Characterization, Mechanical, and Thermal Properties of Gamma Irradiated Starch Films Reinforced with Mineral Clay

Sayeda M. Ibrahim

Department of Radiation Chemistry, National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt

Received 12 February 2010; accepted 2 May 2010
DOI 10.1002/app.32732
Published online 27 July 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Composite fabricated from starch and different concentrations of clay was prepared by solution casting method. The casted film was irradiated to different gamma irradiation doses 10, 20, 30, and 40 kGy. The dispersion of clay into starch was investigated by using X-ray diffraction (XRD). The structural morphology of the composite was measured by scanning electron microscope and infrared spectroscopy. Film properties, such as water vapor transmission, mechanical, and thermal properties were also measured. The gel content and swelling behavior of the starch/clay composite were investigated. It was found that the gel content increases with increasing clay content and irradiation dose. The results obtained indicate that the starch/clay composite showed an increase in the tensile strength, thermal stability. Moreover, there is a decrease in water vapor transmission (WVRT) which improves its barrier properties. Both XRD and infrared spectroscopy showed that starch can be intercalated into the clay galleries. Also antibiotic drug Chlortetracycline HCl was loaded into the starch/clay composite by direct adsorption method. Chlortetracycline HCl adsorption capacity of composite was found to increase from 1.13 to 4.20 mg Chlortetracycline HCl per gram dry film with increasing amount of drug concentration. In vitro drug release studies in different buffer solutions showed that the basic parameters affecting the drug release behavior of the film are pH of the solution, drug concentration, and time. J Appl Polym Sci 119: 685–692, 2011

Key words: starch; clay; gamma radiation; nanocomposite

INTRODUCTION

In recent years, polymer/clay nanocomposites have received considerable attention because they combine the structure, physical, and chemical properties of both inorganic and organic materials. Compared to the pure polymers these nanocomposite demonstrate excellent properties, such as improved storage modulus, decreased thermal expansion coefficients, reduced gas permeability, and enhanced ionic conductivity.[1–4]

Starch is a low cost polysaccharide derived from agricultural plants and it is sensitive to biological attach. Natural starch exists in granular form and it has been used as filler in polymers. However, starch based materials have some drawbacks, such as poor water resistance and relatively poor mechanical properties. This is due to its hydrophilic nature and thus its sensitivity to moisture content, which is a factor that is difficult to control.[5–10] Consequently, starch is usually blended with hydrophobic biodegradable polymers to improve water resistance and mechanical properties.

Another method for improving starch properties is based on adding nanoclay to different starch formulations.[11–13] Nanoclay has been incorporated into synthetic polymers, to improve barrier, mechanical, and heat resistance properties.[14,15]

Park et al.[13] had shown that incorporating only 5 wt % nanoclay into potato starch reduced water vapor transmission rates by nearly one half. In addition, nanoclay samples exhibited higher dynamic elastic modulus and tensile strength. The reason for this improvement is that the nanoclays became intercalated, resulting in better dispersed platelets. Consequently, water molecules need to follow a more tortuous path through the composite, leading to lower water vapor transmission rates.

In addition, the dispersed platelets provide more surface area for starch/nano clay interactions, resulting in better reinforcement and improved mechanical properties.

Thermoplastic starch (TPS)/clay nanocomposites were prepared through melt intercalation method. The dispersion of the silicate layers in the TPS hybrids was characterized by using wide angle X-ray diffraction (WAXD). The effect of clay contents on the tensile, dynamic mechanical, thermal properties, and

Correspondence to: S. M. Ibrahim (sayda.ibrahim@yahoo.com).

the barrier properties of the nanocomposites was investigated. It was observed that the clay nanocomposites showed higher tensile strength and thermal stability, better barrier properties to water vapor.[13]

Thermoplastic starch (TPS)/clay nanocomposites were prepared by melt processing. Thermal stabilities of starch/clay nanocomposites were evaluated under N_2 atmosphere using thermogravimetric analysis (TGA). Transparent films of starch/clay hybrids were fabricated by hot pressing. Intercalation of starch into clay galleries and crystalline structure of starch were investigated using X-ray diffraction (XRD). It was found that the increase in d-spacing of organically modified clay was due to starch molecular intercalation.[16]

The effects of incorporating various montmorillonite nanoclay into wheat, potato, corn, and waxy corn starch samples were examined by rheology and X-ray diffraction. During gelatinization, the leached amylase interacted with the Cloisite Na+ interlayer, producing better reinforcement and higher modulus values. The samples containing wheat and corn starch showed comparable elastic modulus values during gelatinization. However, the potato and waxy corn samples had modulus values that rapidly decreased at higher temperatures.[17]

Preparation of starch/clay nanocomposite materials is proposed and analyzed by XRD, TGA, and scanning electron microscopy (SEM). Increase of the clay loading (>5 wt %) causes intercalation. The introduction of low content (≤5 wt %) of MMT improves the thermal stability and the stiffness of the materials. There is a limit content of clay that can be added to improve the thermal and thermomechanical properties of the composites.[18]

In modern medicine[19,20] polymeric materials have been used for a wide range of applications as drug delivery systems because they are nontoxic, high swellable, and much of them are compatible with blood, tissues, cells, i.e., in the human body.

This work concerned with the preparation of starch/clay composite with different clay concentrations. The effect of different doses of gamma radiation was studied. The dispersion of clay into the starch matrix and the effect of its addition on the mechanical, thermal properties, and morphology of starch/clay composite films was studied. The suitability of starch/clay composite as carrier material for the controlled release of drug Chlortetracycline HCl has been investigated.

EXPERIMENTAL

Materials

Maize starch used throughout this study was supplied by the Egyptian company for starch and glucose, Cairo, Egypt.

Clay Montmoeillonite (MMT) was supplied by Zhejiang Fenghong clay chemicles, People's Republic of China.

Preparation of starch/clay composite films

Starch/clay composite films were prepared from starch/clay aqueous suspensions by casting. The starch/clay rations were 100/0, 99/01, 98/02, 97/03, 96/04, and 95/05 (w/w), relative to dry starch, with a total mass of 5 g. The clay was dispersed in distilled water (10 mL) for 24 h, producing a gel that was added to an aqueous dispersion of starch. This suspension was degassed and heated to boiling point for 30 min with continuous stirring to gelatinize the starch granules. *N,N′* methylene bisacrylamide as crosslinking agent (0.1 wt %) was added to the solution. Glycerol (20% w/w, relative to starch on dry basis) was added to the hot solution and the solution was then poured on to polypropylene dishes and solvent evaporated to dryness at 40–50°C.

Determination of gel fraction

A known weight of the starch/clay composite (W_0) was extracted in a refluxing system by boiling in bidistilled water for 24 h. The samples were then removed and dried in a vacuum oven at 50°C, to eliminate excess water, to reach a constant weight (W_1). Finally, the soluble fraction was calculated according to the following equation:

$$\text{Sol. Fraction } (\%) = [(w_0 - w_1)/w_0] \times 100, \quad (1)$$

where W_0 is the initial weight of the dry sample and W_1 is the weight of the dry, insoluble part after extraction.

$$\text{Gel. Fraction } (\%) = 100 - \text{sol. fraction} \quad (2)$$

Swelling behavior of starch/clay composite films

A known dry weight of the insoluble part of the sample (W_1) after calculation of the soluble fraction were immersed in distilled water at room temperature for 24 h. The swollen part of the sample at equilibrium was weighed (W_2). The swelling percentage is determined by:

$$\text{SW}(\%) = W_2 - W_1/W_1 \times 100,$$

where W_1 and W_2 represent the weights of the dry and wet sample, respectively.

Measurement of water vapor transmission

The water vapor transmission rate (WVTR) was measured according to monograph of the European

Pharmacopeia. It consists of measuring the weight loss of a bottle which contains 25 mL of water. The bottle has a mouth with a diameter of 35 mm. The sample with a diameter of 40 mm was then put at the bottle mouth as a cap, and placed in an oven at 35°C for 24 h. The water vapor transmission rate (WVTR) was calculated by using the following formula:

$$\mathrm{WVTR} = \mathrm{W_i} - \mathrm{W_t}/\mathrm{A} \times 24 \times 106\ \mathrm{gm^2/h},$$

Where WVRT is expressed in gm^2/h, A is the area of bottle mouth (mm^2), W_i and W_t are the weight of bottle before and after placed in oven, respectively.

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°.

Thermogravimetric analysis

TGA studies were carried out using a TGA-30 apparatus (Shimadzu, Kyoto, Japan), at a heating rate of 10°C/min. in air, over a temperature range from room temperature to 500°C. Duplicate runs of the TGA thermograms of some starch/clay composite films were performed to check the reproducibility of the thermal data.

Tensile mechanical properties

Mechanical tests including break stress and strain were performed at room temperature using an instron machine (Model No. 1195) at a crosshead speed of 5 mm/min. Starch/clay composite films were cut with a die into dumbbell shape of 40 mm length and 4 mm width. The recorded value for each mechanical parameter is the average of five measurements.

Spectroscopic analysis

Infra red spectra of the film samples were obtained by using an ATI Mattson

Genesis spectrophotometer made by Unicam (England).

Scanning electron microscopy

The morphology of the fracture surfaces of the starch and starch/clay composites was examined. The scanning electron micrographs were taken with a JSM-5400 instrument (Joel, Japan). A sputter coater was used to precoat conductive gold onto the fracture surface before observing the microstructure at 25 kV.

Preparation of chlortetracycline HCl-loaded starch/clay composite

Aqueous solution of drug was prepared by dissolving different concentration of chlortetracycline HCl (30, 50, 80 mg) in 100 mL H_2O. The dry starch/clay composites were soaked into the drug solution at room temperature until the complete absorption.

Release of chlortetracycline HCl

Release experiments were performed by placing the load composite in 10 mL of buffer solution (pH 7) for 3 h at room temperature. The release amount of chlortetracycline HCl was measured by UV Spectroscopy (UNICAM UV/Vis Spectrometer. 1000 model) after the complete release the composites.

RESULT AND DISCUSSION

One major problem in the uses of starch as one of the component for the preparation of composite is its limited process ability due to its big particle sizes (5–100 xn). Therefore, it is difficult to make a good film for package application. To overcome this problem, starch is mixed with different composition of nanoclay (1, 2, 3, 4, and 5%). It was found that incorporating 4% clay in the starch/clay composite lead to the formation of good casting film. The starch/clay composite was irradiated to several irradiation doses 10, 20, 30, and 40 kGy to study the effect of irradiation doses on the properties of this composite as gel fraction % and swelling behavior.

Gel fraction %

The dependence of the gel fraction of starch/clay composite on clay compositions as a function of irradiation dose is shown in Figure 1. From this figure, it was found that for all samples, the gel fraction increased with the increase of clay content up to 4 wt %. Moreover, the gel fraction increases with the increase of irradiation dose up to 30 kGy. Hence, 30 kGy was found to be the favorable dose for gel formation. However, 40 kGy cause degradation for all composite compositions. These results of gel fraction clearly demonstrate that the formation of starch/clay composite was promoted in the presence of clay. Also, ionizing radiation could induce the crosslinking of the composite under high concentration of starch.[21–23] The presence of clay stimulated the formation of radicals from starch and also sustained the life of radicals longer which resulted in high efficiency of gel formation in the composite.

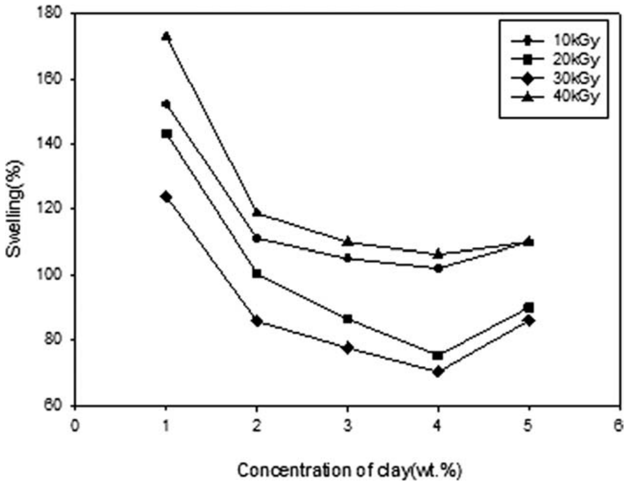

Figure 1 Effect of clay concentration on gel fraction (%) of starch/clay composite at different irradiation doses.

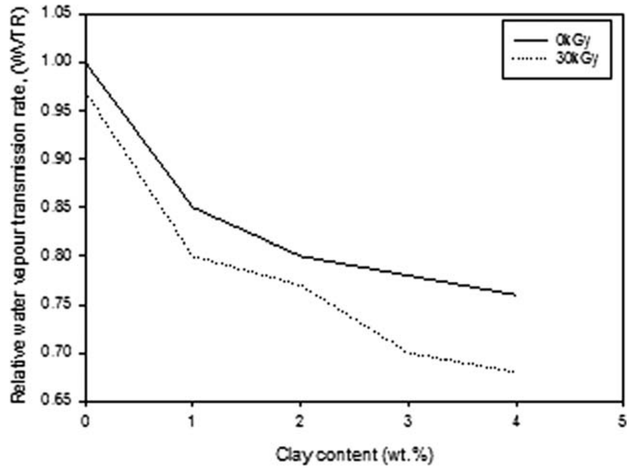

Figure 3 Effect of different concentration of clay content on the relative water vapor transmission rate behavior at 30 kGy.

Swelling behavior

The swelling of the starch/clay composite with different clay content as a function of irradiation dose is shown in Figure 2. From this figure, it was found that the swelling of starch/clay composite decreased with increase of clay content in the composite and with the increase of irradiation dose. Thus, the lower swelling ratios observed in the composite systems might be explained by the occurrence of hydrogen bonding between Na-MMT and starch, which leads to a sort of physical crosslinking.[24] The number of intermolecular crosslinks increases with the increase of irradiation dose up to 30 kGy, which leads to the decrease of the degree of swelling.

Water vapor transmission rate (WVTR)

Figure 3 shows the relative water vapor transmission rate (WVTR) versus the contents of clay in the unirradiated and irradiated starch/clay composite. The results obtained from this figure show that for the starch films the WVTR decreased remarkably with adding small amounts of clays for both unirradiated and irradiated composite. It means that the layered structure of clay blocks the transmission of moisture vapor through the film matrix. The decreasing of WVTR in composite is due to the presence of

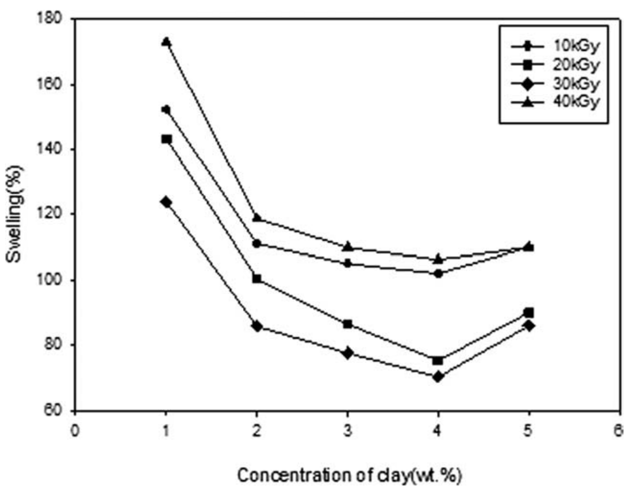

Figure 2 Effect of clay concentration on the swelling (%) of starch/clay composite at room temperature for 24 h.

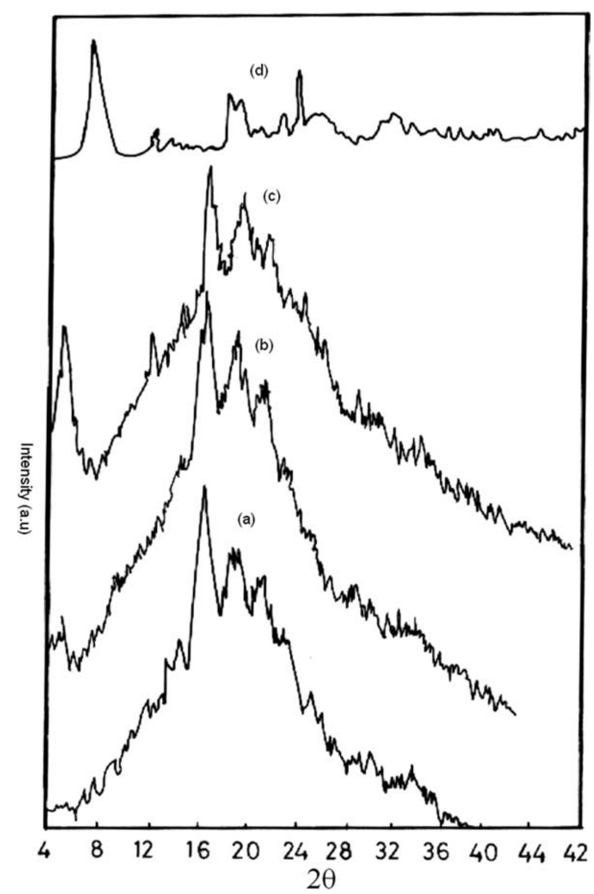

Figure 4 XRD spectra of (a) pure starch, (b) 1% clay, (c) 4% clay, and (d) pure clay.

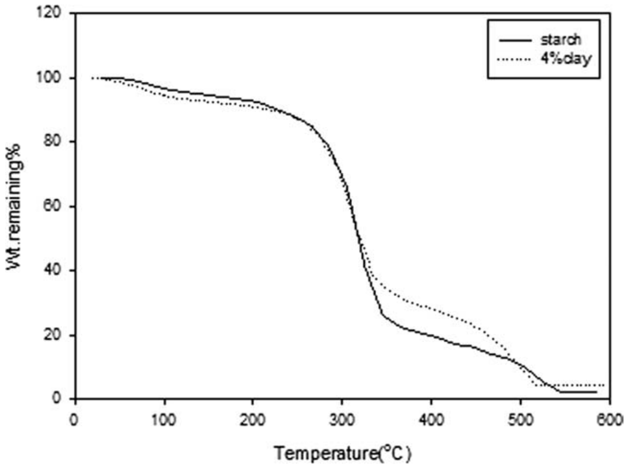

Figure 5 Thermogravimetric analysis of unirradiated starch/clay (4 wt %) nanocomposites.

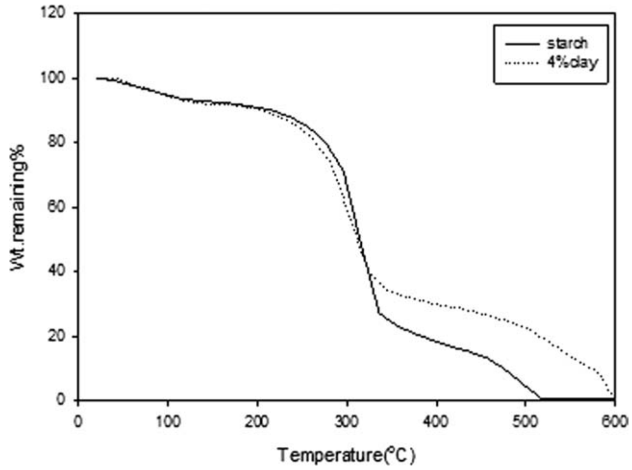

Figure 6 Thermogravimetric analysis of starch/clay (4 wt %) irradiated to 30 kGy.

dispersed large aspect ratio silicate layers in the polymer matrix as seen in other polymer–layered silicate composites.[25,26] The observed decrease in WVTR is of great importance in evaluating starch/clay composite for use in food packing, protective coatings, and other applications where efficient polymeric barriers are needed. Furthermore, reduced WVTR in biodegradable polymer composite films may have the added benefit for modifying degradation rates, because hydrolysis of the matrix polymer is likely to depend on the transport of water from surface into the bulk of the material.[27] The addition of clay is carried out to improve the rigidity of the film. The amount of clay added to the composite film should be controlled due to its synergetic effect on the mechanical strength and WVTR of the film.

X-ray diffraction

Figure 4 shows XRD patterns of starch and starch/clay composite with different clay contents (1 and 4 wt %). It was found that the appearance of the new peak at $2\theta = 5.6°$ (d-spacing = 1.77 nm) lower angle than native MMT which appears at $2\theta = 6.9°$ (d-spacing = 1.23). The angle of the native MMT is shifted with increasing starch content in the composite films. It is generally thought that during the intercalation process the polymer enters the clay galleries, thus increasing the gallery spacing (d-spacing).[11] According to Bragg's law, a shift of the diffraction peak toward a lower angle and the increase of d-spacing indicated the formation of nanocomposite structure of the silicate layers of MMT.

Thermal stability

TGA results of unirradiated and irradiated starch/clay composite films in the temperature range from room temperature to 600°C are shown on Figures 5 and 6.

The thermal decomposition of plasticized starch followed a three-step reaction with a maximum decomposition at 289°C. The first step corresponds

TABLE I
Tensile Properties of Starch/Clay Composites with Different Concentrations of Clay at Different Irradiation Doses

		Blend composition (starch/clay)			
Property	Irradiation dose (kGy)	99/1 wt %	98/2 wt %	97/3 wt %	96/4 wt %
Tensile strength (MPa)	0	0.625	1.5	2.7	3.8
	10	2.0	2.7	2.9	4.1
	20	3.7	4.4	8.3	10.4
	30	5.8	6.6	11	12.5
	40	2.7	3.4	3.7	3.8
Elongation at break (%)	0	28.7	26.3	25.2	24
	10	27	25.4	24.5	23.4
	20	26.2	24	23.3	22.5
	30	25	23.5	23.3	22.4
	40	26.5	24	23	22.0

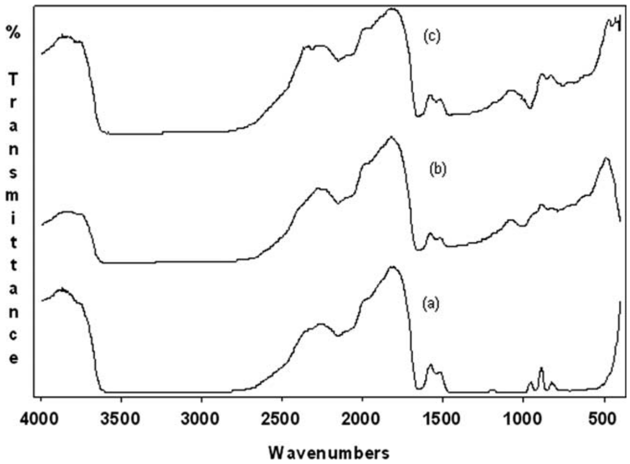

Figure 7 IR spectra of (a) pure starch, (b) 1% clay, and (c) 4% clay.

to water loss, the second to starch and glycerol decomposition, and the third to the oxidation of partially decomposed starch. Pure clay shows two degradation steps attributable to water loss (first step) and to clay dehydroxylation at $\sim$ 725 (second step).[26] From the data obtained in Figures 5 and 6, it was found that the thermal stability increases with the addition of clay up to 4 wt % and irradiated at 30 kGy. The results obtained by these figures indicate that the starch/clay composite decompose at a higher temperature with good thermal if compared with the pure starch before it intercalate with clay which is undergo decomposition at relatively low temperature, indicating the enhancement of the thermal stability of the prepared nanocomposite. This enhancement may be due to that clay is inorganic material with high thermal stability and great barrier properties and can prevent the heat from transmitting quickly and can limit the continuous decomposition of the nanocomposite.

Tensile properties

Table I shows the tensile properties of the starch/clay composite with different concentrations of clay at different irradiation dose. It can be seen that the tensile properties of the unirradiated and irradiated starch/clay composite are generally increased with increasing the concentration of clay. While tensile strength increases on increasing irradiation dose up to 30 kGy then there is a decrease in tensile strength on increasing the irradiation dose more than 30 kGy. It is important to mention that the maximum tensile strength is shown with concentration 4% clay at 30 kGy. The increase of tensile strength is affiliated with the radiation induced crosslinking of the composite. On the other hand and as expected, the elongation at break values have in counter a systematic decrease with increasing the clay content in the composite and with increasing the irradiation dose for the same composition.

FTIR spectroscopy

The FTIR spectra of irradiated starch and starch/clay composite are illustrated in Figure 7. The absorption band which characteristic for starch [Fig. 7(a)] appears at 3346.7 is due to hydrogen–bonded hydroxyl groups that contribute to the complex vibrational stretches associated with free inter- and intra molecular bound hydroxyl groups, which are responsible the gross structure of starch. The absorption bands for starch/clay composite with different concentration of clay (1 and 4 wt %) are shown in Figure 4(b,c). The characteristic band with a peak at 3625 cm^{-1} ascribed to the stretching vibrational band of –OH group on the surface layers of the clay accompanied with other peak at 917 cm^{-1} which is also characteristic to –OH bending group are shown in this figure. Moreover the absorption band at 1157 cm^{-1}, 1079 cm^{-1} are probably due to silicon linkage in the structure of clay. A weak absorption band at 524 cm^{-1}, 472 cm^{-1} are due to the presence of Al—O stretching and Si—O bending vibrations of MMT, respectively.

Structural morphology of starch/clay composite

Figure 8 shows SEM micrographs of the fractured surface of the starch and starch/clay (4 wt %)

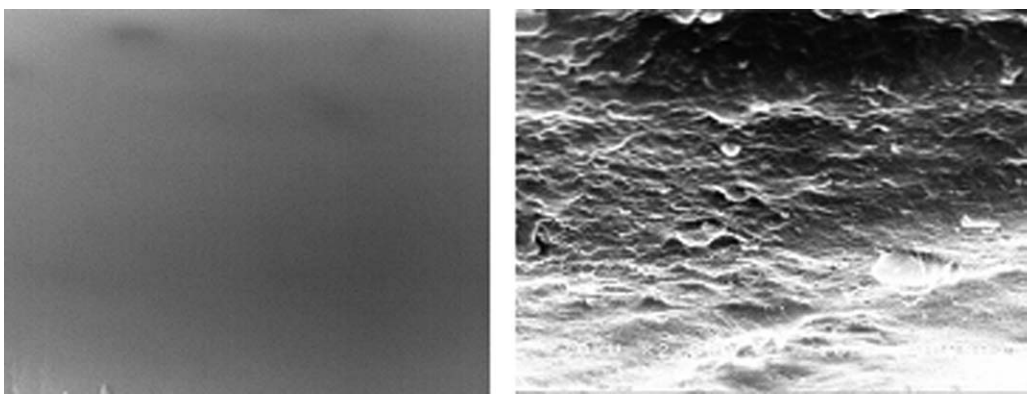

Figure 8 Scanning electron micrography of (a) starch and (b) starch/clay (4 wt %) irradiated at 30 kGy.

composite. The SEM micrograph of pure starch is characterized with smooth surface. On the other hand, the SEM micrographs of starch/clay composite (4 wt %) showed homogeneously dispersed clay particles, though it has an increase in surface roughness and show a denser dispersion of layers of clay in starch.

Adsorption of chlortetracycline HCl

For the investigation of cationic drug adsorption behavior of starch/clay composite prepared. In this study, composites were initially swollen in different concentration of Chlortetracycline HCl solution at pH 7. The total amount of chlortetracycline HCl adsorbed into 0.1 gm of dry starch/clay composite at different initial drug concentrations is given in Figure 9. As can be seen from this figure, the amount of total chlortetracycline HCl taken increased with increasing initial drug concentration. The reason for this increase was attributed to the specific bonding of positively charged drug to partially ionized composite and to the higher free volume available for diffusion. The amount adsorbed of drug per gram of dry adsorbent is calculated from the following equation:

$$qe = C_i - C_e/m$$

where qe is in mg adsorbate per gram of dry adsorbent, C_i and C_e are the initial and equilibrium concentrations of adsorbate solution (mg/mL) and m is the mass of dry adsorbent (g).

Release of chlortetracycline HCl

The release experiment was carried out at buffer solution of pH 7 which is similar to that of the intestine medium. Figure 10 shows the drug release behavior of composite loaded with different concentrations of the initial drug as a function of time at pH 7. The results obtained, show good agreement with previous workers that the amount released depends upon the initial amount of the drug present in the polymer matrix.[28]

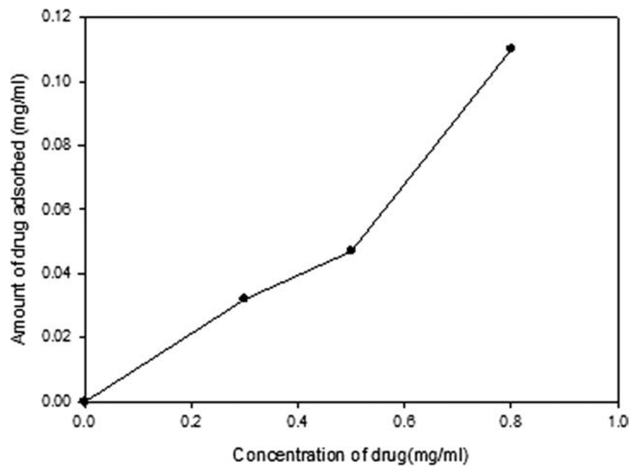

Figure 9 Effect of initial concentration of drug (mg/L) on the amount of adsorption of drug by starch/clay (4 wt %).

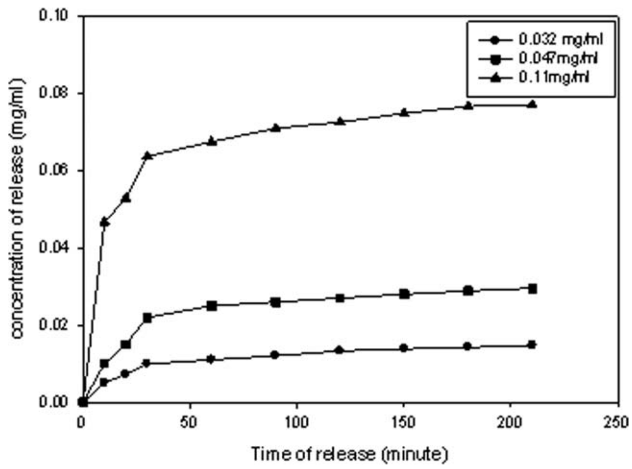

Figure 10 Chlortetracycline HCl released from starch/clay composite as a function of time for different loaded amount of drug at pH 7.

CONCLUSION

Formation of starch/clay composite at various clay contents (1–5%) were prepared by solution casting method. The prepared films were exposed to various doses of gamma radiation up to 40 kGy. The introduction of MMT content up to 4 wt % clay leads to significant improvement in thermal stability, tensile properties, and lower water vapor transmission than the pure starch. The results also showed that adding only 4 wt % of clay to the starch matrix to improve the tensile strength and barrier property of the composite.

References

1. Yao, K. J.; Song, M.; Hourston, D. J.; Luo, D. Z. Polymer 2002, 43, 1017.
2. Sun, T.; Garces, J. M. Adv Mater 2002, 14, 128.
3. Usuki, A.; Tukigase, A.; Kato, M. Polymer 2002, 43, 2185.
4. Wu, J. H.; Lerner, M. M. Chem Mater 1993, 5, 835.
5. Butler, M. F.; Cameron, R. E. Carbohydr Polym 2000, 41, 2249.
6. Chang, Y. P.; Cheah, P. B.; Seow, C. J. Food Sci 2000, 65, 445.
7. Gaudin, S.; Lourdin, D.; Forssell, P. M.; Colonna, P. Carbohydr Polym 2000, 43, 33.
8. Lim, S. T.; Chang, E. H.; Chung, H. J. Carbohydr Polym 2001, 46, 107.
9. Moates, G. K.; Noel, T. R.; Parker, R.; Ring, S. G. Carbohydr Polym 2001, 44, 247.
10. Standing, M.; Westling, A. R.; Gatenholm, P. Carbohydr Polym 2001, 45, 209.

11. Mcglashan, S. A.; Halley, P. J. Polym Int 2003, 52, 1767.
12. Park, H. M.; Li, X.; Jin, C. Z.; Park, C. Y.; Cho, W. J.; Ha, C. S. Macromol Mater Eng 2002, 287, 553.
13. Park, H. M.; Lee, W. K.; Park, C. Y.; Cho, W. J.; Ha, C. S. J Mater Sci 2003, 38, 909.
14. Alexandre, M.; Dubois, P. Mater Sci Eng 2000, 28, 1.
15. Vaia, R. A. In Polymer–Clay Nanocomposites; Pinnavaia, T. J., Beall, G. W., Eds.; Wiley: New York, 2000; pp 229–266.
16. Zhang, Q. X.; Yu, Z. Z.; Xie, X. L.; Naito, K.; Kagawa, Y. Polymer 2007, 48, 7193.
17. Bor- Sen, C.; Emma, Y.; Greg, M. G.; William, J. O. Carbohydr Polym 2005, 59, 467.
18. Schlemmer, D.; Angélica, R. S.; Sales, M. J. A. Compos Struct 2010, 92, 2066.
19. Shantha, K. L.; Ravichandran, P.; Panduranga, R. K. Biomaterials 1995, 16, 1313.
20. Hoffman, A. S. Adv Drug Delivery Rev 2002, 54, 3.
21. Wach, R. A.; Mitomo, H.; Yoshii, F.; Kume, T. J Appl Polym Sci 2001, 81, 3030.
22. Wach, R. A.; Mitomo, H.; Nagasawa, N.; Yoshii, F. Radiat Phys Chem 2003, 68, 771.
23. Yoshii, F.; Zhao, L.; Wach, R. A.; Nagasawa, N.; Mitomo, H.; Kume, T. Nucl Instrum Methods Phys Res Sec B: Beam Interact Mater Atoms 2003, 208, 320.
24. Bignotti, F.; Lebon, F.; Peroni, I. Eur Polym J 2007, 43, 1996.
25. Kojima, Y.; Kukumori, K.; Usuki, A.; Okada, A.; Kurauchi, T. J Mater Sci Lett 1993, 12, 889.
26. Yano, K.; Usuki, A.; Okada, A. J Polym Sci Part A: Polym Chem 1997, 35, 2289.
27. Messersmith, P. B.; Giannelis, E. P. J Polym Sci Part A: Polym Chem 1995, 33, 1047.
28. Park, K. Controlled Drug Delivery: Challenges and Strategies; ACS: Washington, DC, 1997.