Influence of Poly (Ethylene Glycol) on the Characteristics of γ Radiation-Crosslinked Poly (Vinyl Pyrrolidone)-Low Molecular Weight Chitosan Network Hydrogels
(Kesan Poli(etilena glikol) ke atas Ciri-ciri Jaringan Hidrogel Kitosan Berjisim Molekul Rendah-Poli(vinil pirolidon)Tertautsilang melalui Teknik Sinar Gamma)

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ABSTRACT

PEG at compositions of 10, 15 and 20 g were added into the initial formulation of hydrogel L, which was composed of 6 g low molecular weight chitosan (LMC) and 14 g poly (vinyl pyrrolidone) in 100 g of 2% lactic acid. The mixtures were moulded and exposed to γ radiation at 7 kGy. The hydrogels obtained were characterized in term of gel fraction, swelling property, syneresis effect, FTIR, XRD and cross section morphology. The results indicated PEG reduces almost 27% crosslinking density of the LMC-PVP hydrogel yet increased hydrogel's water holding capacity from 450% and 480% to 750% and 650% in phosphate buffer solution (PBS) at pH5.5 and pH7.0, respectively. Also PEG enhanced the ability of LMC-PVP hydrogel to retain its moisture from dehydration at body temperature. The morphological study showed PEG developed thick pores wall and reduced the pores size of the hydrogels' network.

Keywords: Covalent-crosslink; plasticizer; porosity; swelling-equilibrium; syneresis

ABSTRAK

PEG dengan komposisi yang pelbagai iaitu 10, 15 dan 20 g telah ditambah ke dalam formulasi asal hidrogel L yang telah disediakan melalui pengadunan 6 g kitosan berjisin molekul rendah (LMC) dengan 14 g poli (vinil pirolidon) dan 100 g asid laktik berkepekatan 2%. Semua adunan dimasukkan dalam acuan dan didedahkan kepada sinar γ pada dos 7kGy. Hidrogel yang diperoleh dibuat pencirian daripada aspek kandungan gel, sifat pembengkakan, kesan sineresis, FTIR, XRD dan morfologi hidrogel menggunakan mikroskop imbasan elektron (SEM). Keputusan pencirian menunjukkan 10 g PEG telah mengurangkan ketumpatan jaringan taut silangan hidrogel sebanyak 14% tetapi meningkatkan keupayaan memegang air daripada 450% dan 480% kepada 750% dan 650% masing-masing dalam larutan penimbal fosfat (PBS) pada pH5.5 dan pH7.0. PEG juga meningkatkan keupayaan hidrogel LMC-PVP untuk mengekalkan kelembapannya daripada terhidrat pada suhu badan. Kajian morfologi juga menunjukkan PEG telah membentuk satu jaringan hidrogel berliang lebih kecil dengan dinding liang yang lebih tebal.

Kata kunci: Keliangan; pembengkakan ekuilibrium; pemplastik; sineresis; taut silang kovalen

INTRODUCTION

Hydrogels are polymeric materials with three dimensional (3D) networks. The networks are developed by crosslinking reaction of polymers induced by chemical or physical agents. Conventionally, crosslink networks of hydrogels are prepared by chemical reaction with the presence of crosslinker such as gluteraldehyde and epoxides (Dergunov et al. 2005; Yang et al. 2010). Due the toxicity issue, the chemical crosslinker are unfavourable in biomaterials preparation (Pollock & Healy 2010). There are natural crosslinkers for instance genipin which is safer and biocompatible. However, the preparation cost is higher since the natural crosslinker is more expensive and requires longer time for preparation (Pu et al. 2013). The reaction condition should also be concerned since natural material can denature easily. Meanwhile, ionizing radiation is an efficient tool to induce crosslinking reaction of polymers. The preparation of hydrogels via ionizing radiation such as gamma (γ) ray and electron beam has been established for decades. It is considered as green technology because it requires no reaction initiator and chemical crosslinker, no harmful chemicals utilized, the reaction can be done at ambient temperature, requires no purification on the end products and gives no toxic chemicals leftover (Nguyen & Liu 2013; Soler et al. 2012; Yang et al. 2010).

Hydrogels imbibe large amount of water as well as biological fluids up to hundreds even thousands times higher than its weight (Zhang et al. 2015a). The water absorption ability of hydrogels is dependent on the presence of functional groups in the hydrogels, the state of water (pH and ionic content), density of the crosslinked-network and the hydrophilic/hydrophobic polymer content (El-sherbiny & Smyth 2012; Nguyen & Liu 2013; Riva et al. 2011; Zhang et al. 2015b; Zhao et al. 2006). Although hydrogels are very hydrophilic, hydrogels are not soluble in the aqueous media due to the presence of crosslink networks. In order to meet special property for certain purpose, hydrogels are prepared from natural polymers

such as chitosan, gelatin and agar and synthetic polymers such as poly(vinyl pyrrolidone) (PVP), poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA). The hydrogels prepared using natural polymers are biocompatible, biodegradable and non-toxic but they are inferior in mechanical strength. Addition of synthetic polymers can overcome this disadvantage (Das et al. 2012; El-sherbiny & Smyth 2012).

Chitosan is amongst the most opted natural polymers to prepare hydrogels. Hydrogels contain chitosan exhibit good swelling property in acidic solution, which is caused by the protonation of amine group (-NH$_2$). Chitosan also formulated into hydrogels for drug carrier application. This cationic polymer interacts with negatively charged drugs and protects the drugs from degradation by enzymes (Archana et al. 2013; Dergunov & Mun 2009). Besides chitosan, degraded chitosan or low molecular weight chitosan (LMC) also demonstrates special property. LMC is more soluble than chitosan. It possesses lower viscosity and better flow-ability compared to chitosan (Park et al. 2011; Tahtat et al. 2012). Hydrogels composed of chitosan and PVP prepared via radiation are well established (Hill et al. 2011). PVP enhances the crosslinking density of hydrogels and give good transparency characteristic to the hydrogels (Zhao et al. 2006). Mostly, PVP-chitosan hydrogels are used for wound and burn dressing. PVP encourages the healing process by absorbing excess body fluid, retain exact moisture on the wound and let the accessibility of air to the wound. Plus, PVP increases the bioadhesion property of hydrogels on the mucosal surfaces. However the presence of PVP in the chitosan hydrogels does not increase the mechanical property of the hydrogels (Archana et al. 2013; Soler et al. 2012).

PEG is non-ionic hydrophilic synthetic polymer increases the elasticity, adhesion and tacky property of the hydrogels. PEG forms H-bond with the mucosal surface same like PVP (Soler et al. 2012). Yet, the Das et al. (2012) addition of PEG in PVP hydrogel decreases the crosslinking density since PEG chains settle among the PVP chains and avoiding crosslinking reaction. Nevertheless, PEG still improves the elasticity characteristic of hydrogels and also promotes better hydration to the hydrogels (Park et al. 2012). Also, the presence of PEG in PVP-chitosan hydrogels increases the release rate of active ingredients such as drugs embedded in the hydrogel networks (Das et al. 2012).

This study aimed at producing hydrogels from LMC and PVP via gamma radiation and to evaluate the effect of

PEG on hydrogels in term of crosslinking density, liquid intake ability, syneresis effect at different temperature and morphological structure, respectively.

MATERIALS AND METHODS

MATERIALS

LMC was purchased from Dungeness Environmental, Bothell, Washington. The average-weight molecular weight, Mw of LMC is 48.80 kDa which was determined by SEC -MALLS (size exclusion chromatography-multi angle laser light scattering). PVP (Mw = 10 kDa) and PEG (Mw = 4 kDa) were analytical grade from Sigma and Acros, respectively. All the materials were used as per received.

METHODS

Preparation of PEG Reinforced LMC-PVP Hydrogel The 6 g of dry LMC was dissolved overnight in 100 mL of 2% lactic acid. Then 14 g of PVP was added in each LMC solution. The mixture was stirred for 2 h or until the homogenous paste formed. Then PEG was added into the PVP-LMC paste. Then the paste was poured into the mould and vacuum-packed prior to irradiation. The vacuum-packed paste was irradiated at 7 kGy produced from Co-60 source facility at Sinagama, Malaysian Nuclear Agency. The dose rate was 1.62 kGy/h. The dose was selected based on the previous study by Mahmud et al. (2015), which indicated 7 kGy produced highest gel fraction of hydrogel L among 3, 5, 10, 15, 20, 25 and 30 kGy. The absorbed dose was monitored using Ceric Cereous dosimeter. The formulations' details are described in Table 1.

FTIR The Fourier transform infrared (FTIR) spectra was recorded on Bruker TENSOR FTIR Spectrometer. The spectra was recorded with the sum of 32 scans at resolution 4 cm^{-1} with a range of 400–5000 cm^{-1}. The hydrogels samples were dried prior to measurement.

Gel fraction Dried hydrogels were crushed into small pieces at size 10 × 10 mm rectangles (Hashemi et al. 2013; Park & Nho 2003). The hydrogel pieces were weighed and placed in the tea bag and tighted. The tea bags were soaked in the water at temperature of 60ºC for 8 h. The tea bags were taken out from the hot water, rinsed with distilled

TABLE 1. The formulation and condition of hydrogel preparation

Sample Code	LMC (g)	PVP (g)	PEG (g)	Dose, kGy
L	6	14	0	7
L10	6	14	10	7
L15	6	14	15	7
L20	6	14	20	7

water and placed into drying oven at 60ºC (Nguyen & Liu 2013). The drying process was done until the weight of tea bags and hydrogel constant. The gel fraction of hydrogels was calculated using (1).

$$\text{Gel fraction (\%)} = \frac{W_t}{W_i} \times 100\% \qquad (1)$$

where W_i and W_f are the initial weight of 10×10 mm dry hydrogel and final weight of hydrogel after extraction, respectively.

X-ray diffraction study The crystallinity of hydrogels was evaluated by X-ray diffractometer, PANAlytical Model PW 3040/60 X'pert Pro. Scanning was done up 2θ of 80º for LMC, PVP, PEG and hydrogels.

Swelling The swelling profiles of hydrogels prepared were determined by immersing 10×10 mm specimens in 40 mL of buffer solution (PBS), pH5.5 and pH7.0 at ambient temperature for 24 h with gentle agitation (Yuan et al. 2007). The swollen hydrogels were then taken out from the solution and the surface liquid was blotted with lab tissue before weighing the swollen hydrogels (Archana et al. 2013). The water uptake was calculated from the following relationship in (2).

$$\text{Water uptake (\%)} = \frac{(W_s - W_i)}{W_i} \times 100 \qquad (2)$$

where W_i and W_s are initial weight of dried 10×10 mm hydrogel and weight of the swollen hydrogel after 24 h immersion, respectively.

Syneresis The syneresis effect was determined by placing the pre-weighed hydrogel on petri dish, uncovered at 2 different temperatures, ambient and -37.0°C + 2.0°C for 2 h. The syneresis of hydrogel creates internal osmotic stress on the physical network and it occurs spontaneously under certain elasticity conditions (Ako 2015; Meena et al. 2009). The fluids releasing rate usually depends on the temperature, salt concentration (if available) in the hydrogels, type of polymer and polymer concentration. The shrunk hydrogels were weighed and syneresis effect was determined by (3) as follows.

$$\text{Syneresis ratio} = \frac{(W_i - W_f)}{W_i} \times 100 \qquad (3)$$

where W_i and W_f are initial weight and final weight of hydrogel after 2 h, respectively.

Morphology The morphological study was carried out by scanning electron microscope (SEM), Phenom G2 Pro. The hydrogels were freeze-dried at -90°C for 5 days. The observation was done on the cross section of hydrogels at 400× magnification.

RESULTS AND DISCUSSION

Figure 1 demonstrates the spectra of LMC, PVP, PEG and series of hydrogel L which contained vary compositions of PEG. The IR spectra of Figure1(a) and 1(b) shows broad absorption band at 3360 and 3434 cm^{-1} were assigned to the overlapped of O-H stretching and N-H stretching vibrations of amide (II) of LMC and O-H stretching vibration of PVP, respectively (Abad et al. 2003; Archana et al. 2013). The broad absorption band around 1010 - 1080 cm^{-1} of Figure1(a) attributes to the glycosidic linkages of LMC (Abad et al. 2003). The strong band at 1653, 1421, 1287 and weak band at 2917 cm^{-1} of PVP Figure 1(b) were assigned to C=O stretching, C-N stretching, O-H bending and C-H stretching vibrations, respectively (Can 2005; Singh & Pal 2011; Yang et al. 2010).

As in Figure1(c), the band of overlapped O-H and N-H shifted to 3376 cm^{-1} due to the interruption of intramolecular H bonds in LMC by H bonds (intermolecular) of the incorporated PVP (Archana et al. 2013; Yang et al. 2010). Also in Figure 1(c) the absorption bands of C=O, C-N and O-H bending shifted to the lower frequency with lower intensity caused by the intermolecular H interation between PVP and chitosan.

The IR spectra of PEG in Figure 1(d) shows strong and medium absorption bands at 2880, 1471, 1342 and 1099 cm^{-1} which are characteristics of aliphatic C-H stretching, C-H bending, CO-H stretching and C-O-C stretching vibrations, respectively (Shameli et al. 2012).

The spectra in Figure 1(e), 1(f) and 1(g) indicates lower intesity of band at 1650 and 1658 cm^{-1} caused by the intermolecular inter-polymer H bonds of -OH, NH$_2$ of LMC, C=O of PVP and -OH of PEG. The C-O stretching band of PEG in Figure 1(d) indicates strong intensity at 1279 and 1099 cm^{-1}. The IR spectra of hydrogel L10, L15 and L20 in Figure 1 shows the intensity of C-O band increased as the PEG content increased. The secondary frequency of C-O at 1099 cm^{-1} shifted to higher frequency due to the interaction of CO-H.

The broad band with less absorbance of CH bending around 2950 - 2900 cm^{-1} was observed in Figure 1(c) compared to Figure 1(b) because of the formation of crosslink network of PVP (Singh & Pal 2011). The covalent bond of PVP crosslinked attributed by the weak vibration of -CH$_2$- at 1420 cm^{-1} of hydrogel L. The aliphatic C-H stretch at 2880 cm^{-1} band indicated intense peak in PEG yet weakened in (e). The reduced intensity of aliphatic C-H stretching vibration caused by H interaction among carbonyl, hydroxyl and amine groups in the hydrogel. However, as the PEG concentration increased, the intensity of C-H vibration gets greater yet the band remains at the same wavenumber i.e 2883 cm^{-1}, as shown in Figure 1(e), 1(f) and 1(g). The spectra in Figure 1(e), 1(f) and 1(g) proves that PEG undergoes entanglement in this PVP-LMC hydrogel instead of crosslink. The addition of PEG increased the intensity of -CH$_2$- bending and shifted the -CH$_2$- band to the higher wavenumber which was around 1460 cm^{-1}.
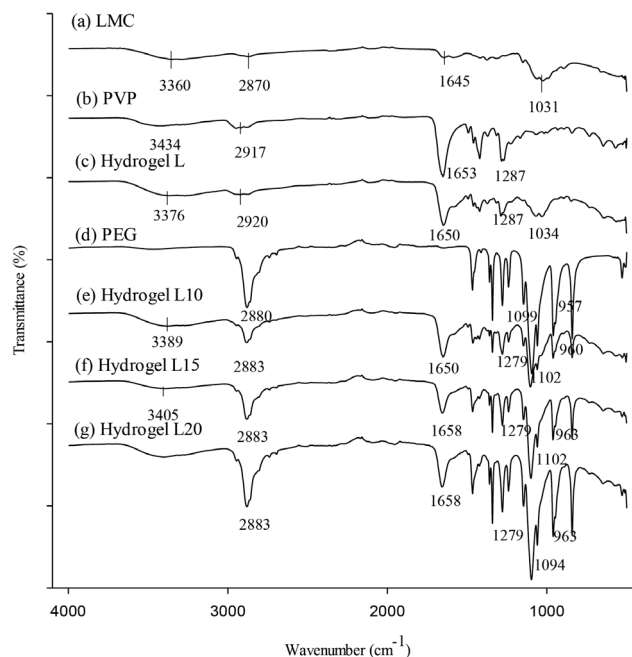
FIGURE 1. FTIR spectra of (a) LMC, (b) PVP, (c) Hydrogel L, (d) PEG, (e) Hydrogel L10, (f) Hydrogel L15 and (g) Hydrogel L20

The formation of PVP covalent crosslinked network is shown in Figure 2. At the primary stage, γ radiation induces the dissociation of water molecules by radiolysis as Figure 2(i). The reactive hydroxyl radicals (·OH) generated from the radiolysis of water molecules abstract the hydrogen (H) from PVP and unstable PVP-radicals formed. The PVP-radicals recombine to the stable stage by developing inter- and intramolecular interactions which generate the formation of crosslink networks via covalent interactions, -C-C- (Can 2005; Jin et al. 2006; Makuuchi 2010). Meanwhile, chitosan undergoes degradation due to the glycosidic-linkages breakage by ·OH radicals. The irradiation of LMC-PVP solution generates the formation of semi interpenetrating polymer network (semi-IPN) hydrogel, where LMC physically entangle with the crosslinked-PVP (Abad et al. 2003; Berger et al. 2004).

Figure 3 illustrates the hydroge L, without presence of PEG gives highest gel fraction. Exposuring of PVP-polysaccharides blends to γ radiation would result in crosslinking of PVP chains, degradation of polysaccharides chains and grafting of polysaccharides on the PVP, simultaneously (Abad et al. 2003). The irradiation of PVP-LMC blends yield to the formation of hydrogel consisting of semi interpenetrating polymer network (semi-IPN), where LMC chains entangled within the crosslinked PVP (Dergunov & Mun 2009). Hydrogel L has highest density of crosslinked network among series of hydrogel L (L10, L15, L20) due to the highest gel fraction indicated.

The addition of 10 g PEG in hydrogel L indicated the drastic reduction in gel fraction. According to Park et al. (2012), PEG reduces gel fraction of PVA hydrogel because PEG remains between the PVA chain and avoiding
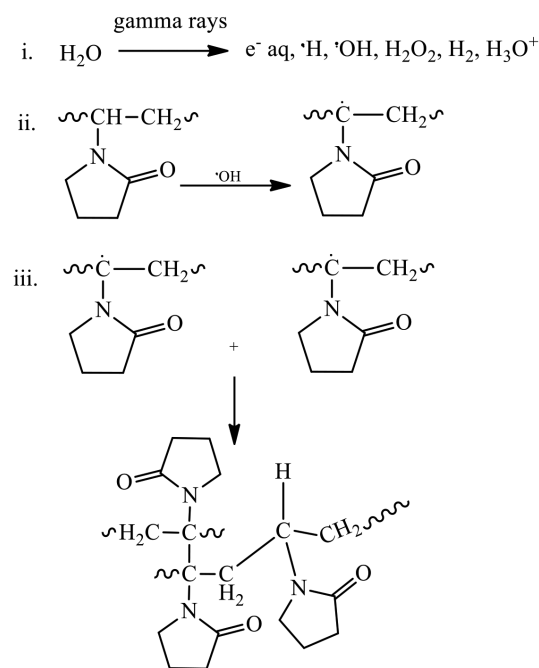

FIGURE 2. The radiolysis of water molecule, the formation of PVP-radicals by reactive ·OH radicals and the recombination of PVP-radicals to form covalent crosslinked network (Can 2005; Pasanphan et al. 2010)

the progressive crosslinking reaction of PVA chain. The incorporation of hydrophilic polymer whose hydrophilicity is different from the initial hydrogel system interrupt the crosslinking reaction and hence reduces the crosslinking density (Berger et al. 2004). The same situation also

occured here, the addition of PEG reduces the density of crosslinked network of hydrogel L. PEG disrupts the crosslinking efficiency of PVP.

Nevertheless, hydrogel L15 indicates higher gel fraction compared to the LMC-PVP L10, yet the difference is insignificant. The entanglement of PEG in the hydrogel L formed the physical interaction or molecular interaction (H bonding) with LMC and PVP. This interaction developes the hydrogel internal strength. However this kind of interaction is reversible and non-covalent interaction (Jin et al. 2006). Gel fraction of LMC-PVP hydrogel with 20 g of PEG reduced due to the disruption of physical interaction between PEG-LMC- PVP chains enhanced by the saturation of H-bonding interaction.
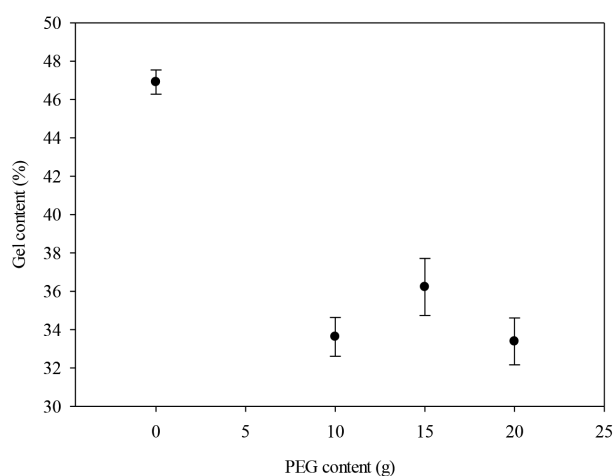

FIGURE 3. Effect of PEG on the gel fraction of hydrogel L after being irradiated at 7kGy

Figure 4 demonstrates the diffractograms of LMC, PVP, PEG and siries of hydrogel L. The LMC has 2 broad peaks at $2\theta = 10°$ and $20°$ with the same pattern, where at $2\theta = 20°$ has sharper and more intense peak. This indicates degradation of chitosan by gamma ray does not change the crystallographic orientation of chitosan as semi-crystalline polysaccharide (Duy et al. 2011). Meanwhile, PVP has double broad diffractions at $2\theta = 10°$ and $22°$ which indicate the amorphous nature of PVP (Sivaiah et al. 2011). PEG shows highly crystalline form with very intense crystalline peak at $2\theta = 19°$ and $23°$. The hydrogel L10, L15 and L20 have semi crystalline dispersion system. As in Figure 4, the PEG reinforced hydrogel L illustrates semi crystalline materials. All hydrogels indicate broad crystalline peaks at range of $2\theta = 9°$ to $12°$ and very intense crystalline peaks around $2\theta = 19°$ and $23°$.

According to the XRD diffractograms obtained, addition of PEG introduces the sharp and intense crystalline peak to the hydrogels. Although PEG introduces new crystalline regions to the hydrogels, the diffraction peaks of PEG in hydrogels show reduction in intensity compared to the PEG alone due to the interaction between components in the hydrogels (PVP-LMC-PEG) (Farag & Mohamed 2012). The intensity of diffraction peaks at $2\theta = 19°$
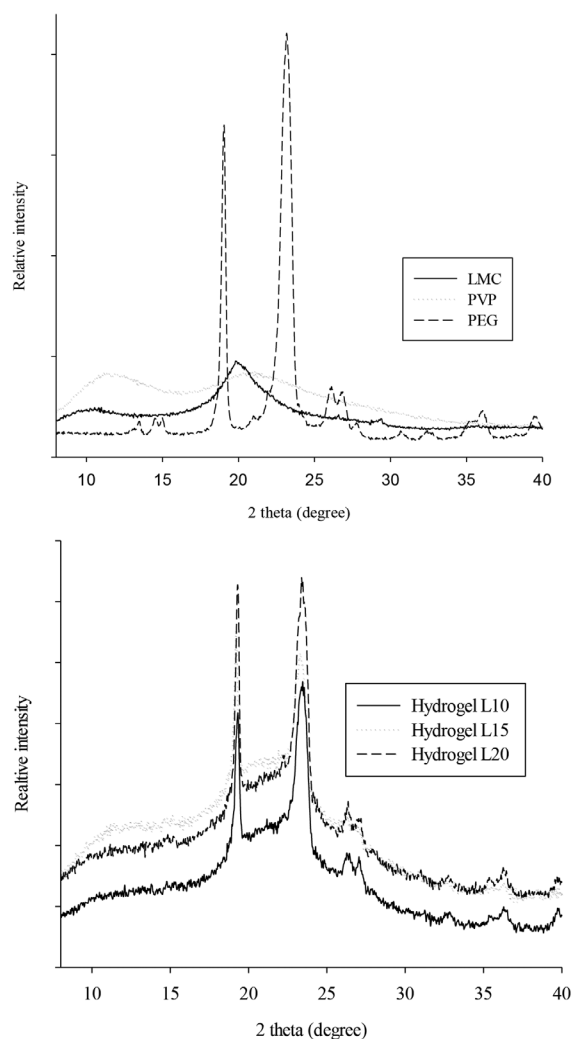

FIGURE 4. XRD diffractograms of LMC, PVP, PEG and dispersion systems of LMC-PVP with PEG in different compositions

and $23°$ increases with the increased of PEG content. The intensity of crystalline regions of L15 is higher than L10 but addition of 20 g PEG in the LMC-PVP hydrogel show reduction at the crystalline regions of L20 yet still higher than L10. The blend of LMC-PVP-PEG introduces fabrication of hydrogels with great semi crystalline properties such as good in transparency, elasticity and form stability. The LMC-PVP-PEG hydrogel able to retain its original form even in swollen state.

Swelling is influenced by crosslinking density of hydrogel network structure, hydrophilic nature of the hydrogel, pH of the swelling solution (aqueous) and hydrophilicity and hydrophobicity of the new polymers or monomers incorporated in the initial hydrogel (Berger et al. 2004; El-sherbiny & Smyth 2012; Park et al. 2012). Figure 5 demonstrates the equilibrium swelling ratio of hydrogel L with PEG in phosphate buffer solution (PBS) at 2 different pH conditions. The hydrogel L shows low water uptake due to its high crosslinking density and tighter pores. These properties decrease the water molecules movement into its network (Nguyen & Liu 2013). The hydrogel L in pH7.0

indicates better swelling behavior than pH5.5. Hezaveh and Muhamad (2013) reported that hydrogel prepared with materials which can protonate in acidic environment lead to the formation of hydrogen bonds resulting in more compact hydrogel network structure. Consequently H-bonds restrict the movement and relaxation of network chain. Therefore hydogel L has better swelling property in pH7.0 than pH5.5.
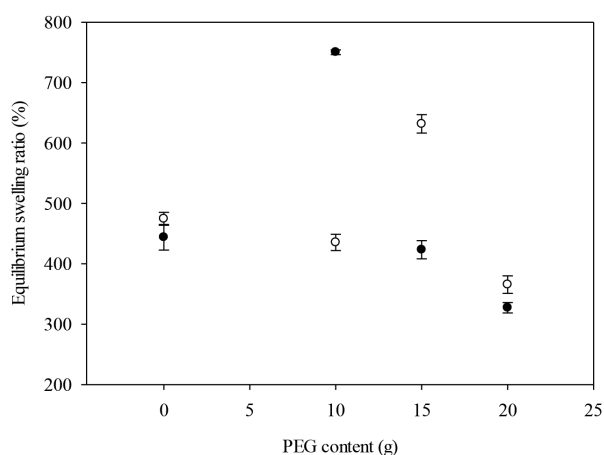

FIGURE 5. The swelling property of LMC-PVP hydrogel with and without PEG in PBS at pH 5.5 (●) and pH 7.0 (○)

In PBS at pH5.5, hydrogel L10 shows highest water uptake. The protonation of amino groups of chitosan molecules in acidic solution causes the matrix expanded by electrosatic repulsion thus allowing water molecules to get into the hydrogel structure (Berger et al. 2004; Tanuma et al. 2010). Besides, hydrophilicity of PEG also attracts more water into the hydrogel structure (Berger et al. 2004; Park et al. 2012). However, addition of 15 and 20 g of PEG in LMC-PVP hydrogel reduces equilibrium swelling ratio of hydrogel drastically. This is because of incorporation of high concentration of PEG in the LMC-PVP hydrogel creates more formation of H interaction between LMC-PEG-PVP. The H interaction inhibits hydrogel to absorb more water molecules into its structure. The results also showed that H bonds hinder the protonation of amino groups in chitosan molecules in acidic medium.

Meanwhile at pH7.0, the 10 g of PEG does not affect much on the equilibrium swelling ratio of LMC-PVP hydrogel. Despite amino groups of LMC do not undergo protonation at pH7.0, the presence of PEG at 10 g also impotence to absorb more water. The hydrogel L15 indicates increment in water uptake and drop remarkably after addition of 20 g PEG. The increment in water uptake probably caused by the disruption of H interaction among the polymers chains and more water molecules are brought into the hydrogel structure. The 20 g of PEG is the saturated amount for hydrogel L according to the lowest and weakest water uptake ability at both pHs.

Figure 6 demonstrates the syneresis effect of the hydrogels after being left uncovered at ambient temperature and at 37.0°C + 2.0°C for 2 h. Syneresis is a condition whenever hydrogel expels water spontaneously and over the time it will become stiffer due to the loss of water in its matrix (Divoux et al. 2015; Pollock & Healy 2010). According to the previous studies done, syneresis of hydrogels are influenced by many factors, such as solvent quality, presence of salt, temperature, humidity, hydrogels' network density, composition of polymers as well as the hydrophilicity and hydrophobicity of the polymers (Ako 2015; Divoux et al. 2015; Kruif et al. 2015; Meena et al. 2009; Pollock & Healy 2010; Simões et al. 2012). Temperature is an external stress that influences the water loss rate of the hydrogel. At the higher temperature, water is evaporated faster compared to the lower temperature (Divoux et al. 2015). Figure 6 indicates hydrogels kept at -37°C + 2.0°C have higher percentage of water loss compared to the hydrogels kept at ambient temperature.
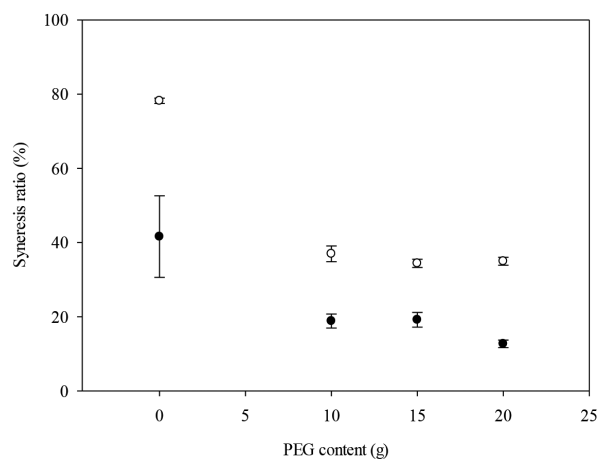

FIGURE 6. Effect of PEGs on sineresis of LMC-PVP hydrogel at -37°C + 2.0°C (○) and ambient temperature (●)

Also, addition of PEG reduces the syneresis ratio of hydrogels at both temperatures. As the PEG content increased, syneresis ratio of hydrogels also decreased. The hydrophilicity of PEG increases the water holding capacity of the hydrogels. This hygroscopic polymer is also able to attract and absorb moisture from the environmanet to retain its moisture. The addition of PEG also increases the porosity of the hydrogel network (Meena et al. 2009; Pollock & Healy 2010). PEG reduces gel fraction of the hydrogel. PEG avoids progressive development of crosslinking network and hence enhances the porosity of hydrogels. Hydrogels absorb and retain more water in their networks. As presented in Figure 6, at ambient temperature, hydrogels with addition of hydrogel L10 and hydrogel 15 show insignificant difference of syneresis ratio. The addition of 20 g PEG in hydrogel L reduces synesresis ratio of hydrogel at ambient temperature. At the higher temperature, addition of 10, 15 and 20 g of PEG do not show significant change in syneresis ratio. The results indicated as low as 10 g of PEG helps hydrogel to reduce water loss and inhibits shrinkage and avoid its
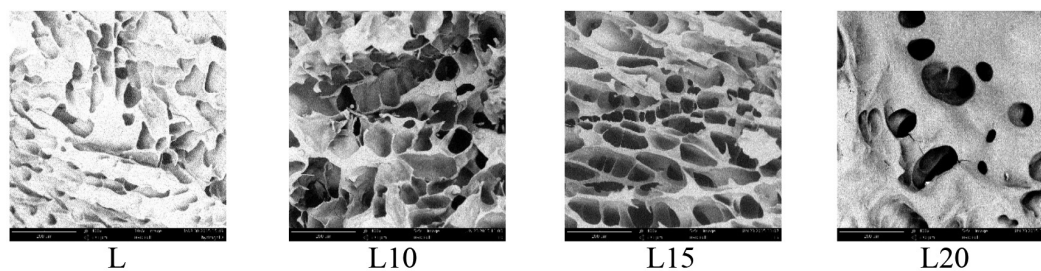
FIGURE 7. Effect of PEG on the morphology of LMC-PVP hydrogel

network from collapse at fast rate due to the syneresis at ambient as well as at elevated temperatures.

The morphological property of LMC-PVP hydrogel reinforced PEG at different composition is shown in Figure 7. The L image shows very dense network with small pores. The pores are arranged close to each other and seperated with very thin walls. The entanglement of LMC in the PVP crosslinked-chains induces the formation of homogenous-thickness of pores' wall and tighter structure. Meanwhile in L10 and L15 images, the networks are less dense with bigger pores. The hydrogel L10 shows interconnecting pores with uniform pore size contribute to better swelling property (Nguyen & Liu 2013). Meanwhile hydrogel L15 with unlinked pores and nonuniformity of pore size indicate weak swelling behavior. The images show pores are surrounded with thin to medium thick wall. Addition of PEG at 10 to 15 g in LMC-PVP hydrogels reduces the formation of crosslink network density. The entanglement of PEG between the PVP crosslinked-chains induces formation of various thickness of pores' wall. As the PEG content increased the thickness of pores' wall increased. The L20 image illustrates smaller pores, least dense network and very thick pores' wall. The presence of 20 g PEG in LMC-PVP hydrogel diminishes the formation of 3D network. The pores located far from each other, randomly and irregularly. The morphological image of L20 indicates that 20 g PEG is the saturation composition of PEG in the LMC-PVP hydrogel.

CONCLUSION

The irradiation of LMC-PVP induces the formation of crosslink network. Addition of PEG in LMC-PVP hydrogel reduces the density of crosslink network. Nevertheless, PEG enhances swelling property, water holding capacity and ability of the hydrogels to retain its water content at higher temperature. PEG also strengthen the mechanical property of LMC-PVP hydrogel by developing homogeneous and miscible blend with LMC and PVP according to the XRD result. The morphology images also show addition of PEG reduces brittleness of the LMC-PVP hydrogel by inhibiting more pores development and increasing the thickness of pores' wall. Overall results indicated addition of PEG as low as 10 g shows better changes in physical and chemical properties of the initial LMC-PVP hydrogels.

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