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Study on preparation of radiation-crosslinked hydrogel of CMS/PVP/KC/MMT by electron beam irradiation

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Abstract: Hydrogel of carboxymethyl starch (CMS)/polyvinyl pyrrolidone (PVP)/kappa – carrageenan (KC)/montmorillonite (MMT) was prepared by electron beam (EB) crosslinking irradiation on an EB linear accelerator UERL-10-15S2 (10 MeV, 15 kW, Russia). The crosslinking capacity of the resulting hydrogels was determined based on gel content and degree of swelling. The mechanical properties, adhesion force on the PE surface and water vapor transmission rate (WVTR) were measured. The preliminary results suggested that the mixture hydrogels (CMS/PVP/KC/MMT) can be used for personal care applications such as facial mask, moisturizing membrane for skin and so on.

Keyword: *hydrogel, CMS, radiation, crosslinking, EB accelerator.*

I. INTRODUCTION

Nowadays, people's demands of beauty and personal care are ever increasing. The more modern and developed life is, the more necessary demands of cosmetics are. Many developed countries in this field such as the USA, Korea, Japan have done a lots of researches [1,2,3,4] and created many kinds of product in the market. And the products have many different puposes of use such as: facial mask, moisturizing membrane or scream for skin and so on.

Various materials such as gel, hydrgel, nanoparticle have been studied and applied in this field and they should have suitable properties that include aseptic, non – toxic, biodegradable, biocompatible and do not cause skin allergy [5,6]. Radiation crosslinking is the best way for preparing these materials that can be used for the cosmetic field.

This paper reported our results on radiation preparation of the crosslinked hydrogels from carboxymethyl starch (CMS)/polyvinyl pyrrolidone (PVP)/kappa – Carrageenan (KC)/montmorillonite (MMT) by the EB. And there will be first steps for researching on hydrogel which is applied to prepare the moisturizing membrane for the skin care by EB irradiation method.

II. MATERIALS AND METHODS

A. Materials

PVP, BASF Kollidone 90, Mw: 1,000 kDa (Germany); CMS, Emsize CMS 150, M_W = 600 kDa, DS = 0,85, Emsland –Stärke (Germany); kappa – carrageenan, Marcel (Phillippines); Montmorillonite (reinforcing agent), Merk (Germany) and pure water.

B. Methods

Preparation of sample and irradiation

Hydrogel membrane was prepared from: CMS, PVP, KC and distilled water, and the other hydrogel membrane was prepared from:

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CMS, PVP, KC and distilled water with the reinforcing phase MMT. The best formulation was of PVP:CMS:KC:H_2O = 10g:5g:1g:100ml (MT0). The mixture has been homogeneously mixed in the Erlen for 4 hours and kept at the room temperature overnight. Then the mixture was heated to 80°C for 3 hours and kept at 70°C for 1 hour to remove the air – bubbles. The obtained homogenous mixture was put into the PET mould with dimension of 100 mm × 100 mm × 3 mm at 45°C. To prepare reinforced hydrogel membrane (MT2), MMT has been added to the formulation. The PET mould containing hydrogel components were packed in PE plastic bags which were finally irradiated by EB accelerator (UERL – 10 – 15S2, 10 MeV, Russia).

Determination of gel content

The obtained hydrogel sample was dried at 65°C until constant weight. Extraction of the dried sample in the nonwoven PE bag was carried out on a Soxhlet system using water as a solvent in 24 hours. After extraction, the sample is dried until constant weight. Gel content was calculated in the following formula (1):

$$\text{Gel content (\%)} = (m_1/m_0) \times 100 \quad (1)$$

Where m_0 is the dried weight of the initial sample (g) and m_1 is the dried weight of sample after extraction (g).

Analysis of the water swelling degree of hydrogel membrane

Hydrogel membrane sample was put into the pure water in 24 hours at pH = 6 – 7. Before weigh the hydrogel samlple, filter-paper is used to soak the surplus water on its surface. Swelling degree of water was calculated in the following formula (2):

$$\text{Water swelling degree (g/g)} = 100 \times (m_t - m_0)/m_0 \quad (2)$$

Where m_0 is the weight of the sample (g) and m_t is the weight of the sample after swelling (g).

Determination of adhesive properties of hydrogel membrane

Sample with the dimension 150 mm × 20 mm × 3 mm covered and rolled with a force about 5N on the test plate's surface made of nonwoven PE fiber at the room temperature in 3 hours. Adhesive force (F_{ad}), required to remove adhesive coated hydrogel membrane from surface square of PE test plate, was measured by the tensile machine QCTech (Taiwan) at angle of peel of 90° to the direction of plastic surface and peeling speed 50 mm/minute [8,9].

$$F_{ad}\ (\text{N/cm}) = \frac{F}{d} \times 10$$

Where F is the tensile force measured by QCTech machine (N) and d is the thickness of the sample (mm)

Analysis of the water vapor transmission rate (WVTR) of hydrogel membrane

Cylinder vases with 35 mm diameter and 50 mm height containing the same 25ml water volumes were used for analysis of WVTR. The hydrogel membranes with 40 mm diameter and 3 mm thickness were covered on the vases. These blanketed container was kept in the incubator at 35°C [7]. The WVTR was determined by weighing the weight loss of the vase or the water vapor over the period of 24 hours.

$$\text{WVTR (g/m}^2\text{/h)} = \frac{(m_{b0} - m_{b1}) \times 10^6}{A \times 24} \quad (3)$$

Where, m_{b0} is the weight of the vase before incubating (g); m_{b1} is the weight of vase after incubating in 24 hours (g) and A is the square of the vase's surface (mm^2).

III. RESULTS AND DISCUSSION

A. Effect of the absorbed dose on the gel content

As can be seen in the figure 1, the gel content of MT0 and MT2 had the same overall tendency increasing steadily in absorbed dose from 10 kGy to 25 kGy. They were saturated at 20 kGy, at which the gel contents are 67.5% and 65% for MT0 and MT2, respectively. It was observed that gel content of the MT0 sample was higher than that of MT2 in the tested dose range. Assuming that reinforcing phase MMT restrained the activity of free radicals for the crosslinking process, the gel content of reinforced hydrogel sample MT2 decreased. Based on the obtained result and the results reported by other researchers [1,3], the best dose for crosslinking dose to prepare hydrogel membranes is also in range of 20 – 25 kGy.

In hydrophilic polymer, its gel proportion was opposite to its swelling degree of water. So, the swelling degree of MT0 was lower than that of MT2 and both of them decreased over the increasing of absorbed doses. Result is illustrated that their water swelling degree was rather small. After irradiation at 25 kGy, swelling degrees were 4.5 and 5.0 g/g for MT0 and MT2, respectively.

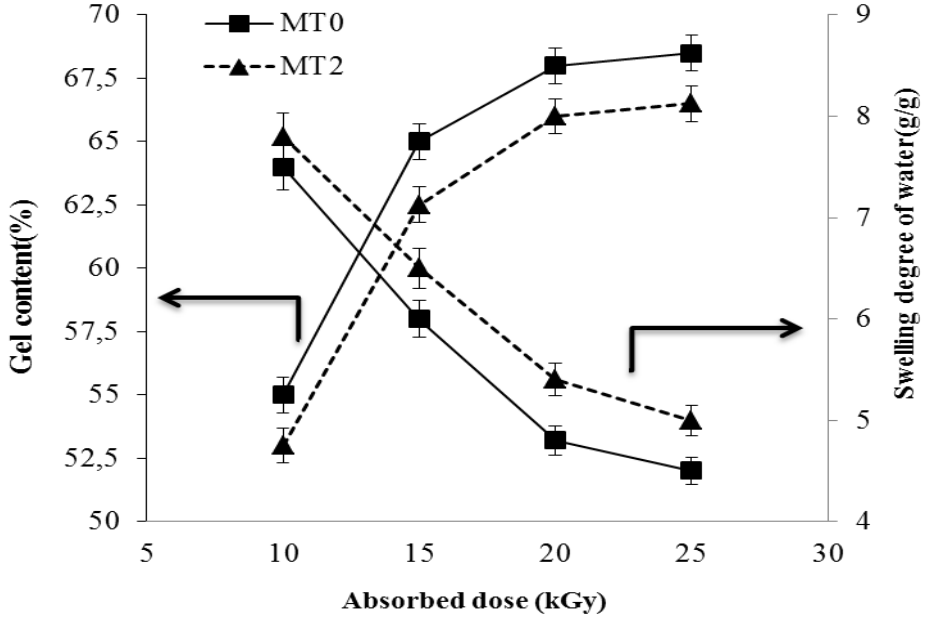

Fig. 1. Effect of the absorbed doses on the gel content and swelling degree of water of hydrogel membranes

B. Effect of absorbed dose on the tensile strength and elongation at break

Results in the figure 2 showed the tensile strength and elongation at break of hydrogel membranes with and without reinforcing MMT substance in the studied dose range of 10 – 25 kGy.

It indicated in figure 2 that tensile strength of samples increased linearly and reached a maximum value at 20 kGy, then decreased at 25 kGy. As was observed that hydrogel membrane with MMT component had better mechanical property than that of MT0 in tested dose range. MMT is a kind of reinforcing agents improving the tensile strength of MT2. For example, tensile strength of MT2 is 0.102 MPa which was higher than that of MT0 (0.095 MPa) at saturated dose of 20kGy.

The elongation at break of MT0 and MT2 decreased dramatically over the studied dose range. In dose range of 10 – 15 kGy, elongation at break of MT0 is higher than that of MT2. It could be argued that MMT component was the main reason causing partial break and reducing MT2 elongation at break. After that, this difference was only in statistical error of calculation at higher doses, in which degree of crosslinking had the main role in decreasing the elongation at break.

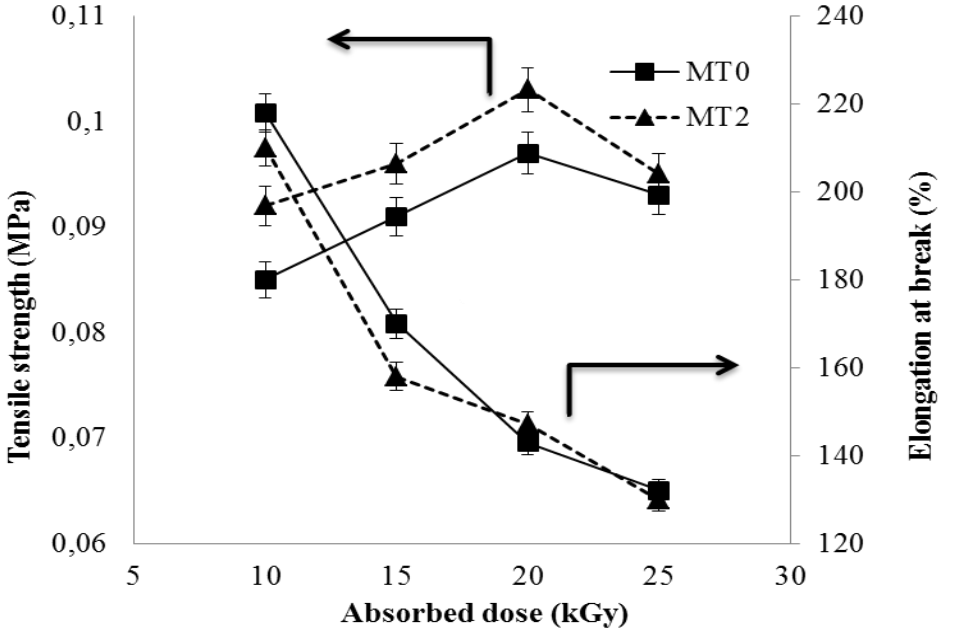

Fig. 2 . Effect of the absorbed doses on the tensile strength and elongation at break of hydrogel membrane

C. Adhesive property

The effect of the absorbed doses on the adhesive property of hydrogel membrane MT0 and MT2 was shown in the figure 3. MT0 and MT2 had the same overall tendency. Their adhesive forces decreased steadily over the dose range of 10 – 22.5 kGy.

At low doses, from 10 to 15 kGy, adhesive force of MT2 was lower than that of MT0. However, this difference was in statistical error of calculation at higher doses from 17.5 to 22.5 kGy. So, the result showed that MMT component did not affect the adhesion property of membrane at this dose range. For example, it was alternately 0.04 N/m and 0.043 N/m for MT0 and MT2, respectively at 20 kGy (see table I). Until now, there was no standard method of estimation in adhesive force of hydrogel membrane applied in skin care.

Table I. Adhesive force of hydrogel membrane with and without the MMT reinforcer at the absorbed dose of 20 kGy

	Adhesive force (N/cm)
MT0	0.042 ± 0.003
MT2	0.046 ± 0.002

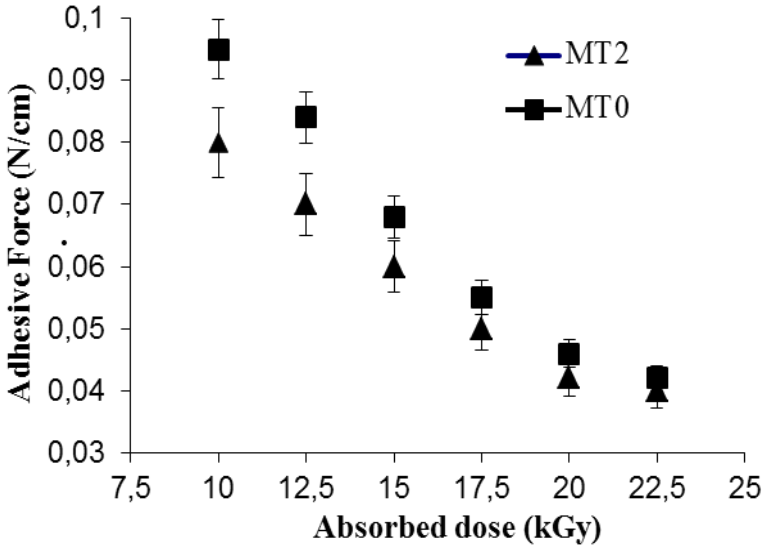

Fig. 3 . Effect of the absorbed doses on the adhesive force of MT0 and MT2 hydrogel membrane

D. Determination of the WTVR

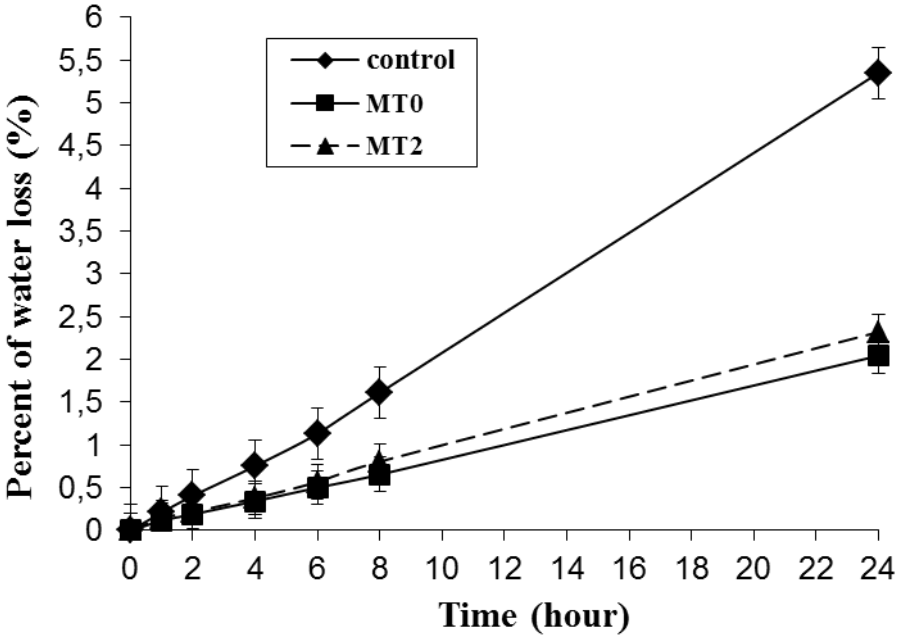

Fig. 4. Percent of water loss versus the vapor time

Results in the figure 4 showed the proportion of water loss in vases covered by the hydrogel membranes irradiated at 20 kGy over the period of 24 hours. The higher percentage of water loss, the lower moisturizing ability is. The control sample is not covered by hydrogel membrane.

As presented in the figure 4, proportion of the water loss increased linearly with the increase of vapor time. The result showed that percentage of water loss of MT0 and MT2 are the same and the MMT reinforce did not affect the moisturizing. From table II, their WVTR had a difference in deviation of calculation and

at low values 23.60% and 24.97% for MT0 and MT2, respectively.

As the result in table II, MT0 and MT2 had moisturizing ability better than Biabrone and Vigilon and same with Viewgel membrane. These products have been commercialized for a long time. So, WVTR of MT0 and MT2 is suitable for preparation of membrane for skin care, especially for dry one.

Table II. WVTR of MT0 and MT2 samples at the absorbed dose of 20 kGy and commercialized kinds of hydrogel membrane

	WVTR (g/m^2/hour)
Control	57.54 ± 4.54
MT0	23.60 ± 3.12
MT2	24.97 ± 4.95
Biabrone [10]	154
Vigilon [11]	139 ± 23
Viewgel (Japan)	18 ± 2.5

II. CONCLUSION

Different crosslinked hydrogel membranes have been prepared from the mixture of PVP/CMS/KC with the ratio of 10g/5g/1g in 100 ml water by EB irradiation in the dose range from 10 to 25 kGy. MMT content 50 – 100 mg has been added in order to prepare reinforcing hydrogel with better machenical properties. The result suggested that the obtained hydrogels with rather good mechanical properties, swelling degree and WVTR, which are suitable for preparing the moisturizing membrane for the skin care.

However, at high dose rate during EB irradiation, bubbles may be produced in the hydrogels. Then further study should be done for improving the appearance property of the radiation crosslinked CMS mixture hydrogels in cosmetic field.

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