Biodegradable Hydrogel Film for Food Packaging

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Abstract: - Disposal of waste plastic packaging materials has raised a serious problem worldwide leading to environmental pollution due to the fact that most of the plastic packaging materials are generally non-biodegradable. In this article we have reported about a novel synthetic and biopolymer based biodegradable hydrogel film as a food packaging material. The water vapour transmission (WVT) test proves that oxygen can pass through the hydrogel film, i.e. the film is breathable. Biodegradability study of the hydrogel film was carried out by soil burial-test in a composting environment up to 5 weeks. SEM analysis shows structural deformation of the hydrogel film with time. The hydrogel film shows sharp weight loss until 4 weeks, and after that no significant residues of the hydrogel films were found in the compost bed.

Key-Words: - Breathable, biodegradable, biopolymer, compost, hydrogel, packaging.

1 Introduction

Hydrogels are extremely hydrated polymer gels with macromolecular three dimensional networks that swells but do not dissolve in water [1]. They have wide range of applications: in agriculture [2], bio and chemical sensors [3-4], water purification and removal of metal ions [5-6], oil spill removal [7], DNA separation [8], largely in the biomedical field (contact lens, wound dressing, tissue engineering, drug delivery, etc.) [9-12], and for food packaging as well [13]. There are different materials available for packaging. Papers and clothes are flexible and light weight and recyclable. Glass and metals are also widely used for packaging as they are corrosion resistant and stronger, respectively. However, among the packaging materials, polymers, specifically plastics are most demanding. They exhibit many worthwhile characteristics, such as: transparency, softness, heat seal ability, and good strength to weight ratio. In addition, they are generally low cost materials, show efficient mechanical properties such as tear and tensile strength, and they are good barrier to oxygen and heat [13, 14]. But, most of the plastic food packaging materials are practically non-degradable, and the waste packaging materials have raised a serious global environmental problem. The use of biodegradable polymer has been limited because they show some problems in their performance and processing, such as brittleness and heat distortion temperature, respectively [15, 16]. Initially, using of starch as a biodegradable thermoplastic material grabbed the attention of the researchers. However this concept did not turn out into a very fruitful one because of the poor performance of starch regarding water sensitivity, limited mechanical properties with high brittleness [15]. To face this challenge, many researchers as well as companies worldwide are now emphasizing on the development of eco-friendly packaging solutions by using the ecological advantages of biopolymers in food packaging applications [13]. Even though researchers have focused on applying these techniques to the food industry, there seems to be a gap between research and its implementation in the industry [14]. To overcome this problem up to a greater extent, as an

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alternative, hydrogels can also offer new opportunities for the design of efficient biopolymer packaging materials with desirable properties [13]. In this regard, development of poly-ion complex hydrogels is an alternative approach for the production of bio-based polymers for food packaging applications [13, 17]. Single biopolymer based films generally show poor mechanical properties, however polymer-polymer interactions can be strengthened by combining biopolymers with bio- or synthetic polymers with different structures and introducing predominantly charge interactions rather than hydrogen bonding. In this way, three different forms of hydrogels may be obtained: physical hydrogels, chemical hydrogels and interpenetrating polymer network (IPN) [13]. There are several examples for the approach to develop food packaging or food wrapping materials by using more than one biopolymers, such as whey protein isolate/mesquite gum, starch/cellulose fibers, chitosan/pectin, gelatin/sodium alginate, soy protein isolate/gelatin, gelatin/konjac glucomannan, chitosan/gelatin, gelatin/pectin, methylcellulose/whey protein, zein/starch, etc [13].

2 Problem Formulation

This paper reports about a novel approach to develop a breathable physical hydrogel film for food packaging using synthetic (polyvinylpyrrolidone; PVP) and biopolymers (carboxymetyl cellulose; CMC and agar) and designated as PVP-CMC hydrogel film. Special attention was given for the breathability of the hydrogel films, as some food materials, mainly fresh vegetables needs aeration, i.e. flow of oxygen to maintain their freshness. Hydrogels possess high water absorption capacity. This is important, because some food materials release moisture, and that should be absorbed by the packaging materials to avoid the food from fast decay. The packaging material must be flexible and non-brittle, so that it can be folded as desired during packaging. The most important parameter is the biodegradability of the packaging material to avoid environmental hazards. The degradation scenario of the above mentioned hydrogel film was studied under controlled environment (30ºC, pH 6.0-8.5, and moisture content ~ 60%) using commercially available compost.

3 Problem Solution

3.1 Experimental

3.1.1 Materials

Polyvinylpyrrolidone K 30 (PVP: molecular weight 40,000), polyethylene glycol 3’000 (PEG: average molecular weight 3,015-3,685) and agar were supplied by Fluka, Switzerland; sodium carboxymethyl cellulose (CMC) was purchased from Sinopharm Chem. Reagent Co., Ltd, China; glycerin was obtained from Lachema Ltd, Czech Republic. Compost (ZAHRADNICNY KOMPOST) was ordered from www.agrocs.cz.

3.1.2 Preparation of hydrogel film

The hydrogel film was prepared by solution casting method [18-22] using aqueous solution which is consisted of PVP: 0.2, CMC: 0.8, PEG: 1.0, agar: 2.0, glycerine: 1.0, and water: 95.0 in w/v %. The polymer solution was prepared in sealed glass bottles under physical stimulation of pressure and heat [15 lbs (107 kPa) pressure and 120°C temperature for 20 minutes]. The hot polymer solution (20 ml each) was poured into petridishes (80 mm diameter) and allowed to cool at room temperature (22-25°C). Finally, a round thin film was obtained and termed as PVP-CMC hydrogel film.

3.1.3 Breathability test

Breathability of PVP-CMC hydrogel film was measured by the water vapour permeability test (WVT) [20, 23, 24]. Each aluminium foil dish (internal diameter of 5.5 cm and height 1 cm) was filled with 10 ml of distilled water (100% RH). A circular piece of dry hydrogel film was placed on the dish and sealed with glue. Another circular piece of the same film was fixed on another dish without water as a reference. Both samples and references were accurately weighed and then placed in a desiccator containing calcium chloride ($CaCl_2$) as a desiccant, and filled with silica gel (0% RH). At specific intervals (24, 48, 72 and 96 hours) the dishes were weighed and the profile of mass change was plotted versus time. The experiment was conducted in triplicates. The amounts of water vapour transmission through the films were measured using the following equation 1.

$$WVT = \frac{Wx}{tAP_0(RH_1-RH_2)} \quad (1)$$

In this equation, WVT is the water vapour transmission. W/t is the mass change (flux, g/h) resulted from the slope of profile of the mass change

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versus time; x is the thickness of the film used in the scale of mm. A is the area of the film in the scale of m^2, which is equal to the surface of the dish. P_0 is the vapour pressure of pure water vapour transmission that is equal to 3.159 kPa at 25ºC. (RH_1-RH_2) is the relative humidity gradient of the inside and outside moisture contact of the examined dish.

3.1.4 Assessment of biodegradability

The biodegradability of the PVP-CMC hydrogel films were investigated by soil-burial test. The whole round PVP-CMC hydrogel films (diameter: 80 mm, thickness: 0.12-0.15 mm) were introduced into the controlled compost environment (30ºC, pH 6.0-8.5, and moisture content ~ 60%) [25]. Total time of biodegradation was 5 weeks. The influences of microbial action on the morphology and weight loss were studied weekly.

Hydrogel films interior morphologies (before and after degradation) were evaluated by scanning electron microscopy (SEM) analysis (VEGA II LMU (TESCAN) operating in the high vacuum / secondary electron imaging mode at an accelerating voltage of 5-20 kV).The samples were sputter coated with a thin layer of palladium / gold alloy to improve the surface conductivity and tilted 30° for better observation. The surface views of the hydrogel films were taken at magnification of 100 x – 10 kx.

The weight loss profile of the PVP-CMC hydrogel film was studied until 5 weeks because of two reasons. Firstly, it comes under general methods of determination of polymer biodegradability in solid state. Moreover, it does not demand any special instrumentation [25].

3.2 Results and Discussion

3.2.1 PVP-CMC Hydrogel film

The polymer film is smooth, flexible, and transparent (diameter: 80 mm, thickness: 0.12-0.15 mm). They show high water absorption and water holding property when immersed into water [18, 19], which is the evidence that PVP-CMC is a hydrogel film. An image of PVP-CMC hydrogel film is depicted in Fig. 1.

3.2.2 Breathability

The oxygen diffusion property of polymer film was confirmed by measuring water vapour transmission (WVT) rate and loss of water in time under controlled environment and the results are presented in Fig. 2. It can be seen from Fig. 2 that rate of water vapour permeation was constant for PVP-CMC hydrogel film. It is well known that increasing the hydrophilic nature of a polymer membrane induces water vapour tendency and as a result increases water vapour permeation [20].

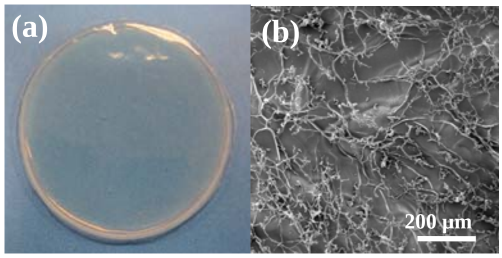

Fig.1: (a) Image of PVP-CMC film in the form of hydrogel, (b) cross-sectional view of freeze dried PVP-CMC hydrogel

The PVP-CMC hydrogel film contains a combination of hydrophilic polymers, i.e. PVP, CMC, PEG and agar which are responsible for high rate of water vapour transmission through the hydrogels. On the other hand, due to the presence of moisture absorbing materials ($CaCl_2$, silica gel) in the desiccators, the water molecules come out of the other side of the film are absorbed by the water absorbing materials. This indicates that the hydrogel films are porous as well as permeable for oxygen.

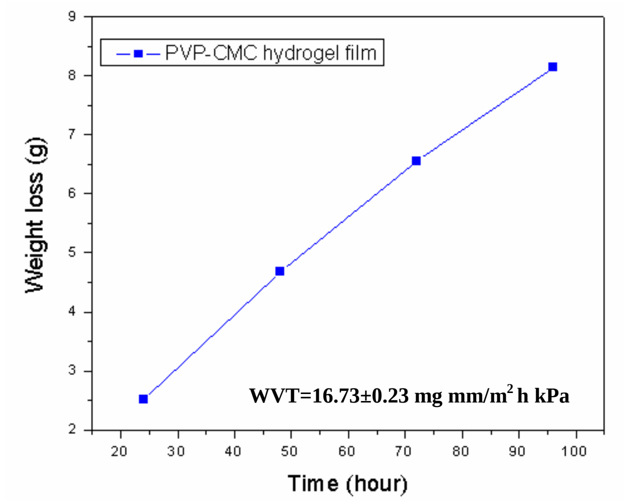

Fig. 2: Profile of water vapour transmission through PVP-CMC hydrogel film

3.2.3 Biodegradability

Biodegradability of the PVP-CMC hydrogel film was studied under composting environment. Fig. 3 (a) shows the image of PVP-CMC hydrogel film before biodegradation. The film is almost transparent, smooth and flexible but non-brittle, which is ideal as a packaging material. Fig. 3 (b) shows the optical view of the compost bed prepared to place the PVP-CMC hydrogel film inside for biodegradation. The composting environment was maintained at 30ºC, having pH 6.0-8.5, and moisture content ~ 60%, which is very favourable for the growth of microorganisms, who play the active role in biodegradation. Fig. 3 (c) displays the residue of a PVP-CMC hydrogel film recovered after four weeks of degradation. After five weeks of biodegradation no recoverable amounts of residues of hydrogel film were remained inside the compost bed, which refers that the whole film was degraded totally after four weeks. Fig. 3 (d) shows the view of the microorganisms present in the compost.

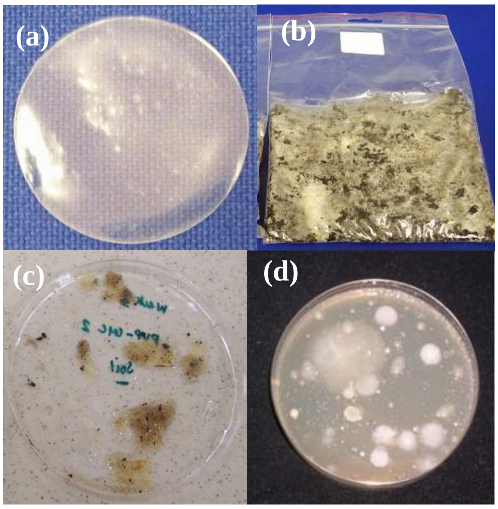

Fig.3: Biodegradability of PVP-CMC hydrogel film (a) hydrogel film before degradation, (b) compost bed where the film was buried for degradation, (c) hydrogel film after biodegradation (after 4 weeks degradation), (d) an image of microbes which are present in compost bed.

The SEM images provide very good evidence in favour of the biodegradation of PVP-CMC hydrogel films. It can be seen from the Fig. 4, before degradation the hydrogel surface was almost smooth and even. After two weeks, irregularities can be observed on the hydrogel film surface, which means that the internal structure of PVP-CMC hydrogel film has started to degrade. After four weeks, hydrogel film surface becomes more irregular, with some depositions (most probably deposition of microorganisms). Thus, the SEM evaluation of the PVP-CMC hydrogel film samples before and after degradation supports that PVP-CMC hydrogel films are biodegradable. Another direct proof for biodegradation is the observation of weight loss with time. It is clear from Fig. 5 that the weight of PVP-CMC hydrogel film was reducing sharply with

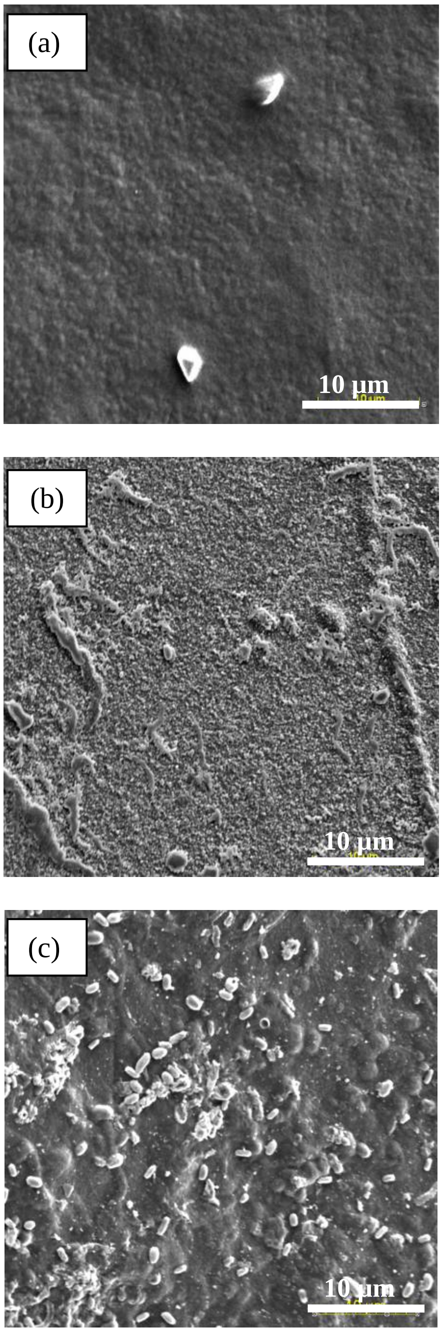

Fig. 4: SEM micrograph of PVP-CMC hydrogel film. (a) Initial and after (b) 2 weeks and (c) 4 weeks of bio-degradation.

time until four weeks, and after that measurement was not possible because the whole hydrogel film was diminished in compost. The major part of PVP-CMC hydrogel film is made of biopolymers like CMC and agar, which may provide some nutrition to the microorganisms to grow. This may lead the degradation process faster. This weight loss profile is direct evidence for biodegradation of PVP-CMC hydrogel film.

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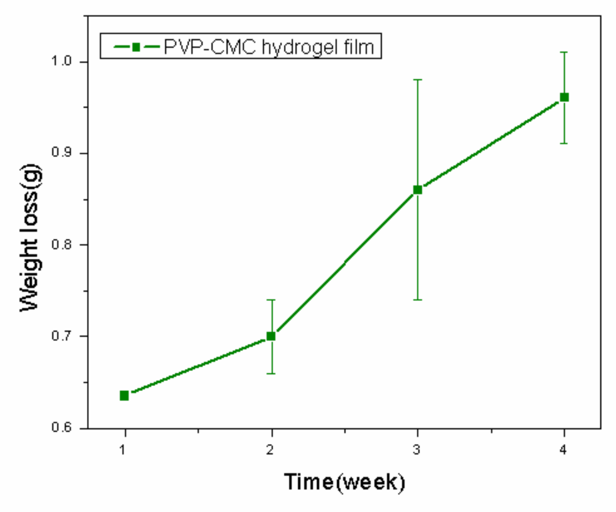

Fig. 5: Weight loss profile of PVP-CMC hydrogel film under compost environment.

4 Conclusion

The results obtained from this research investigation on PVP-CMC hydrogel film successfully prove that the PVP-CMC hydrogel film is breathable and on the other hand completely biodegradable. The film is transparent and flexible too. As a whole this PVP-CMC hydrogel film seems very promising as a food packaging material and to meet up to a certain limit the challenges raised by environmental pollution created by plastic waste materials.

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