

Structure-Property and Swelling Behavior of Electron Beam Irradiated Poly(vinyl alcohol)/Acrylamide/Sodium Montmorillonite Clay Composites

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ABSTRACT: Composites based on poly(vinyl alcohol) (PVA), acrylamide monomer (AM) and sodium montmorillonite clay (MMT) were prepared, in the form of thin films, by solution casting. The PVA/AM/MMT composites films were then exposed to electron beam irradiation to form crosslinked network structure. The structure-property behavior of PVA/AM/MMT hybrids was demonstrated by x-ray diffraction (XRD), scanning electron microscopy, gel content, color intensity, thermogravimetric analysis (TGA) and swelling behavior in aqueous solutions. The results indicated that the introduction of MMT clay ratio up to 5% decreased the gel content of PVA/AM hydrogels. The color measurements indicated that the introduction of MMT clay

ratio up to 5% was shown to affect the color intensity of composite films. It was found that both PVA/AM hydrogels and PVA/AM/MMT composites reached the equilibrium swelling state in water after four hours; however PVA/AM/MMT composites displayed higher swelling than PVA/AM hydrogels. However, the swelling of PVA/AM hydrogels or their composites at the equilibrium state increased with increasing temperature up to 60°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2634–2643, 2011

Key words: electron beam irradiation; composites; poly(vinyl alcohol); acrylamide; sodium montmorillonite clay; swelling

INTRODUCTION

Hydrogels are hydrophilic three-dimensional cross-linked polymeric structures, which are capable of swelling and absorbing large amounts of water or biological fluids allowing a wide usage in medical applications and the removal of toxic pollutants from wastewater.^{1–6}

The naturally occurring sodium montmorillonite clay (MMT), general formula: $(\text{Na,Ca})_{0.3}(\text{Al},\text{g})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2\text{nH}_2\text{O}$, is a favorite filler for a wide range of polymer composites.⁷ MMT have ability to exchange ions and this process is used for structure modification necessary to mixing with hydrophobic polymers. MMT exhibits tendency to agglomeration, thus, in some polymeric matrices it forms microcomposites with larger particles. Polymer/MMT clay composites have been reported to exhibit unique properties and lead to environmentally friendly and inexpensive composites. The synthesis and charac-

terization of polymer composites with the inorganic Na-MMT clay have been the topic of many research works in recent years.^{8–14} The dispersion of the clay within the polymer has significant influence on the properties of the material because of the hydrophilicity of clays, which hinders the formation of homogeneous dispersion in organic polymers. Nanocomposite hydrogels were prepared by crosslinking of aqueous solutions of sulfonated polyacrylamide/sodium montmorillonite with chromium triacetate.¹⁵ The gelation process and effects of clay content and ionic strength on swelling behavior were investigated. X-ray diffraction patterns indicated that exfoliated type of microstructure was formed. Polyacrylate intercalated bentonite superabsorbent hybrid was prepared by solution polymerization with intercalating, polymerizing and crosslinking reaction.¹⁶ The partially neutralized acrylic acid (NaA) was intercalated, polymerized and crosslinked to bentonite. The initiator was potassium persulfate and the crosslinking agent was sugar. The optimum conditions showed that the ratio (wt) of bentonite to monomer was 1/2, the degree of neutralization was 75% (mol), the initiator content was 3%, and the crosslinker content was 5%. The cost of the superabsorbent has decreased by 30%, whereas its water absorbency was about 120 g/g for water, and 30–

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36 g/g for saline solution. Poly(vinyl alcohol), PVA, microcomposites with montmorillonite, MMT, were prepared by their mixing in aqueous colloidal solution. Thin films of composites obtained by solvent evaporation were exposed to 254-nm radiation.⁷ The course of photochemical reactions leading to various products was monitored by FTIR and UV-vis spectroscopy. The chain scission reaction was confirmed by measurement of average molecular weights and polydispersity using gel permeation chromatography (GPC) method. The crosslinking was minor process whereas oxidation and degradation appeared more efficient in exposed PVA/MMT. It was found that the presence of clay filler (MMT) has slight influence on PVA photooxidative degradation. A series of superabsorbent composites were synthesized by copolymerization reaction of partially neutralized acrylic acid on unexpanded vermiculite (UVMT) micro powder using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and ammonium persulfate (APS) as an initiator in aqueous solution.¹⁷ The samples were characterized by Fourier-transform spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The effects of vermiculite content on water absorbency were studied. Swelling behaviors of the superabsorbent composites in various cationic salt solutions (NaCl, CaCl₂, and FeCl₃), anionic salt solutions (NaCl, Na₂SO₄, and Na₃PO₄) and pH solutions were also investigated. It was showed that the equilibrium water absorbency increased with increasing UVMT content and the concentration of 20 wt % clay gave the best absorption (1232 g/g in distilled water and 89 g/g in 0.9 wt% NaCl). Data achieved also suggested that the water absorbency in various saline solutions decreased with an increase in the ionic strengths of these solutions. It was found that at a higher ionic strength ($>1 \times 10^{-3}$ M), the water absorbency in monovalent cationic solutions was higher than those in multivalent cationic solutions. However, at the same ionic strength ($>1 \times 10^{-3}$ M), the effect of three anionic salt solutions on the swelling has the following order: NaCl < Na₂SO₄ < Na₃PO₄. A series of composite and nanocomposite hydrogels were also synthesized by copolymerization reaction of partially neutralized acrylic acid (SA) on bentonite micropowder (BT) using *N,N'*-methylenebisacrylamide (MBA) as a crosslinker and potassium persulfate as an initiator in aqueous solution.¹⁸ The influences of Na⁺-BT, organoBT (O-BT), and the content of the BT in the copolymeric gels on the swelling behavior in deionized water and saline solution [0.2 wt % NaCl(aq)] were investigated. Results showed that the equilibrium swelling was decreased by adding a small amount of the BT; however, at higher BT contents,

the W1 increased with the increase of the amount of clay. It was found that a concentration of 14 wt % Na⁺-BT gave the best results absorption (955 g/g). The thermogravimetric analysis indicated that introduction of clay to the polymer network resulted in an increase in thermal stability.

As can be seen above, the synthesis of the majority of polymer/clay composites was based on chemical initiation. The radiation synthesis of hydrogels has special technical advantages; not only is the interaction between chains through covalent bonds but also it will solve the problem of sterilization, in which it allows the fabrication of noncontaminated products.^{19–25} In this work, electron beam irradiation was used to form hydrophilic composites based on poly(vinyl alcohol)/acrylamide/montmorillonite clay (PVA/AM/MMT) mixtures. The structure of the PVA/AM/MMT hybrids was determined by x-ray diffraction (XRD) and characterized in terms of gel fraction, thermal stability and swelling characters in different conditions.

EXPERIMENTAL

Materials

Sodium montmorillonite clay (Na-MMT) was collected from the Nile river banks; its cation exchange capacity is 74.6 mequiv/100 g. Poly(vinyl alcohol) (PVA) used in this study is a laboratory grade powder, 1.700 MW, purchased from Osaka, Japan. The acrylamide monomer (AM) was purchased from BDH Chemicals Company, England.

Preparation of PVA/AM/MMT composites

Sodium montmorillonite clay (MMT) was first purified by repeated cycles and filtration. The suspension was sonicated in ultrasonic bath for 60 min, allowed to stand over night, filtrated, and left to dry in vacuum oven. The PVA and AM were dissolved in distilled water at 80°C and 60°C, respectively. The polymer blend solutions and MMT clay were mixed with continuous stirring for 15 min, then poured into glass dishes and exposed to different doses of electron beam irradiation to obtain crosslinked films. Electron beam irradiation was carried out on the electron accelerator (1.5 Mev and 37.5 kW) facility of the National Center for Radiation Research and Technology.

Gel content determination

Sample of the prepared hydrogels films were accurately weighed (W_0) and then extracted with distilled water using Soxhlet system for 6 h. After extraction, the samples were removed and dried in vacuum

TABLE I
Gel Content of Hydrogels Based on PVA and Different Ratios of PVA/AM and PVA/AM/MMT Composites with Different Ratios of MMT Clay Prepared at Different Doses of Electron Beam Irradiation

EB dose (kGy)	Gel content (%)								
	PVA (100%)	PVA/AM (90/10%)				PVA/AM (80/20%)			
		Pure	MMT (1%)	MMT (3 %)	MMT (5 %)	Pure	MMT (1%)	MMT (3 %)	MMT (5 %)
20	85.0	93.0	75.0	80.0	60.0	95.0	80.0	70.0	66.0
30	87.0	95.0	77.0	65.0	63.0	98.0	85.0	77.0	74.0
40	90.0	99.0	80.0	66.0	65.0	100.0	90.0	85.0	80.0

oven at 50°C to constant weight (W_1). The gel content was calculated according to the following equation:

$$\text{Gel content (\%)} = (W_1/W_0) \times 100$$

Color intensity measurements

A computerized micro-colorimeter unit made by Dr. Bruno Lange, GmbH, Königsweg 10, D-1000, Berlin, Germany, was used for color measurements. The L^* , a^* , and b^* system used is based on the CIE-color Tri angle (Commission International De' Clair units X , Y , and Z). In this system, the L^* value represents the dark-white axis, a^* represents the green-red axes, and b^* represents the blue-yellow axes. The intercept L^* in which the integers zero and 100 represent the standard dark and white color, respectively. The positive value of a^* and b^* represent the red and yellow color components, while the negative value of a^* and b^* represent the green and blue color component, respectively. The L^* , a^* , and b^* value of pure PVA film was first measured and taken as reference. The color intensity (ΔE^*) of the different samples was determined according to Judd-Hunter standardization, 1976 as follows:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

X-ray diffraction analysis

X-ray diffraction (XRD) experiment of the samples was performed at room temperature by a Philips PW 1390 diffractometer (30 kV, 10 mA) with copper target irradiation at a scanning rate of 8°/min in a 2θ range of 4–90°.

Scanning electron microscopy

The morphology of the fracture surfaces of the PVA/AM/MMT composites was examined by scanning electron microscopy (SEM). The SEM micrographs were taken with a JSM-5400 instrument (Joel, Japan). A sputter coater was used to precoat conduc-

tive gold onto the fracture surfaces before observing the microstructure at 30 kV.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) studies were carried out on a shimadzu-50 instrument (Japan) at heating rate of 10°C min⁻¹ under flowing nitrogen of 20 mL min⁻¹ over a temperatures range from room temperature up to 600°C.

Swelling measurements

Swelling was determined gravimetrically, in which a known dry weight of the different materials (W_0) was immersed in distilled water for different time intervals up to 24 h at room temperature. The samples were removed at each time and blotted on filter paper to remove the excess water on the surface and weighed (W_2). The percentage swelling was calculated according to the following equation:

$$\text{Swelling (\%)} = [(W_2 - W_0)/W_0] \times 100$$

The hydrogels or composites in the equilibrium state (W_E) were immersed in water at different temperatures (10–60°C) and then weighed (W_T). The swelling was calculated as follows:

$$\text{Swelling (\%)} = [(W_T - W_E)/W_E] \times 100$$

RESULTS AND DISCUSSION

Effect of MMT ratio on gel content

The effect of MMT ratio and electron beam irradiation dose on the gel content of hydrogels based on pure PVA and PVA/AM of different ratios as well as PVA/AM/MMT composites is shown in Table I. It can be seen that the gel content of PVA hydrogel was greatly increased by increasing the ratio of AM up to 20% and irradiation dose up to 40 kGy. This can be explained on the basis that AM monomer undergoes crosslinking higher by electron beam

irradiation higher than PVA and that the increase of irradiation dose is associated with increasing the number of free radicals in the system. It is also clear that the gel content of all the PVA/AM/MMT composites was decreased with increasing the ratio of MMT clay, regardless of AM ratio and irradiation dose. However, the higher the ratio of AM in the initial composition, the lower is the decrease in gel content. The decrease in gel content observed by increasing the MMT ratio is due the blocking of limited number of active sites by MMT particles and thus led to a decrease in gel content.

The mechanism of crosslinking of the PVA polymer and AM monomer in dry state by electron beam irradiation may be briefly outlined as follows:

1. The polymer or monomer (M-H) absorb radiation and go to the transient activated states MH^* .
2. The concentration of radicals increase and the transfer of radicals from adjacent carbon atoms also increase and thus the rate of crosslinking and gelation increases, in which two polymer radicals PM^* with m and n repeat units combine to form a crosslinked point:



Effect of MMT ratio on color intensity

PVA polymer and AM monomer are water soluble, having the minimum functional groups required to achieve miscibility and competition of hydrogen bonding. The water solubility of the two materials would eventually facilitate mixing and processing of a wide range of hydrogel compositions. Visual observation showed that all the solutions of PVA/AM mixtures were clear at room temperature and highly stable, neither macroscopic phase separation nor appearance of precipitates were being observed. The films of PVA/AM at different compositions appeared also transparent to visual examination. The effect of MMT clay ratio on the color properties was examined by a method based on the measurement of analyzed reflected beam of light to different color parameters after passing through the hydrogels or composites films as shown in Figure 1. It should be noted that a white opaque material was placed under the films to be measured and that the measured films were of constant weight. As shown, the L^* values indicate that the films of PVA/AM hydrogels are transparent, however the increase of AM ratio causes a slight change in the transparency in the PVA/AM hydrogel films. The proportions of the red color component (a^*) and blue color component

(b^*) is also high, in accordance with the values of the L^* intercept. On the other hand, the whiteness (L^*) and blue (b^*) color proportions were found to decrease systematically with increasing the MMT ratio in the hydrogel composition. In the same time the red (a^*) and color intensity (ΔE^*) proportions were found to increase with increasing the MMT ratio in the hydrogel composition. In this regard, the increase in color intensity (ΔE^*) of the films of PVA/AM hydrogels containing 10 and 20% AM was increased by 214 and 425% upon the introduction of 3% MMT clay, respectively. The redness (a^*) of the same order of materials was increased by 186 and 175% by introducing 3% MMT clay, respectively. On the basis of these findings, it may be concluded that PVA/AM hydrogels are miscible at any composition and the introduction of MMT clay affects the color properties to large extents. This is possibly due to intercalated polymers with MMT clay.

Effect of MMT ratio on X-ray diffraction patterns

X-ray diffraction is a powerful tool for examining the crystalline structure of polymer composites, in which it gives valuable information about the changes of structure, intensity and width of polymer crystals. Figures 2-4 show the XRD patterns of the hydrogels based on pure PVA and PVA/AM of different ratios as well as their composites with different ratios of MMT clay, prepared at a dose of 20 kGy of electron beam irradiation (as examples). However, the XRD parameters of the different PVA/AM composites prepared at 20 and 40 kGy are summarized in Table II.

On the basis of the XRD study, few points may be addressed:

1. For pure MMT clay, XRD reports the spacing between ordered layers of the d_{001} or basal spacing, in which water expanded sodium clay normally exhibits a peak associated with a spacing of 12.5 Å, in accordance of the data on Table II. The absence of this basal peak is commonly taken as evidence for a high dispersion of clay platelets, whereas a peak associated with higher spacing would indicate intercalated nanocomposites.
2. The position of the XRD peak was affected by increasing the AM ratio from 10 to 20% in the initial hydrogel composition, in which 2θ was increases from 19.000 to 19.548 Å; however, a decrease can be observed in the intensity and distance between layers.
3. The increase of MMT ratio and irradiation dose were associated with an increase in the value

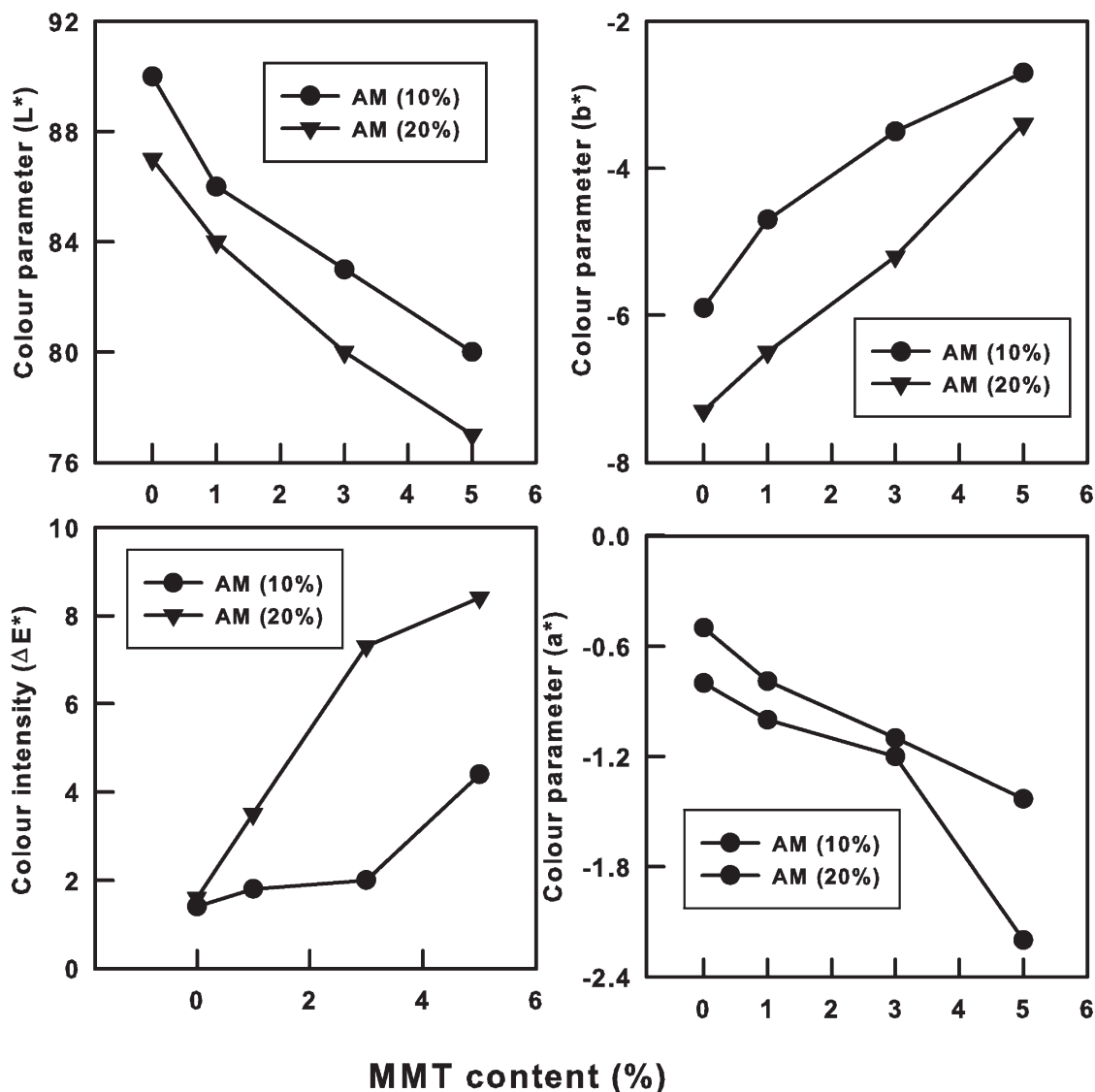


Figure 1 Effect of MMT clay ratio on color parameters of thin films of PVA/AM composites of different ratios, prepared at the dose 40 kGy of electron beam irradiation.

of 2θ and a decrease in the XRD peaks intensity due to the decrease in crosslinking density (gel content) by the introduction of MMT clay in the network structure.

Effect of MMT on morphology

The strength of interfacial interactions between the polymer matrix and layered clay were investigated by examining the fracture surfaces by scanning electron microscopy (SEM) as shown in Figure 5. The SEM micrograph of pure PVA/AM hydrogel is characterized with smooth surface. On the other hand, the SEM micrographs of PVA/AM/MMT composites showed a different morphology, in which the surface is affected by the intercalation with the MMT clay. It is characterized by the hybrid struc-

ture, which appeared as separated parallel layers of $\sim 4 \mu\text{m}$ apart particularly in the case of the microcomposites with 5% MMT. This layered structure was not clear in case of the composites with low MMT of 1%, in which the fracture surface showed that MMT is highly dispersed indicating the occurrence of intercalation and exfoliation in accordance with XRD analysis and color measurements.

Effect of MMT ratio on thermal stability

Thermal stability may represent an important property in polymer/layered silicate composites. It is generally accepted that the improvement in thermal stability is related to barrier properties and the radical-trapping effect of clay platelets. Theoretically, thermal dissociation of any polymeric material is largely determined by the strength of the covalent

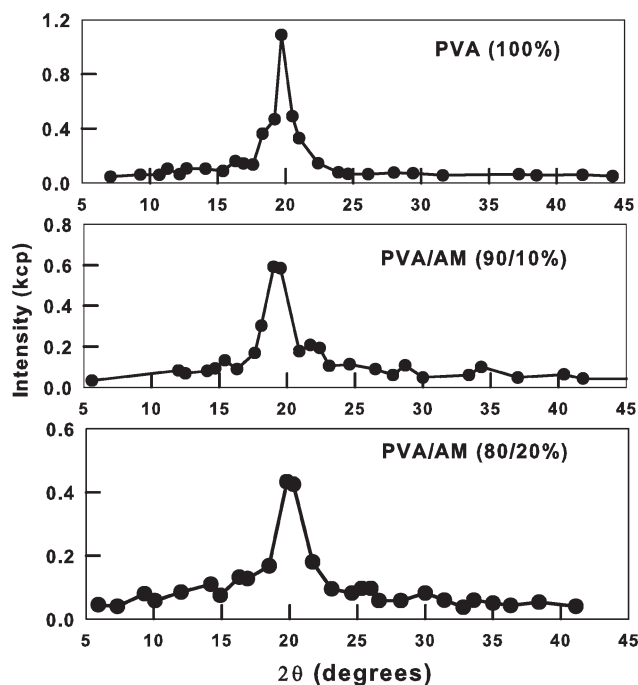


Figure 2 XRD patterns of hydrogels based on pure PVA and different ratios of PVA/AM, prepared at a dose of 20 kGy of electron beam irradiation.

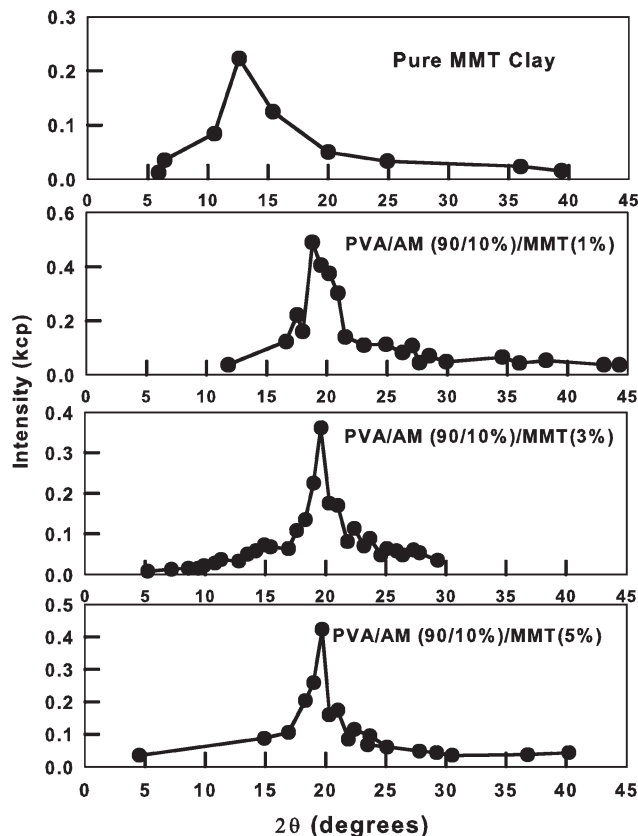


Figure 3 XRD patterns of pure MMT clay and the hydrogels based on PVA/AM (90/10%) with different ratios of MMT clay, prepared at a dose of 20 kGy of electron beam irradiation.

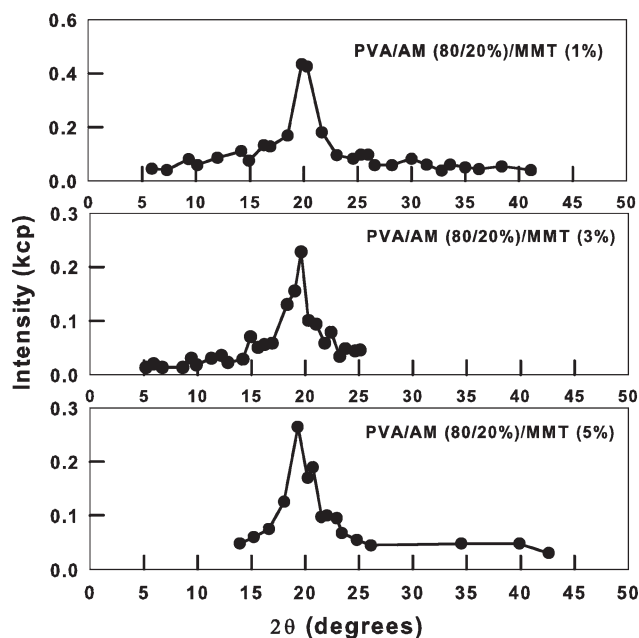


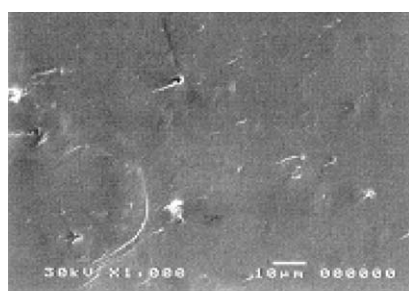
Figure 4 XRD patterns of the hydrogels based on PVA/AM (80/20%) with different ratios of MMT clay, prepared at a dose of 20 kGy of electron beam irradiation.

bonds between the atoms forming the polymer molecules. The dissociation energies of the covalent bonds C–H, C–C, C=O, C–O, and O–H were reported to be 414, 347, 741, 351, and 464 kJ/mol.²⁶ According to these values, the average complete dissociation energy for poly(vinyl alcohol) and polyacrylamide was calculated to be 416.1 and 440.6 kJ/mol, respectively. Thus, it may expect that the copolymerization of PVA and AM will eventually results in hydrogels with higher thermal stability than pure PVA.

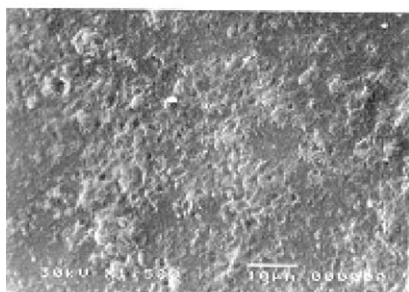
Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of the hydrogels based on pure PVA and PVA/AM as well as the composites with MMT clay. The initial TGA thermograms for all the hydrogels and composites were collected (not shown) and the corresponding rate of thermal decomposition reaction curves were plotted against temperature as shown in Figure 6. The different thermal kinetic parameters for all composites are shown in Table III. It can be seen that the rate of thermal decomposition reaction curves displayed similar trends; however, the different kinetic parameters (T_{onset} , T_{endset} , and T_{peak} temperatures) differ from one material to another. The temperatures at which the maximum values of the rate of reaction (T_{peak}) indicate the single stage of thermal decomposition and the nonexistence of phase separation between the different components forming the composites. Meanwhile, it was observed that there is a T_{peak} in all the curves before 200°C (not shown), which is assigned to the evaporation of

TABLE II
Summary of XRD Patterns of PVA/AM/MMT Composites Prepared at Different Doses of Electron Beam Irradiation

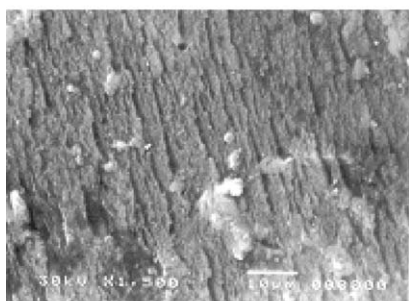
PVA/AM/MMT composites	EB dose (kGy)	2 θ (degrees)	D (\AA)	Intensity (kcp)
Pure MMT clay	0	12.600	13.6733	0.223
Pure PVA (100%)	20	19.718	4.4986	1.090
	40	19.718	4.4986	0.315
Pure PVA/AM (90/10%)	20	19.000	4.6578	0.592
	40	14.618	6.0545	0.068
90/10%/MMT (1%)	20	18.868	4.6993	0.490
	40	14.958	5.9177	0.050
90/10%/MMT (3%)	20	19.685	4.5061	0.362
	40	13.089	6.7586	0.050
90/10%/MMT (5%)	20	19.718	4.4986	0.423
	40	19.700	2.1584	0.423
Pure PVA/AM (80/20%)	20	19.548	4.5374	0.722
	40	19.100	4.1000	0.095
80/20%/MMT (1%)	20	19.888	4.4606	0.433
	40	19.600	0.0650	0.095
80/20%/MMT (3%)	20	19.685	4.5061	0.228
	40	13.1000	0.0350	0.098
80/20%/MMT (5%)	20	19.378	4.5768	0.265
	40	20.298	4.3502	0.068



(A)



(B)



(C)

Figure 5 SEM micrographs of : (A) Pure PVA/AM (80/20%) hydrogel, (B) PVA/AM (80/20%) composite with 1% MMT and (C) PVA/AM (80/20%) composite with 5% MMT.

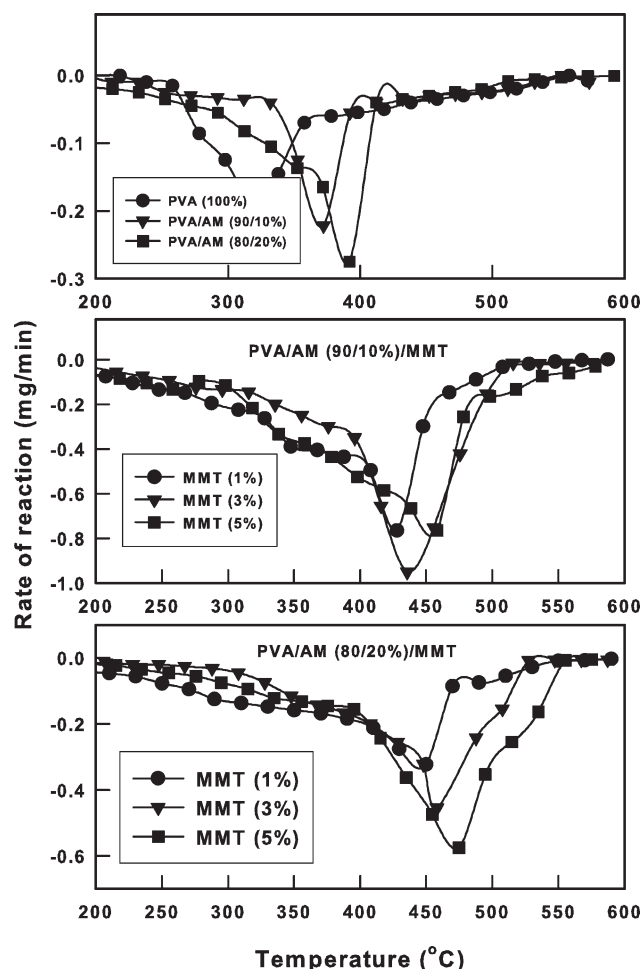


Figure 6 Rate of thermal decomposition reaction curves of PVA/AM/MMT composites prepared at the dose 40 kGy of electron beam irradiation.

TABLE III
Thermal Decomposition Parameters of PVA/AM/MMT
Composites, Prepared at a Dose of 40 kGy of Electron
Beam Irradiation

PVA/AM/MMT composites	T_{onset}	T_{peak}	T_{endset}
PVA (100%)	255	320	357
PVA/AM (90/10%)	316	370	395
PVA/AM (80/20%)	207	390	418
PVA/AM (90/10%)/MMT (1%)	379	427	457
PVA/AM (90/10%)/MMT (3%)	381	436	513
PVA/AM (90/10%)/MMT (5%)	386	452	484
PVA/AM (80/20%)/MMT (1%)	370	444	483
PVA/AM (80/20%)/MMT (3%)	432	457	510
PVA/AM (80/20%)/MMT (5%)	365	471	523

the combined water molecules from the composites. However, the main T peak is probably to the thermal decomposition of the respective composites. It can be seen that the values of T_{peak} , T_{onset} , and T_{endset} are in accordance with the theoretical calculations based on the average complete dissociation energies. The values of different thermal kinetic parameters clearly indicated that the thermal stability of PVA/AM copolymer hydrogels was greatly increased with increasing the ratio of AM and MMT in the initial compositions of preparation.

This is additional evidence that the Na-MMT layers were exfoliated and dispersed in the polymer matrix, although with different grade of dispersion. The improvement of thermal stability can be attributed to the barrier effect of Na-MMT. Na-MMT is a layered structure and small molecules generated

during thermal decomposition process cannot permeate, and thus have to bypass, Na-MMT layers.^{18,27}

Effect of MMT ratio on equilibrium swelling

Figure 7 shows the swelling kinetics in water at 25°C for the hydrogels based on pure PVA and PVA/AM of different ratios; prepared by electron beam irradiated at different doses. It can be seen that the degree of swelling of all the hydrogels was progressively increased within the initial time of swelling up to four hours and then tends to level off. The swelling of PVA/AM hydrogels displayed a systematic trend in accordance with composition, in which swelling increases with increasing the ratio of AM monomer in the initial solutions. In addition, it can be seen that the PVA/AM hydrogels displayed higher degree of swelling than the hydrogel based on pure PVA. However, the swelling content decreases with increasing electron beam irradiation dose. This higher swelling of PVA/AM hydrogels than pure PVA hydrogel may be attributed to the higher hydrophilic character of PAM than PVA. The lower swelling associated with increasing irradiation dose is attributed to the increase of crosslinking density, in which the chains are compact and thus blocks the voids for the diffusion of water molecules.

It was shown that the nonuniform distribution of the electric potential inside inhomogeneous polyelectrolyte gels leads to effective traps for the counter ions.²⁸ The trapped counter ions become osmotically passive and they do not contribute to the osmotic pressure, which is the main cause of gel swelling. In our case, inhomogeneity of charge and potential distribution comes from the anionic plates of the clay inside the gel. Most of the clay counter ions remain mainly in the local volume around the clay particles or between the plates and do not contribute strongly to the total osmotic pressure inside the gel. Thus, counter ions of Na⁺-MMT, contrary to that of the PVA/AM chains, do not contribute significantly to gel swelling. Then the amount of hydrophilic groups in the network decrease with the increase of Na⁺-MMT content, which causes the decrease of osmotic pressure difference between the polymeric network and the external solution, and then the shrinkage of the gel, occurs.

Figures 8 and 9 show the swelling kinetics in water at 25°C for the hydrogels based on PVA/AM of different ratios modified with different ratios of MMT clay; prepared by electron beam irradiated at different doses. It can be seen that the swelling content of all the PVA/AM/MMT composites increases progressively within the initial time of swelling up to four hours and then tends to level off up to the equilibrium state. However, the swelling content

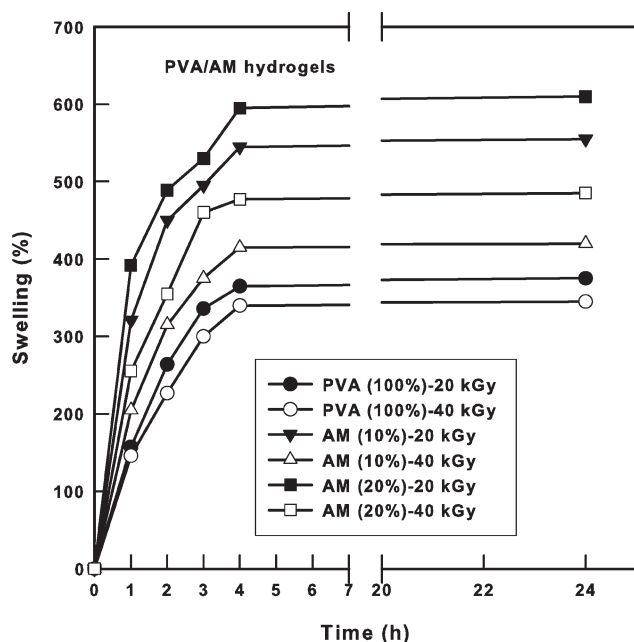


Figure 7 Swelling kinetics in water at 25°C (pH = 7) for hydrogels based on PVA (100%) and PVA/AM of different ratios, prepared by electron beam irradiation at different doses.

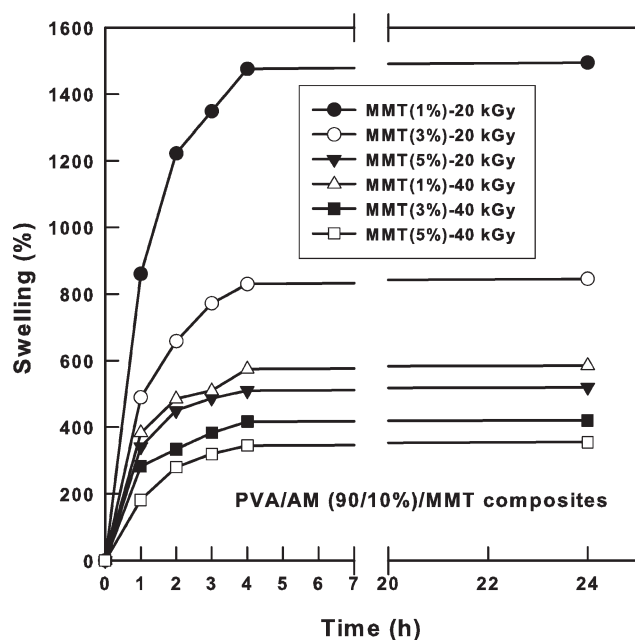


Figure 8 Swelling kinetics in water at 25°C (pH = 7) for hydrogels based on PVA/AM (90/10%) with different ratios of MMT clay, prepared by electron beam irradiation at different doses.

decreases with increasing MMT ratio, regardless of PVA/AM composition due to blocking the voids acceptable for water molecules by MMT clay particles. On the other hand, the swelling content of PVA/AM/MMT composites with higher AM ratio displayed higher swelling content than those with lower ratio of AM.

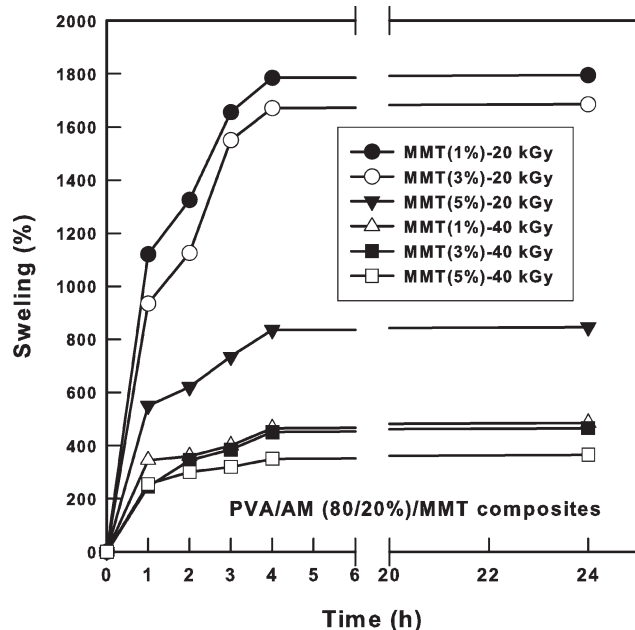


Figure 9 Swelling kinetics in water at 25°C (pH = 7) for hydrogels based on PVA/AM (80/20%) with different contents of MMT clay, prepared by electron beam irradiation at different doses.

Effect of temperature on equilibrium swelling

Figure 10 shows the effect of temperature on equilibrium swelling of PVA, PVA/AM hydrogels, and PVA/AM/MMT composites as a function of time. It can be seen that the ES of all the composites increases with increasing temperature up to 60°C, regardless of composition. However, the ES was found to increase by using 1% MMT and then tends to progressively decrease by increasing the MMT clay content up to 5%. On the other hand, the ES of the hydrogels PVA/AM displayed the highest change in ES with temperature. This change in the ES was found to increase with increasing the ratio of AM in the initial composition. The increase of the degree of swelling with increasing temperature may be explained as follows. At higher temperatures, the voids of the compact structure of composites were increased causes an increase in the mobility of chains and hence facilitate the diffusion of water molecules from the surroundings.

CONCLUSIONS

In this article, superabsorbent crosslinked hybrid composites was prepared by electron beam

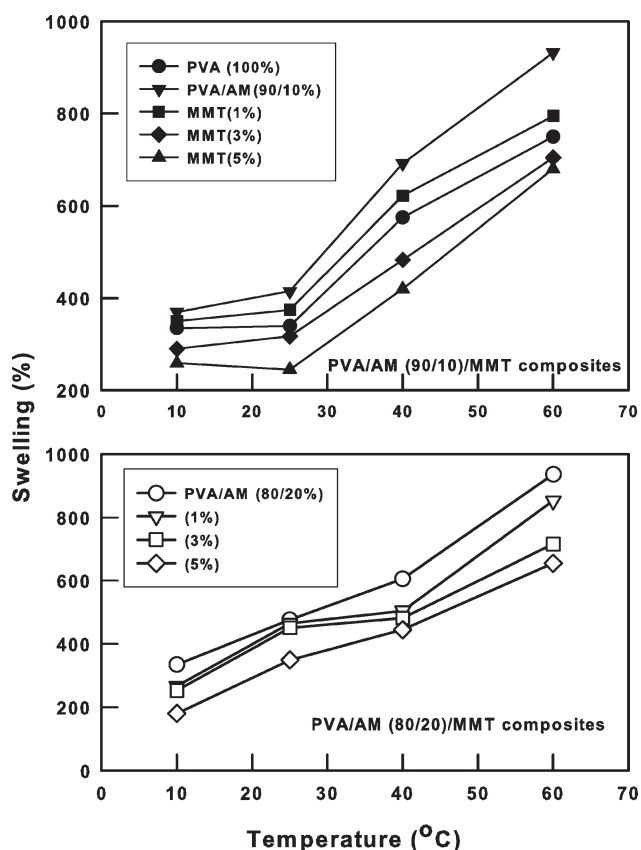


Figure 10 Effect of temperature on equilibrium swelling in water at (pH = 7) for hydrogels based on pure PVA and different ratios of PVA/AM with different ratios of MMT clay, prepared by electron beam irradiation at a dose of 40 kGy.

crosslinking of poly(vinyl alcohol)/acrylamide in the presence of montmorillonite (MMT) clay. Although the MMT clay appeared homogeneously dispersed in the solution casted films by visual observation, the color measurements indicated that the color of the transparent films of pure PVA/AM hydrogels was changed. Based on the results obtained through this work, it may be concluded that there are three factors affecting the structure-property behavior of the formed PVA/AM/MMT composites. These factors were electron beam irradiation dose, AM ratio and MMT content. While, the increase of AM ratio in the initial composition from 10 to 20% was associated with an increase in the gel content and swelling percentage, the increase of dose from 20 to 40 kGy caused a drop in the swelling, regardless of hydrogel composition. The introduction of 1% of MMT clay, on the other hand, improved the swelling; however, relatively higher ratios up to 5% caused a great decrease in the swelling percentage. The thermogravimetric analysis (TGA) indicated that introduction of MMT clay to the hydrogel network caused an increase in thermal stability. Moreover, the thermal stability of the PVA/AM/MMT composites was found to increase with increasing the ratio of MMT clay. This is probably due to the crosslinking of both PVA and AM and the homogeneously dispersed of the MMT inorganic species in hydrogel matrix.

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