Poly(Lactic Acid)/Layered Silicate Nanocomposite Films: Morphology, Mechanical Properties, and Effects of γ-Radiation

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ABSTRACT: Poly(Lactic acid) (PLA)-layered silicate nanocomposite films were prepared by solvent casting method. The films were irradiated with Co^{60} radiation facility at dose of 30 kGy. The effect of γ irradiation on mechanical properties of the neat PLA and nanocomposites was evaluated by data obtained from tensile testing measurements. The tensile strength of the irradiated PLA films increased with addition of 1 wt % triallyl cyanurate indicating crosslink formation. Significant ductile behavior was observed in the PLA nanocomposites containing 4 pph of nanoclay. Incorporation of nanoclay particles in the PLA matrix stimulated crystal growth as it was studied by differential scanning calorimetry. The morphology of the nanocomposites characterized by transmission electron microscopy and X-ray diffraction revealed an exfoliated morphology in the PLA nanocomposite films containing 4 pph of nanoclay. Only very small changes were observed in the chemical structure of the irradiated samples as it was investigated by Fourier transform infrared spectroscopy. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 142–149, 2011

Key words: biodegradable; biomaterial; poly(lactic acid); nanocomposite; γ-irradiation

INTRODUCTION

Poly(lactic acid) (PLA) is a linear aliphatic thermoplastic polyester produced either by the polycondensation of lactic acid or by ring-opening polymerization of lactide cyclic dimmer.[1] Lactic acid is synthesized from fermentation of renewable sources such as corn, sugar beet, and other starch-rich products.[2–5] Direct condensation of lactic acid leads to low molecular weight polymer. Therefore, the ring-opening polymerization of lactide is more popular for producing PLA with higher molecular weight.

Biodegradability and bioabsorbability of this plant-based polymer has drawn many attentions to itself in recent years. Good mechanical properties along with its biocompatibility make it suitable for biomedical applications[6]: such as prosthetic implants,[7] three-dimensional scaffolds,[8] controlled-release drugs,[9] and resorbable sutures. There is also a growing interest in utilizing PLA for packaging and disposable plastic articles, since production cost has been lowered by new technologies and large scale production.[5,10] In spite of many good properties of PLA that makes it a preferred choice for substitution with petroleum-based polymers, existence of a few weaknesses in some aspects such as thermal stability, barrier properties, and toughness seeks a requirement for its modification. The performance of PLA can be enhanced by the incorporation of nano-sized particles. Among the nano-sized inorganic particles that are added to the polymer matrix montmorillonite clay are of particular interest due to their abundance, low cost, and their geometrical features. They consist of numerous layers stacked in parallel called platelet; each platelet has high aspect ratio (length/thickness). Addition of natural clay into polymer matrix very rarely leads to formation of nanocomposites because of incompatibility between inorganic/organic systems.[11] To enhance miscibility between two components, hydrated cations (Ca^{2+}, Na^+) of the interlayer space of montmorrilonite are exchanged with cationic surfactants such as alkylammonium or alkylphsphonium. The ion-exchange reaction lowers the surface energy of inorganic material and makes it compatible with polymers.[11] Two types of intercalated and exfoliated polymer nanocomposites may be resulted from incorporation of nanosized organophilic clay in a polymer matrix, although most of research works show a mixture of the two.[1] Some attempts have been made by researchers to improve various properties of PLA through formation of PLA/organophilic clay

nanocomposites.[1,12,13] Chemical and/or radiation-induced crosslinking is another alternative for improving thermal and mechanical properties of PLA.[14–17]

The main objectives of this study were to investigate the effect of γ-radiation on mechanical properties of the poly(lactic acid)/organoclay nanocomposite films prepared by solvent casting method. Mechanical properties of the irradiated PLA nanocomposite films were examined by stress–strain test. The effect of Nanolin incorporation on crystallinity and thermal behavior of the hybrid films was studied by differential scanning calorimetry (DSC). The chemical structure of the irradiated PLA samples was characterized by Fourier transform infrared (FTIR) spectroscopy. Morphology of the nanocomposite films were studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively.

EXPERIMENTAL

Materials

PLA granules were purchased from a chemical company in China. Nanosized organoclay with the trade name of Nanolin DK4 was used as a polymer additive.

Preparation of PLA and PLA/organoclay nanocomposites

PLA and PLA/Nanolin DK4 nanocomposites were made via solvent casting method.[18] A required amount of PLA granule was weighed and mixed vigorously with enough amounts of chloroform via a magnet stirrer. The temperature maintained constant at 50°C in a water bath until the complete solution of PLA was obtained. The solution was poured into a glass mold and placed on a leveled surface. After 48 h, the prepared PLA film was removed from the mold and placed into a vacuum oven for 24 h at 25°C and 24 h at 40°C. The PLA films containing multifunctional monomer were made by the same procedure except 1–2 wt % triallyl cyanurate (TAC) was added to the PLA solution and mixed again for an hour. Nanocomposite films were made by addition of Nanolin to the PLA solution. Initially, a dispersion of organoclay in chloroform was obtained by introducing various amounts of Nanolin to solvent followed by vigorous mixing in a digital ultrasonic bath for 60 min. The solution of PLA and the dispersion of Nanolin was then mixed together by an ultrasound bath for about 3 h and poured into a glass mold on a leveled surface. Nanocomposites films containing 2, 4, and 6 pph (pph stands for

parts per hundred of the PLA polymer) were made by this procedure.

Irradiation of films

The pristine PLA and nanocomposite films were cut into strips and irradiated with γ-rays at dose of 30 kGy in presence of air. The irradiation was carried out at room temperature and dose rate of 4.6 Gy/s using a Co^{60} irradiator Gammacell model 220 manufactured in Canada. It should be noted that the effect of γ-rays on the mechanical properties of the commercial PLA films at various doses of 5–35 kGy had been previously investigated,[18] and from those results the optimum dose of 30 kGy was applied to the PLA solvent cast films. The optimum dose was the maximum dose that the tensile strength of the commercial PLA film did not have a prominent reduction upon radiation.

Characterization of PLA films

Gel permeation chromatography

Number average of 100,790 g/mol and weight average of 237,560 g/mol were obtained for the PLA granule via gel permeation chromatography (GPC) on an Agilent 1100 GPC at temperature of 30°C and solvent of chloroform. The detector was IR (Refractive Index).

FTIR spectroscopy

Infrared spectra of the neat PLA films before and after irradiation were obtained using FTIR machine Series 8300 manufactured by Shimadzu Company in Japan.

Gel content

Gel fraction of the irradiated PLA films was determined using Soxhlet extraction method by following equation.

$$\text{Gel fraction } (\%) = (W_g/W_0) \times 100$$

where W_0 is the initial weight of the irradiated PLA film and W_g is the weight remaining after 24 h extraction in chloroform followed by drying in a vacuum oven for 48 h.

Mechanical properties

Mechanical properties of the PLA and PLA nanocomposite films were characterized by a Zwick tensile testing machine. The films were cut into the strips with the dimensions of 10-cm length × 2-cm
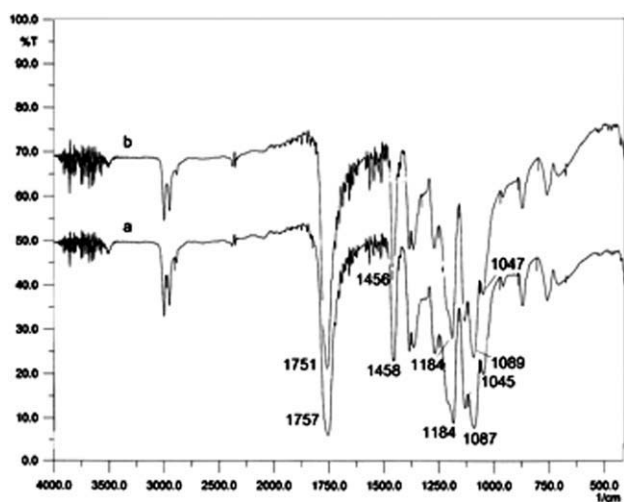
Figure 1 FTIR spectrum of the pristine (a) and γ-irradiated PLA film (b) at dose of 30 kGy.

width and stretched with the gauge length of 4 cm and a speed of 5 mm/min.

Differential scanning calorimetry

Thermal behavior and crystalline structure of the samples were investigated via DSC by the PerkinElmer DSC Model Pyris 1. The test was performed under nitrogen atmosphere between 40 and 200°C at heating rate of 10°C/min.

XRD

The structure of the PLA-Nanolin nanocomposite films were evaluated by XRD measurements. XRD patterns were taken by a Philips Analytical X-Ray Diffractometer, operated at 30 kV and 20 mA, equipped with Cu tube anode at irradiation wavelength of 1.54056 Å. The X-ray diffractograms were collected in the angle range, 2θ, of 2°−10° at continuous scan mode. The d-spacing is calculated from Braggs' equation:

$$n\lambda = 2d\sin\theta$$

where n is taken as unity, λ corresponds to the wavelength of the X-ray radiation, d is the spacing between diffractional lattice planes, and θ is half the angle of diffraction.

TABLE I
Gel Content of the Irradiated PLA Film at 30 kGy

TAC (wt %)	Gel fraction (wt %)
1	71
2	55.5
0	0

TEM

TEM was used to characterize morphology of the PLA nanocomposite films. The TEM was performed on a Phillips EM 208 S electron microscope operating at acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

FTIR spectroscopy

No significant changes are observed in the chemical structure of the γ-ray treated sample compared to that of unexposed one as seen in Figure 1. Only very slight changes occurred at wavenumber position of some of the absorption peaks. For instance, the absorption of carbonyl group at 1757 cm^{-1} shifted to 1751 cm^{-1}. This may be attributed to chain scission and consequent oxidation reactions induced by radiation treatment.

Crosslinking of irradiated PLA films

Degree of crosslinking of the irradiated PLA films was evaluated by measuring the gel fraction as shown in Table I. Surprisingly, increase of the TAC from 1 to 2 wt % decreased the gel content from 71 to 55.5 wt %. It may be due to the fact that multifunctional monomer at 2% value has not been spent totally at dose of 30 kGy. This is also confirmed by the higher elongation at break of this sample compared to that of the pure PLA (Fig. 2) that may imply some residue of the monomer acting like a plasticizer.

Mechanical properties

γ-Rays are known to induce structural changes, such as scission and crosslinking in the exposed polymers. The change in mechanical properties of the
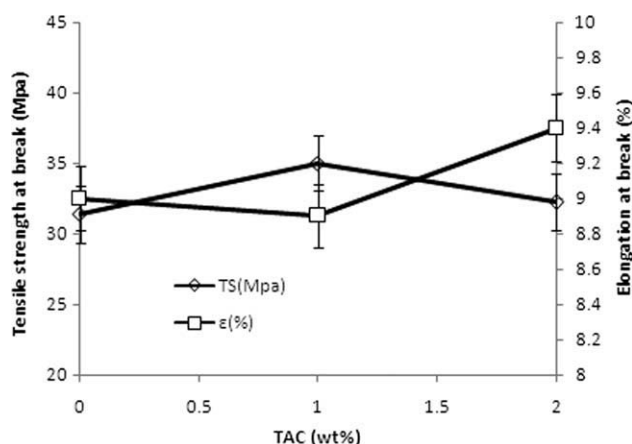

Figure 2 Tensile strength and elongation at break versus TAC value for the PLA + TAC cast films irradiated at 30 kGy.
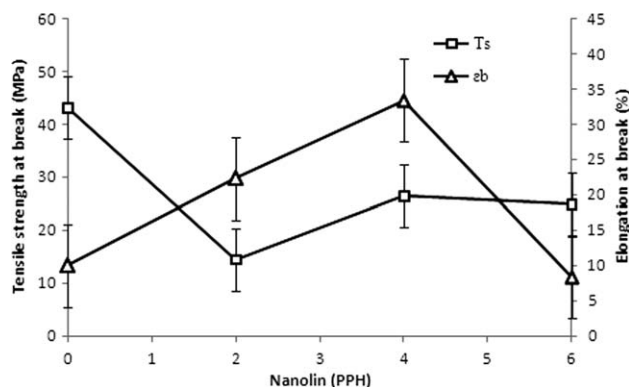
Figure 3 Tensile strength and elongation at break of the unirradiated PLA and PLA/Nanolin nanocomposites.

irradiated PLA film implies some structural changes having occurred in the pristine PLA films after exposure to the high energy ionizing radiation (Figs. 3 and 4). Tensile strength declined markedly from 43.1 to 31.4 MPa and the elongation at break reduced from 10.8 to 9% indicating perhaps some chain scission. Figure 2 shows tensile strength and elongation at break of the pristine and TAC-added PLA films, irradiated at 30 kGy. Addition of the TAC at 1 wt % improved the tensile strength of the irradiated PLA film, but no remarkable change appeared at 2%. The gel content of the PLA film containing 1% TAC reduced from 77 to 55.5% upon increasing of TAC to 2 wt %. This suggests that the optimum TAC value for crosslink formation between the PLA macromolecules at dose of 30 kGy is 1 wt %. The mechanism of formation of crosslinks may be briefly explained as follows. Interaction of high energy γ-rays with PLA film leads to break C—H bond resulting in free radical on the PLA molecular chain. The double bonds of allyl group in TAC are also broken to form a pair of electrons. Combining the electrons generated on TAC molecule with the electron exists on PLA molecular chain forms a three-dimensional network that improves tensile strength of the PLA film. Slight change observed between the elongations at break of the irradiated samples containing TAC is due to their different degree of crosslinking.

Addition of 2 pph layered silicate nanopowder with the trade name of Nanolin DK4 into the PLA film decreased the tensile strength of pristine PLA from 43.2 to 14.3 MPa, while the elongation at break improved from 10 to 23.2% (Fig. 3). Incorporating 4 pph of Nanolin further increased the elongation at break of the PLA film to the value of 33.4% and the tensile strength to the value of 26.4 MPa. In spite of the lower tensile strength of the 4 pph nanocomposites than that of the neat PLA, the elongation at break increased to as much as threefolds. As a matter of fact, formation of nanocomposites through introducing layered silicate nanopowder in the PLA

changed its structure from a stiff-brittle to a ductile-flexible one. It should be noted that unirradiated PLA nanocomposites, particularly those containing 2 and 4 pph organoclay, showed a yield point in their stress–strain curves. Obvious stress whitening and necking were also observed before rupture especially in the 4 pph nanocomposites as shown in Figure 4. Indeed the good dispersion of the clay platelets into the PLA matrix in an exfoliated system and intensive interaction between the two phases is the reason for ductility enhancement of this nanocomposite sample. Increasing the Nanolin content to 6 pph had an adverse effect on the ductility that may be attributed to agglomeration and nonhomogenous distribution of the organoclay platelets.

A similar trend was observed in the mechanical properties of the PLA nanocomposite films having exposed to 30 kGy γ-rays except the 2 pph nanocomposite, which showed some increase in tensile strength and reduction in the elongation at break compared to those of the pure PLA. All the irradiated nanocomposite samples exhibited lower elongation at break and higher tensile strength compared to those of the unirradiated ones suggesting more rigid structure has been formed upon exposure to high energy radiation (Fig. 5).

Morphology

Morphology of the PLA nanocomposites was characterized by XRD method and transition electron microscopy.

XRD patterns

Figures 6 and 7 display XRD patterns of the Nanolin-DK4 powder and PLA nanocomposites films,

Figure 4 Exhibition of stress whitening and necking in the 4 pph PLA nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].
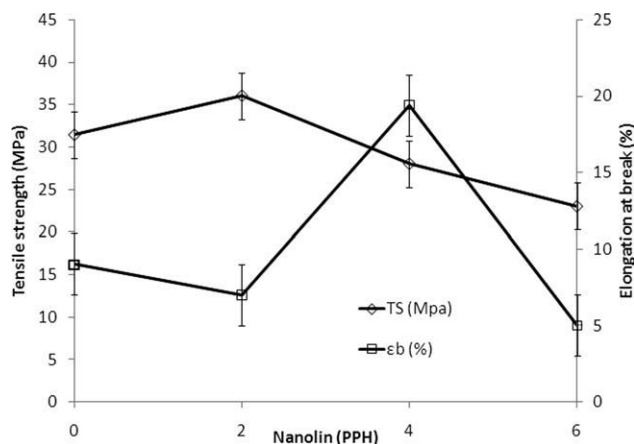
Figure 5 Tensile strength and elongation at break of the PLA and PLA/Nanolin nanocomposites irradiated at 30 kGy.

respectively. The strong sharp peaks in diffractogram of nanocomposites seen at a larger d-spacing and a lower value of 2θ compared to XRD peaks of the Nanolin indicates formation of an intercalated structure, that is, insertion of PLA into the silicate layer spaces without disruption of its arrangement. On the other hand, the diffraction peak at $2\theta = 2.38°$ in the 4 pph nanocomposites has been nearly disappeared (very low intensity of peak comparing to the sharp peak at $2\theta = 2.64$ in the XRD pattern of the layered silicate), which may be evidence of formation of partially exfoliated nanocomposite at this composition. This can also be observed by the TEM micrographs (Fig. 8) of the 4 pph nanocomposites that show fully separated silicate layers randomly dispersed in the polymer matrix.

TEM

Figure 8 shows TEM micrograph of the PLA nanocomposite containing 4 pph of Nanolin. As it is seen most of the platelets seem to be well dispersed in a random manner that exhibits exfoliation of layered
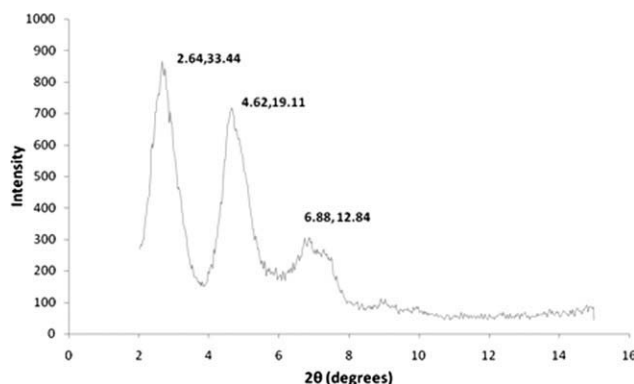

Figure 6 X-ray diffraction pattern of the Nanolin powder. The first number on the peak exhibits $2\theta°$ and the second one, d (Å), is the value of the spacing between silicate layers.
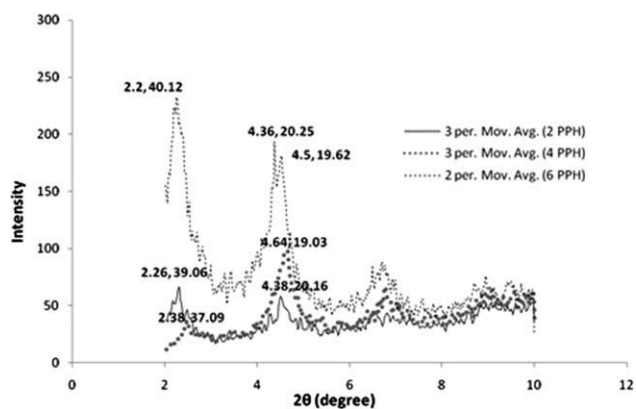
Figure 7 X-ray diffraction patterns of PLA-Nanolin nanocomposites.

silicate by the PLA. The TEM micrographs of the PLA/Nanolin nanocomposites with 2 and 6 pph modified nanoclay content are displayed in Figures 9 and 10.

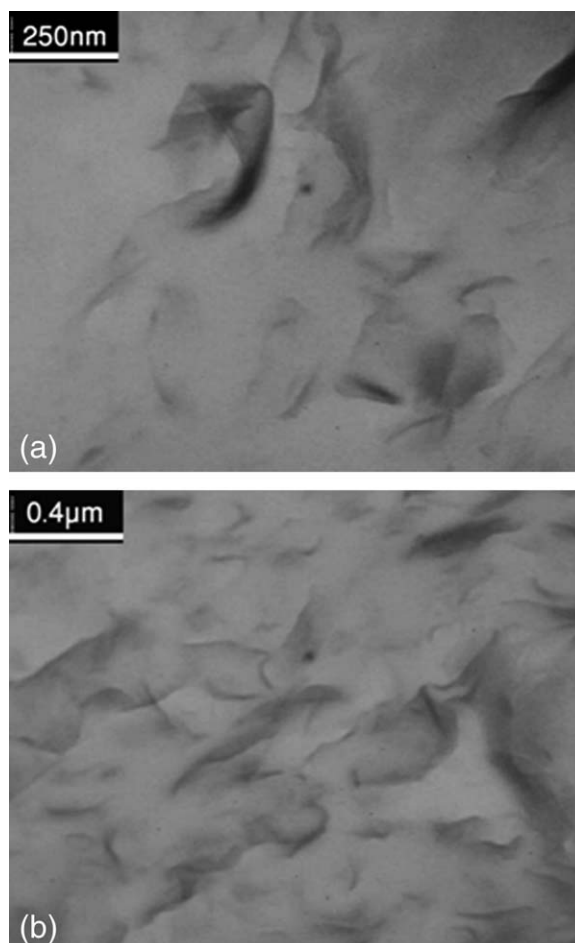In contrast with the 4 pph, the TEM of the 2 and 6 pph nanocomposites exhibit an intercalated

Figure 8 TEM micrographs (a, b) of exfoliated layered silicate in the PLA nanocomposite containing 4 pph Nanolin at different magnifications.
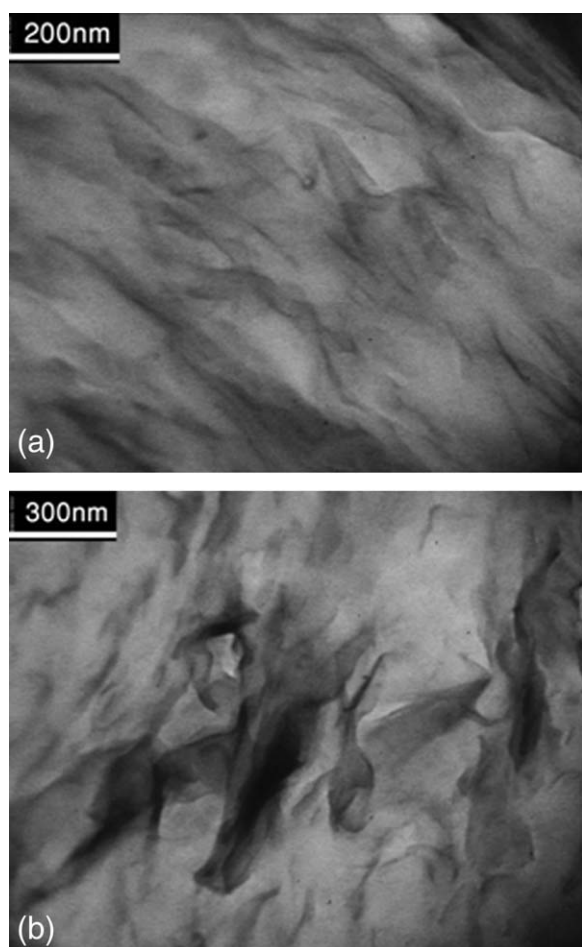
Figure 9 TEM micrographs (a, b) of intercalated layered silicate in the PLA nanocomposite containing 6 pph Nanolin at different magnifications.

morphology, which shows that the individual silicate layers are separated in an organized manner within polymer matrix by an average distance that depends on the clay loading. Figure 9(a) shows dispersion of the clay layers in parallel with each other in the PLA matrix although some agglomeration also exist [Fig. 9(b)]. In 2 pph PLA nanocomposite, the intercalated structure still retained while the distance between the layers increased due to low loading of the nanoclay that leads to better dispersion (Fig. 10).

Crystallinity of the PLA nanocomposite

Crystallinity of the PLA nanocomposites was investigated by DSC. Figures 11–14 display DSC thermograms of the pure PLA and PLA nanocomposite films containing various amounts of Nanolin. An endothermic peak at temperature range from 148 to153°C is observed that represents melting point of the PLA. The other endothermic peak at temperature of around 63°C corresponds to the glass transition of the PLA. No peak is observed in the DSC thermo-

grams during cooling process. Apparently crystallization rate of the PLA melt is very slow and requires more time for formation of crystallites. All the nanocomposites containing 2, 4, and 6 pph of layered silicate show higher enthalpy change and melting point compared to those of the pure PLA, indicating growth of crystalline region in the nanocomposite structure. Incorporation of modified clay enhances crystallites growth as the nanosized particles act as nucleating sites.

CONCLUSIONS

Nanocomposites of the PLA/layered silicate were successfully prepared via solvent casting method. Irradiation of pristine PLA films with γ-rays at 30 kGy deteriorated the mechanical properties of the exposed films. Addition of TAC monomer at 1 wt % slightly increased the tensile strength and decreased elongation at break, suggesting three-dimensional network formations upon exposure to high energy radiation at 30 kGy. Introducing Nanolin DK4 into the PLA films significantly improved
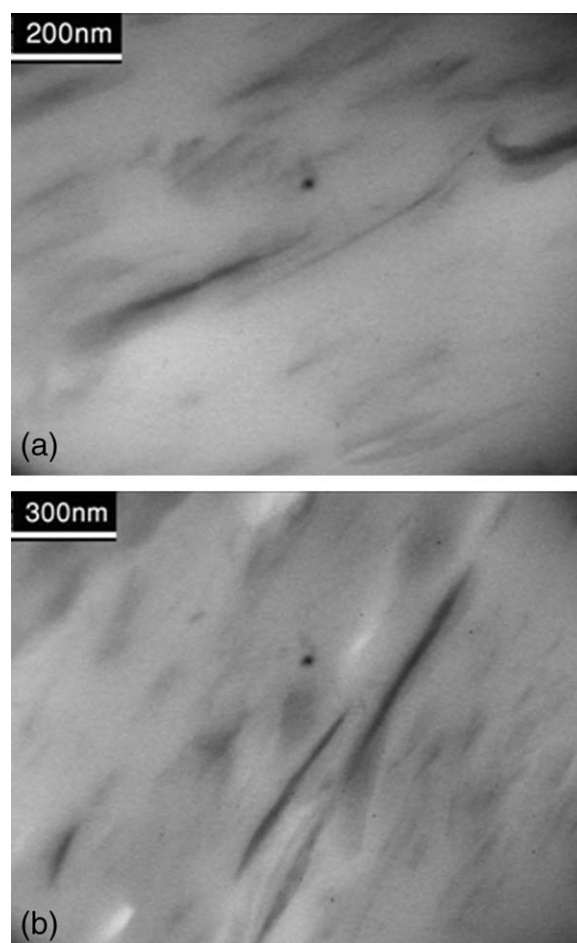

Figure 10 TEM micrographs (a, b) of intercalated layered silicate in the PLA nanocomposite containing 2 pph Nanolin at different magnifications.
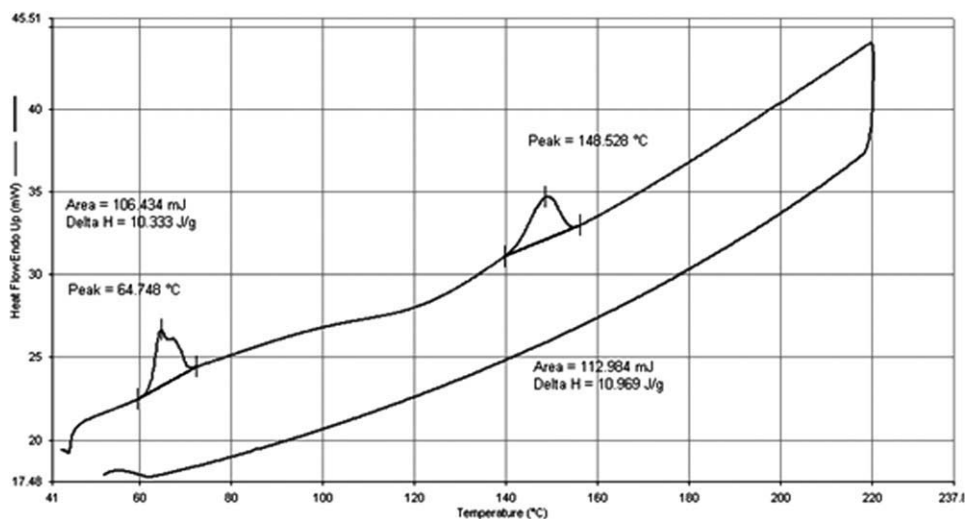
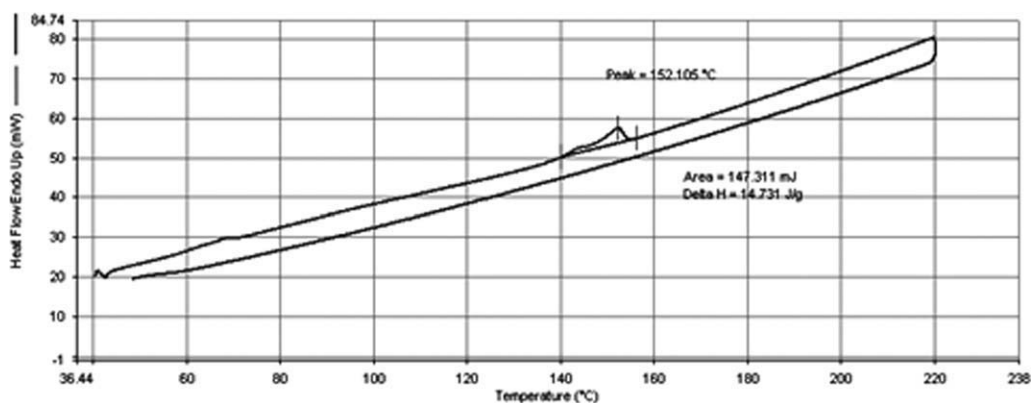**Figure 11** DSC thermogram of the PLA solvent cast film.

Figure 12 DSC thermogram of the 2 pph PLA nanocomposites film.

the elongation at break of the hybrid samples, particularly in the 4 pph nanocomposite sample. Exposing the PLA nanocomposites to 30 kGy γ-rays led to the higher tensile strength and lower elongation at break probably due to interaction of nanoparticles with the polymer matrix induced by ionizing radiation. Formation of nanocomposites was verified by TEM micrographs and XRD difractograms. Incorporation of the nanosized organophilic clay enhanced crystallites growth in the nanocomposite samples due to the action of the nanosized particles as nucleating sites.
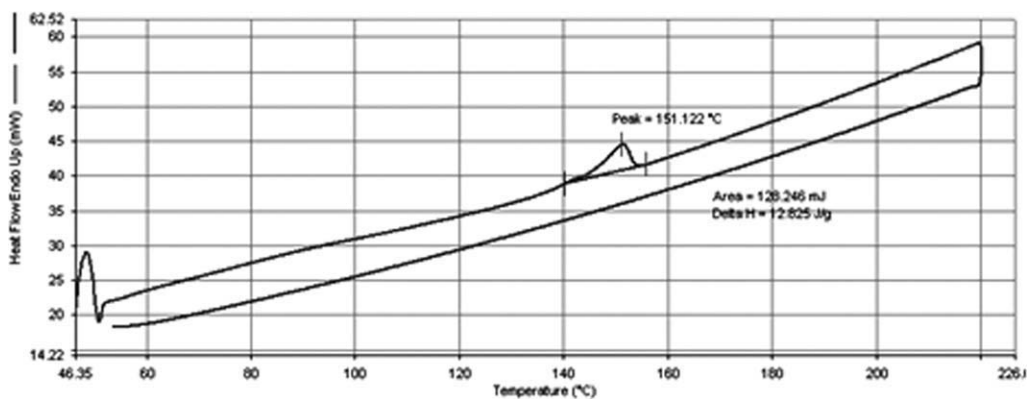
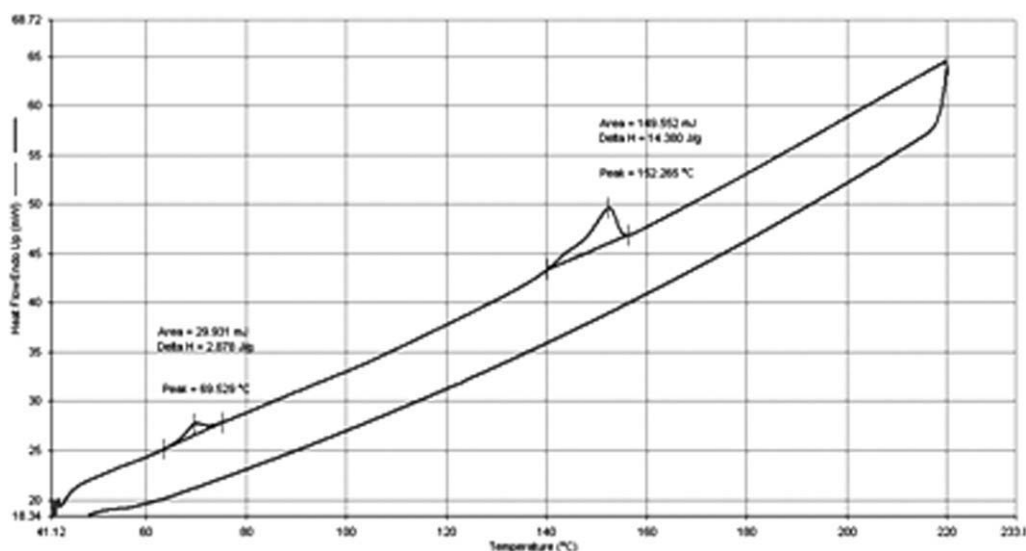**Figure 13** DSC thermogram of the 4 pph PLA nanocomposites film.

Figure 14 DSC thermogram of the 6 pph PLA nanocomposites film.

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