrogels were determined using the DMA frequency/strain experimental setup. The following conditions were used: isotherm at 5 °C for 5, 15, 35, 55 and 95 min (depending on %RH), frequency of 1 Hz, temperature range of 10–80 °C, heating rate of 1 °C/min, and dry or humid atmosphere of 10, 30, 50 and 70%RH. Two parallel measurements for each sample were performed.

3. Results and discussion

3.1. FTIR and XRD spectroscopy

Fig. 1 shows the ATR-FTIR spectra of dry film of PVP, CMC and PVP–CMC hydrogels. Among these three hydrogels, the spectra of CMC and PVP–CMC films are analogous. Even though hydrogel can be prepared from using neat synthetic polymer like PVP or neat natural polymer like CMC, it is also possible to prepare hydrogel mixing both natural and synthetic polymer like PVP–CMC (20:80) to improve the mechanical properties of hydrogel film without drastic change in its physico-chemical nature. It can be seen from Fig. 1 that the chemical structure of PVP–CMC hydrogel does not change much. The spectra of both CMC and PVP–CMC hydrogel films present the characteristic absorptions of cellulose structures, including the absorption around 3400 cm^{-1} (hydroxyl stretch influenced by hydrogen bonding), 2905 cm^{-1} (methylene), 1651 and 1603 cm^{-1} (carbonyl band),1060 cm^{-1} (β-1, 4-glycosidic bond) and 1428 cm^{-1} (skeletal C=C stretching vibrations in the

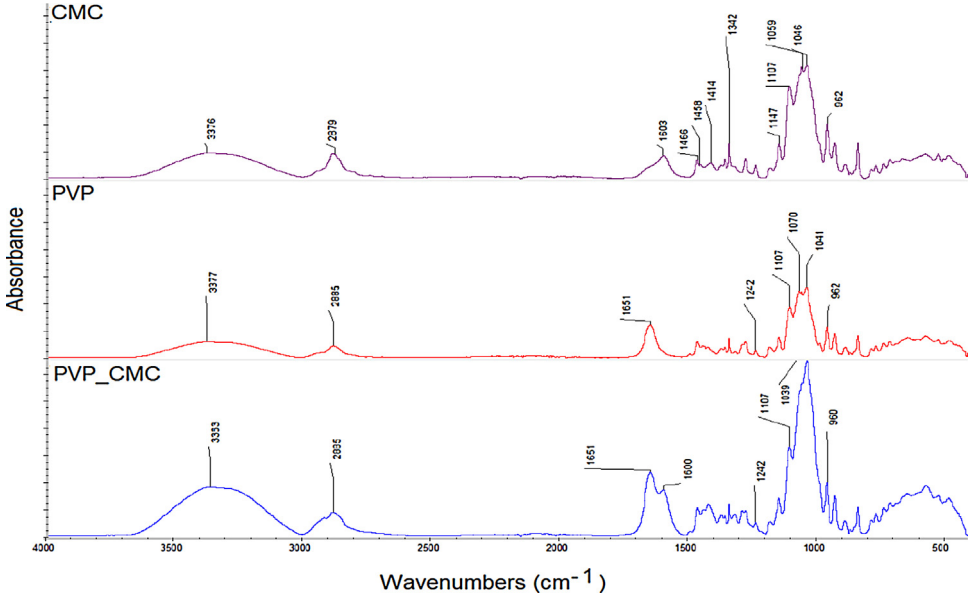

Fig. 1. FTIR spectra of CMC, PVP and PVP–CMC hydrogel film.

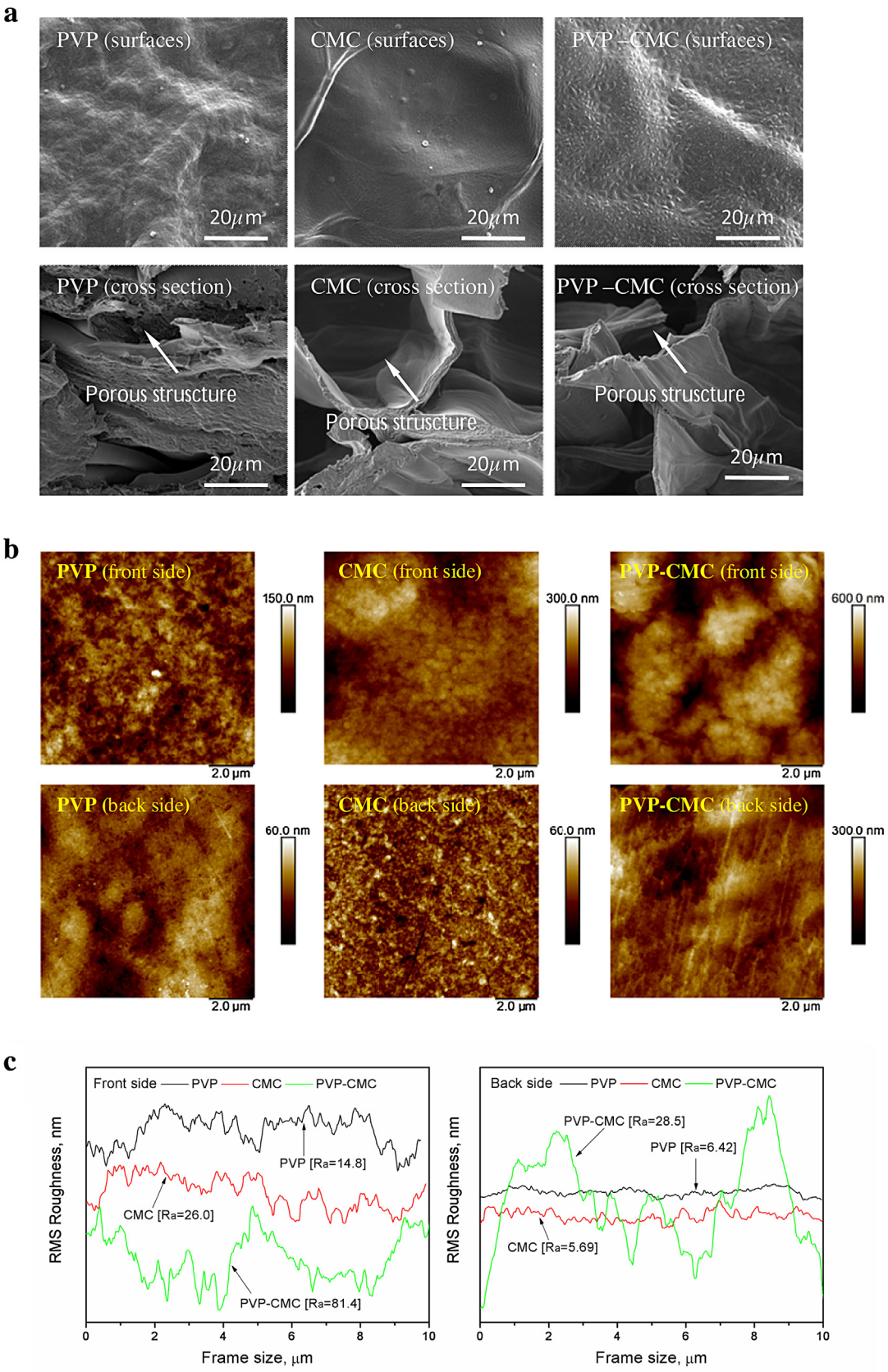

Fig. 2. (a) SEM images of PVP, CMC and PVP–CMC hydrogels (lyophilized film). (b) AFM images of PVP, CMC and PVP–CMC hydrogels (dry film including Z scale). (c) Profile of roughness of PVP, CMC and PVP–CMC hydrogel films where [R_a represents the arithmetic average of absolute values of the profile].

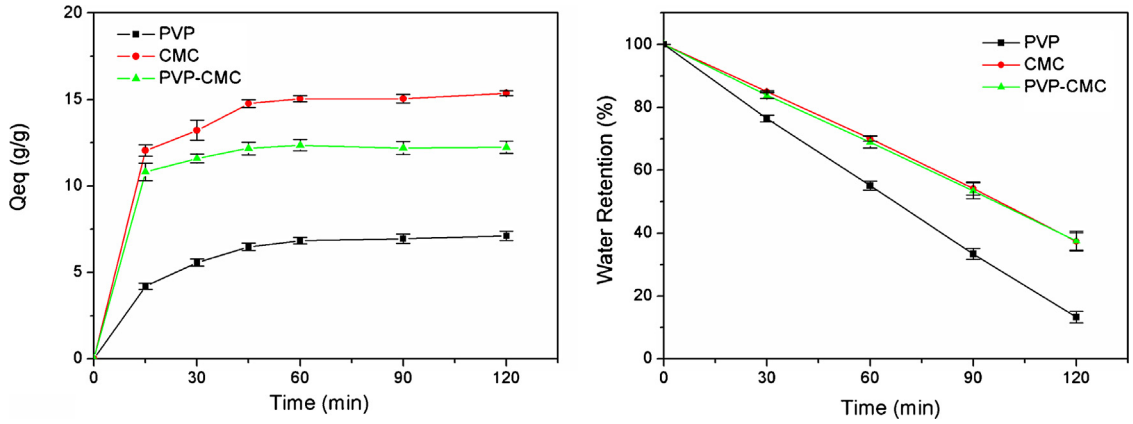

Fig. 3. Swelling (left) and de-swelling (right) kinetics curve of PVP, CMC and PVP–CMC hydrogel film (average value ± SD, $n = 3$).

aromatic rings) (Roy et al., 2010a; Roy et al., 2010b; Roy, Saha, Humpolicek, et al., 2010, Wu, Zhang, Liu, & Yao, 2012; Zhou et.al, 2013). Some characteristic peaks of PVP spectrum: 1286 cm^{-1} for C—N stretching vibration, 1456 cm^{-1} and 1651 cm^{-1} peaks and the typical carbonyl band 1603 cm^{-1} at 1620 cm^{-1} region are clearly visible in PVP–CMC hydrogel film, which confirms the physical interaction between natural (CMC) and synthetic (PVP) polymer, and the developing of the physical nature of cross-link junctions (Ahmed, 2013; Wang et al., 2007) to form such pseudo hydrogel (i.e. physically bonded unstable hydrogel) by applying temperature and pressure (physical stimulating agents). The miscible nature of synthetic (PVP) and natural (CMC) polymers in PVP–CMC hydrogel was investigated with XRD which confirms the physical structural properties. Moreover, the XRD pattern (figure not illustrated) of all these three (PVP, CMC and PVP–CMC) hydrogel thin films exhibits amorphous nature.

3.2. Morphology

The SEM images of PVP, CMC and PVP–CMC (lyophilized films of hydrogels) are depicted in Fig. 2a, AFM images of PVP, CMC and PVP–CMC (dry films of hydrogels) are illustrated in Fig. 2b, and the roughness of each hydrogel films is revealed in Fig. 2c to compare their surface images as well as surface topography of each hydrogel film. The SEM images (surface and cross section) of PVP, CMC and PVP–CMC are showing a clear difference in texture among these three kinds of hydrogels. But exploring their surface topography and roughness investigated by AFM, confirms that each film (PVP, CMC and PVP–CMC) is different from each other; even though each film is exhibiting three dimensional cross linking structure (as shown in Fig. 2a). The AFM images of PVP thin film represent the front/upper view and the back/lower view, similarly CMC exhibits the front/upper view and back/lower view, finally the front/upper view and back/lower view of PVP–CMC are also placed as presented in Fig. 2.b. The SEM and AFM images of PVP, CMC and PVP–CMC exhibit clearly the physical networks of polymers having transient junctions which can arise from either polymer chain entanglements or physical interaction, and as a result the porous structures are developed into the matrix. Therefore, all these three dry thin films are capable to absorb moisture/retain water, even though these films are prepared with water soluble polymer.

3.3. Swelling and deswelling kinetics

The swelling and de-swelling behaviour of PVP, CMC and PVP–CMC hydrogel thin films are shown in Fig. 3. Generally, swelling or de-swelling depends on the crosslinking as well as ionic strength properties of polymer film. The observed trend of swelling kinetics for both CMC and PVP–CMC are quite similar/comparable, but the swelling kinetics of PVP film shows quite a less amount of water uptake capacity though the initial pH of each polymer solution was 6.5. The maximum amount of water uptake is observed within 15 min (i.e. 12.05 ± 0.33 g/g for CMC, 10.82 ± 0.50 g/g for PVP–CMC and 4.20 ± 0.16 g/g for PVP) then their uptake capacity is uniformly increased and within 60 min reaches to more or less equilibrium state. It seems that as ionic strength of CMC is different than PVP, the osmotic pressure difference is higher in the case of CMC and PVP–CMC in comparison with PVP hydrogel film. Actually, during the swelling process, water needs to continuously overcome the osmotic pressure inside the absorbent. The substantial hydrophilic groups (—COO^-, —CHO and —OH) presented in the hydrogel thin film enhance the electrostatic repulsion in the hydrogel network, and thus strengthen the osmotic difference. Thus, the higher value of the osmotic pressure difference enhances the water uptake into the absorbents (Li et al., 2012; Zhou, Fu, Zhang, & Zhan, 2013). Further, it can be noticed from the de-swelling kinetics of PVP, CMC and PVP–CMC hydrogel, shown in right figure in Fig. 3 that, though the observed water uptake capacity of PVP hydrogel film is slow and low (left figure), the swollen film of PVP de-swells at faster rate compared to the swollen hydrogel films of CMC and PVP–CMC. Moreover, both CMC and PVP–CMC hydrogels are exhibiting quite a good amount of water retention capacity until 120 min. It is interesting to mention that at 30 min, the water retention capacity of PVP–CMC was 83.84 ± 1.0% for PVP–CMC, and 84.99 ± 0.38% for CMC and 76.47 ± 0.97% for PVC. But, after 90 min intermission at 120 min, the water retention value of hydrogels shows about 37.34 ± 2.72% for CMC, around 37.54 ± 3.09% for PVP–CMC and 13.27 ± 1.83% for PVP. Finally, it can be concluded that both CMC

Table 1
Stress–strain analysis data of CMC and PVP–CMC film at dry atmosphere (average value ± SD, $n = 5$).

Mechanical property	CMC			PVP–CMC		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
Tensile strength at break (MPa)	43.7 ± 3.3	42.1 ± 7.3	45.7 ± 3.9	45.6 ± 1.5	45.5 ± 1.9	42.2 ± 4.3
Tensile strain at break (%)	6.6 ± 1.9	7.4 ± 2.5	5.9 ± 1.54	7.4 ± 1.7	6.7 ± 0.6	8.2 ± 2.8
E-modulus (MPa)	1722 ± 158	1816 ± 287	1977 ± 380	2183 ± 183	2213 ± 83	1957 ± 55

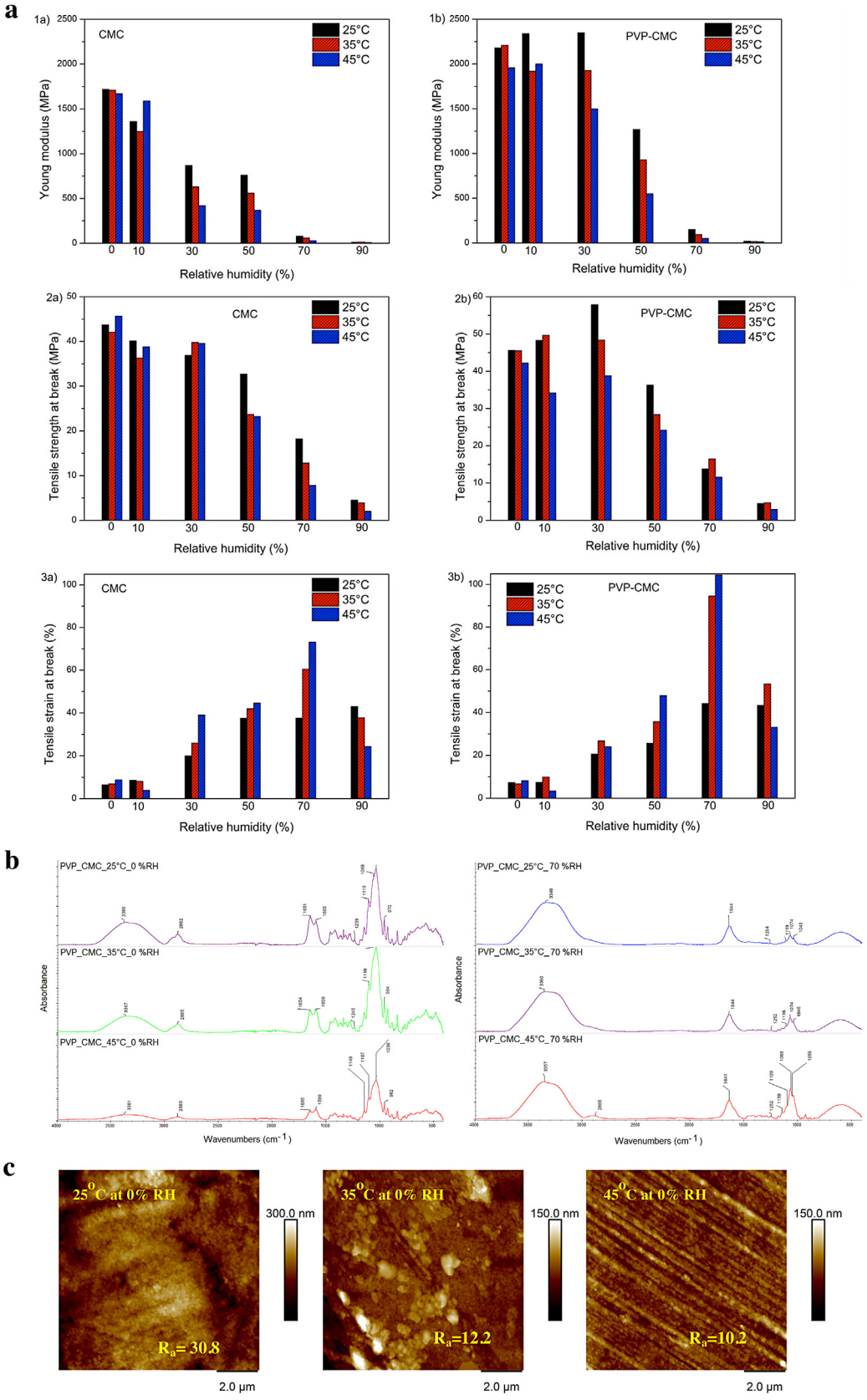

Fig. 4. (a) *E*-modulus (1), tensile strength at break (2), tensile strain at break (3) of hydrogel films at different temperature and relative humidity: (a) CMC, (b) PVP–CMC. (b) IR spectra of PVP–CMC hydrogel film at 0% RH (left) and 70% RH (right). (c) AFM image of PVP–CMC hydrogel film after treatment at 25, 35 and 45 °C [R_a is the arithmetic average of absolute values of roughness profile of the said film].

and PVP–CMC have comparable water retention as well as water uptake capacity.

3.4. Mechanical properties

The mechanical properties of dry hydrogel samples were determined by DMA transient stress-strain analysis at dry (0%RH) or humid (10–90%RH) atmosphere. The means and standard deviations were calculated from five replications. Mechanical properties as a function of the applied temperature at dry atmosphere are tabulated in Table 1. Tensile strength and strain at break of PVP–CMC sample are very similar to the neat CMC sample; however, *E*-Modulus of PVP–CMC increases about 26% compared to CMC. After an increase of temperature from 25 to 35 °C was recorded no significant changes of mechanical properties. Nevertheless, the increase of temperature to 45 °C influenced slightly on E-Modulus or stiffness of both samples, with an increase of about 14% for CMC and a decrease of about 10% for PVP–CMC.

In the service life of hygroscopic materials such as hydrogels, it is necessary to estimate an effect of humid atmosphere on the mechanical behaviour of products. The mechanical behaviour of CMC and PVP–CMC samples depending on relative humidity as well as temperature changes are presented in Fig. 4a. The obtained results show that mechanical properties of PVP–CMC at room temperature (25 °C), in the range of 0–30%RH stay at steady level. In contrast, neat CMC withstands at room temperature only in 10%RH. It can be seen that the increase of temperature together with relative humidity accelerates the loss of E-Modulus or stiffness, decrease of tensile strength and increase of strain at break. The presence of PVP in CMC hydrogel improves the mechanical properties in the whole range of testing temperature and relative humidity. The improvement of mechanical properties or increase in stiffness of PVP–CMC hydrogel is due to the cross-linking of CMC chain with PVP upon drying. Cross linking of CMC chain could occur due to hydrogen bonding, interaction between carboxylic and hydroxyl group of CMC chains. Overall, this could lead to structure collapse due to drying and thus increase in stiffness. It can be seen from IR spectra (Fig. 4b right) that the intensity of hydroxyl, alkyl and carbonyl groups decreases with the increase of temperature. Moreover, the increasing temperature modifies a ratio of the intensity of C=O assigning to PVP (1651 cm^{-1}) and CMC (1600 cm^{-1}), indicating faster diminishing of carbonyl group of PVP. Based on these results it can be concluded that an increase of temperature can initiate an interaction between CMC and PVP, resulting in physical cross-linking and as a result increase of stiffness. The morphology of PVP–CMC film which is measured at different temperatures (25 °C, 35 °C and 45 °C) depicted in Fig. 4c is the evidence of it. It can be seen from the surface morphology that the roughness of the PVP–CMC film gradually decreases with the increase of temperature. Whereas, the same PVP–CMC film in presence of increase relative humidity, significantly increase an intensity of hydroxyl groups and almost diminishes C=O groups of CMC (1651 cm^{-1}). However, C=O groups of PVP were at 70%RH very stable (1641 cm^{-1}) as shown in (Fig. 4b left). It indicates that the presence of PVP in the PVP–CMC blend contributes to the higher stability during hydrothermal treatment. It agrees with the obtained results of stiffness and lower water absorption of PVP–CMC in the comparison with the neat CMC film.

3.5. Accelerated creep behaviour at humid environment

Materials used for packaging must be capable of sustaining some thermal, moisture and mechanical stress during transport and product storage. Very important is the ability of material to withstand hydrothermal aging accelerated by mechanical stress with a minimal change of shape and without failure. Hydrothermal and mechanical stresses can be simulated with DMA–RH analysis (Gregorova et al., 2013). Fig. 5 shows the creep behaviour of neat CMC and PVP–CMC hydrogels during creep/recovery cycle at the applied stress of 10 MPa, temperature of 25 °C and variable (stepwisely changed) relative humidity. As observed, the creep (strain) at 25 °C is about 30–70% higher for neat CMC than for PVP–CMC hydrogel, depending on the applied atmosphere. The increase of relative humidity enlarges the differences between final strains of both samples. PVP–CMC sample exhibits lower creep compliance during creep and higher strain recovery in the recovery phase. Both samples did not withstand the application of 90%RH ambient atmosphere at room temperature and the stress of 10 MPa, and they ruptured during moisture conditioning phase.

In the previous study, the larger deterioration of mechanical properties of Kraft paper due to the temperature accelerated creep in the humid atmosphere was shown (Gregorova et al., 2013). CMC and PVP–CMC hydrogels also belong to the hygroscopic material, therefore the determination of their mechanical behaviour during hydrothermal creep is inevitable to appreciate their properties in the service life. Table 2 shows that the increases of relative humidity along with temperature decrease the elastic response of CMC and PVP–CMC samples to the creep.

3.6. Dynamic frequency/strain

The ability of storing energy and damping properties of dried CMC and PVP–CMC hydrogels at the atmosphere with various relative humidity within the temperature span of 5-80 °C was

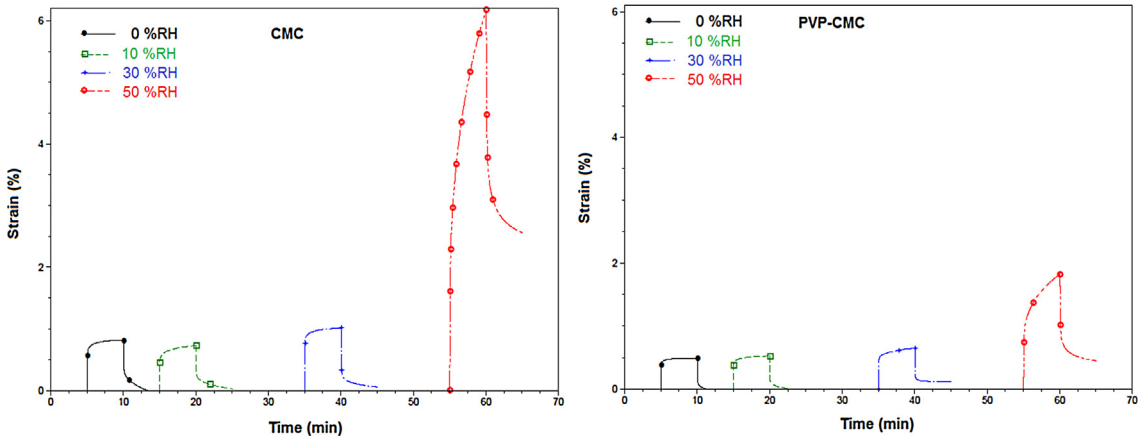

Fig. 5. Dependence of strain during creep experiment with stress of 10 MPa at 25 °C and variable relative humidity: (a) CMC, (b) PVP–CMC.

Table 2
Creep data after displace time and recovery data after recovery time of CMC and PVP–CMC hydrogels.

Relative humidity (% RH)	CMC			PVP–CMC		
	Creep compliance ($\mu m^2/N$)	Strain (%)	Strain recovery (%)	Creep compliance ($\mu m^2/N$)	Strain (%)	Strain recovery (%)
25 °C						
0	812	0.81	100	483	0.48	100
10	735	0.73	95.8	527	0.53	100
30	1014	1.01	93.7	651	0.65	92.3
50	6170	6.16	58.6	1819	1.82	75.2
90	*	*	*	*	*	*
35 °C						
0	1375	1.38	83.3	640	0.64	100
10	1048	1.05	88.2	695	0.70	97.5
30	1326	1.33	77.8	807	0.81	81.1
50						
90	*	*	*	*	*	*

* Sample has broken during conditioning time at this humidity.

Table 3
Storage modulus (E′) and peak values of loss tangent (tan δ) of CMC and PVP–CMC hydrogel films at 25 °C and various relative humidity based atmospheres.

Atmosphere (% RH)	CMC			PVP–CMC		
	E′ (MPa)	Temperature at tan δ peak	tan δ	E′ (MPa)	Temperature at tan δ peak	tan δ
0	2940	43.4 and 67.8	0.08 and 0.09	3260	44.9 and 64.0	0.12 and 0.14
10	2580	67.3	0.09	2990	62.2	0.16
30	1060	32.9	0.18	2020	51.0	0.19
50	90	17.8	0.19	180	23.4	0.20
70	40	10.9	0.19	70	20.0	0.82

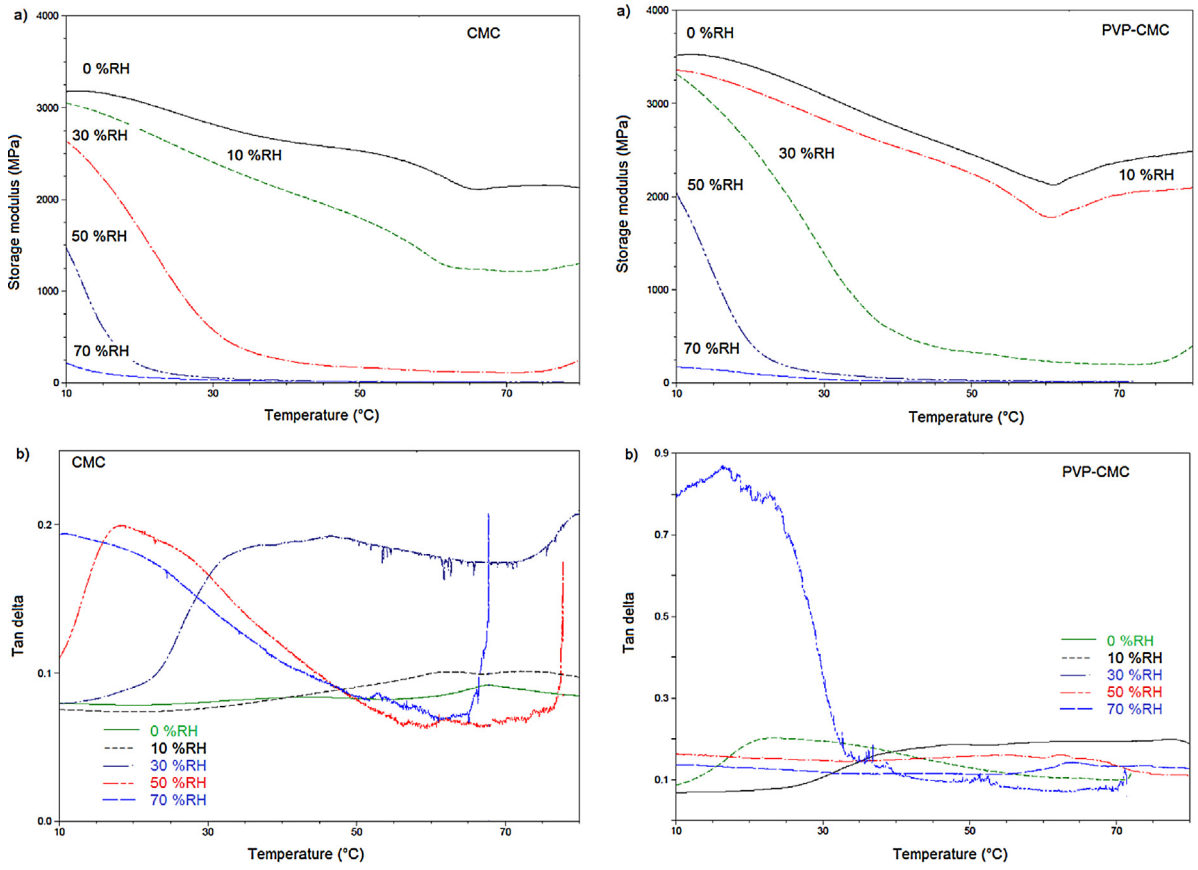

Fig. 6. Effect of temperature on storage modulus (a) and loss tangent (b) nature of CMC and PVP–CMC based hydrogel film in the atmosphere with various relative humidity (0%, 10%, 30%, 50% and 70% RH).

determined by dynamic oscillatory experiments at 1 Hz. The temperature-dependent typical curves of storage modulus and loss tangent of CMC and PVP–CMC samples in dry and wet atmosphere are presented in Fig. 6. The value of storage modulus reflects the stiffness of samples and their ability to store energy.

CMC film exhibits the storage modulus of 2940 MPa at 25 °C and 10%RH, while over the whole temperature span are visible five zones in storage modulus curve: (1) vitreous state (below 13 °C), (2) sharp decrease of stiffness to about 540 MPa (13–39 °C), (3) gradually decrease of stiffness (storage modulus) to about 140 MPa (39–52 °C), (4) additional sharp loss of stiffness (storage modulus) to about 400 MPa (52–66 °C) and (5) plateau (66–80 °C). The presence of 20 wt% of PVP (in PVP–CMC hydrogel) increases the stiffness of CMC to 3260 MPa at 25 °C and 10%RH. Moreover, the storage modulus curve of PVP–CMC at this condition shows some deviations compared to neat CMC. Only three zones can be determined: (1) viterous state (below 17 °C), (2) sharp decrease of stiffness to about 1350 MPa (17–61 °C) and (3) gradually increase of stiffness to about 360 MPa (61–80 °C). All of the E-modulus values shown above are the average values of two parallel measurements.

The aim of this work is to gain more detailed information about the effect of moisture on the viscoelastic properties of neat CMC and PVP–CMC hydrogels. According the results, the humidity change from 0 to 10%RH decreases the stiffness of both CMC and PVP–CMC samples, slightly about 9–13%. It is also found from Fig. 6a that both hydrogels show clearly two transition peaks at dry atmosphere (0%RH), and these properties are kept at 10% RH.

The first tan δ peak at about 43.4–44.9 °C was diminished at humid atmosphere. The atmosphere with the moisture of 30%RH caused a detrimental effect on the stiffness loss about 39–99% and the shifted peak of loss tangent about 13–57 °C (Table 3). The incorporation of PVP in CMC helped to inhibit the plasticizing effect of moisture predominantly up to 50%RH.

4. Conclusion

The main objective of this work was to determine the hydrothermal effect on the static and dynamic mechanical properties of cellulose based hydrogel films i.e. PVP–CMC hydrogel film which could be a promising food packaging material for fruits and vegetables to keep them fresh for longer duration (Saha et al., 2014). Controlled force, creep/creep recovery and dynamic oscillatory testing under thermal, mechanical and moisture stresses were performed using DMA–RH to provide the information for long-term stressed performance of neat CMC and PVP–CMC hydrogels to simulate possible consumer conditions as both the hydrogel film exhibited a comparable water uptake as well as water retention capacity. The neat CMC based hydrogel film has been evaluated to compare and to establish the importance of PVP in PVP–CMC hydrogel film, concerning the improvement of the mechanical stress properties and other hydrothermal effects. Finally, it can be concluded that:

- Not only *composition* of polymeric hydrogel film but also *temperature*, *relative humidity* etc. have great influence on morphology, roughness, physic-chemical behaviour of cellulose based hydrogel film.
- The incorporation of PVP in PVP–CMC hydrogel film helps to inhibit the plasticizing effect of moisture predominately up to 50% RH.
- Presence of PVP in the PVP–CMC hydrogel film contributes to the higher stability during hydrothermal treatment.
- In PVP–CMC hydrogel film, an increase of temperature can initiate an interaction between CMC and PVP, resulting in physical crosslinking and as a result increase of stiffness.
- PVP–CMC hydrogel film exhibits lower creep compliance during creep and higher strain recovery in the recovery phase and ruptured during moisture conditioning phase.

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