Characterization of nano-biocomposite films reinforced with nanofibrillated cellulose and montmorillonite as a potential application for Food packaging industry

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ABSTRACT: In this study, polyvinyl alcohol- Nanofibrillated cellulose –Montmorillonite (PVA-NFC-MMT) and Ethylene-vinyl acetate- Nanofibrillated cellulose –Montmorillonite (EVA-NFC-MMT) nanocomposites containing 2% weight of NFC and MMT were prepared by melt blending method. Then, the effect of NFC and MMT as reinforcing materials on biodegradability, morphology, and mechanical, thermal and barrier properties of films was investigated. Field Emission Scanning Electron Microscopy images of PVA-NFC-MMT and EVA-NFC-MMT indicated simultaneous uniform dispersion of NFC and MMT in the polymer matrix leading to the highest values of transparency and strength compared to control samples. Results for Differential Scanning Calorimetry indicated an increase in glass transition temperature and the crystallinity of PVA-NFC-MMT and EVA-NFC-MMT, compared to films without NFC and MMT. Oxygen permeability was decreased from 28.5 and 760 cc/m^2.day.atm in pure PVA and EVA to 3.7 and 114 cc/m^2. day.atm in PVA-NFC- MMT and EVA-NFC-MMT, respectively. Compared to the control sample, the tensile strength of PVA-NFC-MMT and EVA-NFC-MMT was increased by 20 and 44.4%, respectively. Biodegradability tests of films under soil indicated the improved degradation of PVA and EVA due to the simultaneous presence of NFC and MMT in such a way that they were degraded by 9.56 and 8.36%, after 120 days under soil burial conditions, respectively.

Keywords: *Biodegradation; EVA; Food Packaging; MMT; Nanocomposite; NFC; PVA.*

INTRODUCTION

The adverse effects of packaging produced from non-degradable polymers such as the reduction of natural resources, energy crisis, global warming, and ecosystem-related problems, have attracted attention of researches interested in finding the suitable alternatives for this kind of packaging within the recent years. A good option for solving the problem of non-degradable packaging in the food industry is replacing biodegradable polymers with non-degradable ones due to their biodegradability, biocompatibility, renewability and availability (Tripathi, *et al.*, 2008; Rhim, *et al.*, 2013; Ray and Bousmina, 2015). Biodegradable polymers used in

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the production of biodegradable packaging can be categorized into natural and synthetic polymers. Natural polymers like chitosan, starch, cellulose, agar, gelatin and gluten, in addition to being expensive, lack the mechanical and physical properties and the necessary barriers against water vapor and gas. All of these disadvantages limit their usage in food packaging industry (Sarwar, *et al.*, 2018). However, the emergence of new technologies have provided the ground for modification of non-degradable polymers and the advent of a generation of synthetic biodegradable polymers called polyolefin copolymers. In this generation of polymers, non-degradable polymers are copolymerized with comonomers such as vinyl alcohol or vinyl acetate, and so alcohol and ester groups may enter into the polymer structure resulting in the increased polarity of the polymer chain and its biodegradability.

Ethylene vinyl acetate (EVA) is a synthetic polymer formed from copolymerization of ethylene with vinyl acetate comonomer. Due to its transparency, hardness, tensile properties, not being thermal insulation, capability to prevent radio waves, non-toxicity and odorless, EVA has a variety of applications in the production of adhesives, insulators, foams, and especially packaging films (Salehi, *et al.*, 2003). Polyvinyl alcohol (PVA) is also a polyhydroxy polymer produced from hydrolysis of polyvinyl acetate. It is one of the most abundant synthetic polymers in the world enjoying excellent properties such as water-solubility, film formation, emulsifying agent, adhesion, and barrier-properties against oils, greases and solvents. In addition to being odorless and nontoxic and having oxygen and aroma compounds-barrier properties, these two polymers' biodegradability, ease of processing and mechanical properties are much better than those of conventional polyethylene and polypropylene films. As a result, they are considered to be suitable candidates for packaging films (Jelinska, *et al.*, 2010). Despite these desirable characteristics, these two polymers have some disadvantages such as the increased resistance to permeability in dry atmospheres and the reduced resistance to permeability in humid atmospheres.

Researchers find that entrance of water molecules into the structure of these polymers and interference of their hydrogen bonds between hydroxyl groups causes

this problem, which, in turn, results in breakdown of the physical barriers against permeability. Various approaches have been proposed to solve or improve such problems. One of the most widely used methods in the industry includes protection of polymer film through hydrophobic coatings such as polyethylene which prevent directly exposure of film to water molecules. Another way to reduce the permeability of PVA- and EVA-based films in humid atmospheres is using composite and nanocomposite technology. The permeability of these films in humid atmospheres can be reduced by preparing composite from these films using a suitable micro or nanoparticle. By using nanometer-sized fillers like titanium dioxide, zinc oxide, silicates, clay, nanocellulose and silver nanoparticles in biodegradable polymer matrix, one can improve their mechanical and barrier properties and create antibacterial and oxygen-refining properties, as well. In fact, the presence of nanometer-sized fillers with a greater aspect ratio and surface area improves the properties of the base polymer, while the weight percentage of nanometer-sized fillers gets much less than that of traditional composites (usually containing 40-50% fillers). Given the fact that weight of the nanocomposite is greatly reduced compared to the composite, it can be used in special applications, especially packaging (Zhao, *et al.*, 2008). In recent years, the tendency to use organic and mineral fillers have been appreciated by researchers due to their non-toxicity, low density, proper mechanical properties, and the increased renewability, biocompatibility and biodegradability (Sarwar, *et al.*, 2018).

Montmorillonite with the chemical formula $M_x(Al_{4-x}Mg)Si_8O_{20}(OH)_4$ is one of the most widely used layered silicate compounds with the nanoplate structure. It is used for production of many nanocomposites and nano-biocomposites because of its low prices and availability, relatively easy processing and remarkable improvement properties (Zhao, *et al.*, 2008). Its crystalline structure which belongs to the structural family of 2:1 phyllosilicates consists of two tetrahedral layers of silica with a shared octahedral sheet of aluminum hydroxide which are linked to each other by oxygen ions. Layer thickness is 1 nm and their length ranges from 30 nanometers to several microns and even more in some cases. This clay mineral has a specific surface

area equivalent with 750-800 gr/m^2 (Ray and Bousmina, 2015; Pillai and Ray, 2012; Nouri, *et al.*, 2018). Due to their morphology, the presence of montmorillonite nanoplates in polymer matrix leads to a tortuous path for penetration of the molecules, thereby reducing the permeability of the polymer films which is a highly desirable properties. However, reduction of permeability is associated with removing other important properties such as transparency and ductility. Because of their excellent light diffusion properties, Montmorillonite nanoplates remove transparency of the films produced at relatively low percentage (about 5%) (Noorbakhsh-Soltani, *et al.*, 2018). In this case, nanometer-sized fillers such as nanocellulos should be used in order to prevent the decreased transparency of the film. Nanocellulose, as one of the high molecular weight pseudo-crystalline nano-polymer, exists in all plants. This natural polymer creates a disorderly network through very strong hydrogen bonds between the nanometer-sized components. Indeed, it is a very popular nanometer-sized reinforcing material for production of polymer nanocomposites. Nanocellulose is available in both cellulose nanocrystals and nanofibrils forms.

Nanocrystalline cellulose has a rod-like structure with lengths of 200 to 2000 nm as well as a high degree of crystalline and modulus. In contrast to cellulose nanocrystals, cellulose nanofibrils are composed of filamentous units that have both crystalline and amorphous portions at the same time and are capable of creating a complex network. Due to its excellent properties, Nanocellulos has been used as an ideal reinforcing material in polymers such as starch, polylactic acid, alginate, polyethylene oxide, polycaprolactone, and other polymers (Sarwar, *et al.*, 2018). Given the above-mentioned issues and according to the previous studies, no research has been conducted on the simultaneous addition of cellulose nanofibrils and montmorillonite to synthetic polymers such as polyvinyl alcohol and Ethylene vinyl acetate. With this in mind, the present study sheds light on the effect of simultaneous application of fibrillated nanocellulose reinforcement system and montmorillonite nanoplates in PAV and EVA polymer matrix in order to improve their biodegradability, mechanical and barrier properties for food packaging.

MATERIALS AND METHODS

Materials
In this study, PVA and EVA polymer matrix (Lotte Group, a Korean-Japanese conglomerate) were used in order to study the effect of polymer type on the produced nanocomposite films. Maleic anhydride and benzoyl peroxide with 99% and 98% purity, respectively; Montmorillonite nanoclay (Montmorillonite K10) with specific surface area of 220-270 gr/m^2 (produced by Sigma-Aldrich Company, USA); and nanofibrillated cellulose in the form of gel with 2.5 w% of plant-based nanocellulose with average length and width of 150*700 nm^2 (produced by Nano Novin Company, Iran) were also used.

Production of Nanocomposite Films
PVA- NFC-MMT Nanocomposite Film
In order to produce this film, certain amount of PVA, Nanofibrillated cellulose and Montmorillonite were manually mixed according to contents of Table 1. Melt blending process of the above compounds was done by means of an internal mixer (Internal mixer, brabender, Germany, 2002) at 200°C within 10 minutes. After the extruded nanocomposite was collected from output device, hot press process (Minitest press, Toyoseiki, Japan) was applied on the respective mixture at 220°C and 10 MPa pressure for 20 minutes in order to produce nanocomposite film with specific dimension and thickness. The produced films were finally cooled down, cut and analyzed.

EVA-NFC-MMT Nanocomposite Film
In order to produce EVA-NFC-MMT nanocomposite film, EVA copolymer was graft by the maleic anhydride in order to improve the hydrophilic properties of polymeric matrix chains. Benzoyl peroxide was used to generate the necessary radicals for grafting. To do so, 45 g of EVA copolymer, 1.8 g of benzoyl peroxide and 4.5 g of maleic anhydride were used for grafting by an internal mixer. When the temperature reached 160°C, grafting was carried out at 80 rpm for 10 minutes. To produce a nanocomposite sample, the maleic anhydride-grafted polymer matrix was escaped from chamber of internal mixer. Then, a certain amount of it together with a certain amount of montmorillonite,

Table 1: Summary of names and composition of nanocomposite films Based on PVA and EVA

Number	Samples	Crude Polymer (%)	Nanocellulose (%)	Montmorillonite (%)	Maleic anhydride (%)	Antioxidant (%)
1	PVA	99.5	0	0	0	0.5
2	PVA-NC	97.5	2	0	0	0.5
3	PVA-MMT	97.5	0	2	0	0.5
4	PVA-NC-MMT	90.5	2	2	5	0.5
5	EVA	99.5	0	0	0	0.5
6	EVA-NC	97.5	2	0	0	0.5
7	EVA-MMT	97.5	0	2	0	05
8	EVA-NC-MMT	9.5	2	2	0	0.5

nanocellulose, and antioxidant were again transferred to feeder of internal mixer, as explained in Table 1. After adjusting the temperature ranges of extruder from 100 to 140°C, the above mixture was fed into the extruder and mixing process was performed at 120 rpm. The extruded nanocomposite was collected and a certain amount of it was subjected to hot pressing at 140°C and 20 MPa pressure in order to produce films with certain dimensions and thicknesses. The produced films were finally cooled down and cut and certain areas of them were tested for identification tests.

Characterization
Field Emission scanning Electron Microscopy (FESEM) and Elemental Analysis

Morphology of surface of Polyvinyl alcohol -nanofibrillated Cellulose- Montmorillonite and Ethylene-vinyl acetate -nanofibrillated Cellulose- Montmorillonite nanocomposite films was studied by means of field emission scanning electron microscopy, Hitachi SU8000 model, manufactured by Czech Republic. Surface and cross-sectional imaging of the samples was also performed by FESEM in low vacuum mode at different magnifications. To prepare an electron microscopy image from surface of the samples, they were first glued to the aluminum base by silver paste. The bases were dried in a coating /dispersive machine up to critical point and were coated with gold for 7 minutes. In order to study the cross-sectional area of films, the samples were broken down in liquid nitrogen. Moreover, the EDX analysis was performed to determine elemental maps of nanocomposite films and illustrate the presence of elements in naocomposite structures by using energy dispersive X-ray spectrometer (MIRA3TESCAN-XMU, Czech Republic).

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (Perkin Elmer, the Q100 model made by USA), was used in order to study the thermal properties. The device was calibrated by indium and silver. The empty aluminum container was used as reference, nitrogen atmosphere was used as a neutral medium and liquid nitrogen was used as a cooling medium. Then, 0.3 g of each sample of weighing film was placed on the aluminum container. Samples without a reinforcing material were scanned at a heating rate of 10°C/min in a temperature range of -100 to 100°C and samples with reinforcing material were scanned in a temperature range of 20 to 240°C in three steps. The melting temperature and glass transition temperature were determined based on heat-temperature curves of the second step. The glass transition temperature was considered as the midpoint between the onset and the end of the second-order endometrial changes in the thermal current curve.

Mechanical Properties

Stretching experiments were performed by using stretching machine (ST503 model made by an Iranian company called Santam Co.) based on ASTM D638 standard. Prior to the experiments, the samples were conditioned at a relative humidity of 55% within 24

hours. The films were cut in rectangular shape with dimensions of 50× 20 ×0.5 mm. The distance between two jaws and their movement speed was chosen 30 mm and 5 mm/min, respectively. Stretching experiments were performed on each sample of film and factors such as maximum force at rupture point and maximum displacement were obtained from the force curve in terms of deformation. Tensile strength (TS_3) at Mpa and elongation to breakpoint (EB_4) at percent was calculated using relations 1 and 2.

$$Ts = \frac{F_{Max}}{A} \tag{1}$$

$$EB = \frac{L_{Max} - L_0}{L_0} \times 100 \tag{2}$$

In which F_{Max} denotes maximum tensile force, A denotes cross-sectional area, L_{Max} denotes maximum length at rupture point and L_0 denotes the initial length of film.

Measurement of Oxygen Permeability (OP)

Oxygen permeability indicated the amount of oxygen penetration through the nanocomposite film. Oxygen permeability test of film samples was performed according to ISO 15105-1 by means of MOCON OX-TRAN oxygen permeation analyzer (2.21 MH model manufactured by USA). The film sample was placed in the gas permeation cell having open testing area of 5 cm². The oxygen as permeation gas and nitrogen as carrier gas were continuously passed through the film in in the counter current form. The experiments were carried out at a temperature of 25°C and relative humidity of 60%. The Oxygen transfer rate (OTR) was recorded and oxygen permeability was calculated based on the following equation:

$$OP\left(\frac{cc}{m2.day.atm}\right) = \frac{OTR \times X}{\Delta P}$$

In which X denotes thickness of sample and denotes differences in partial pressure of oxygen on both sides of film.

Measurement of Biodegradability of Films

The biodegradability test of PVA/EVA films and PVA-NFC-MMT and EVA-NFC-MMT nanocomposite films was performed based on the D6868-03 ASTM standard. To do so, film samples were buried in the soil at a depth of 10 cm. The amount of moisture and microbial concentration in the soil were kept constant by the sprayed wastewater. The lost weight arisen from degradation of films was determined every 30 days for 120 days. After being removed from the soil and rinsed with water, samples were placed in oven at 50°C until constant weight was reached and then they were weighed.

DISCUSSION

Surface Morphology Analysis

Figs. 1a, b and c illustrate the electron microscopy images of PVA-NFC, PVA-MMT, and PVA-NFC-MMT nanocomposite films. As shown in Fig. 1a, the PVA-NFC sample had irregular folding (severe plastic deformation) and surface ablation, which indicated that its structure was not stable in terms of mechanical strength. Also, irregular accumulation of carbon-based flake particles was observed in place of folds. In the PVA-MMT sample (Fig. 1b), the folds were more regular and had a specific pattern as parallel strips. The PVA-NFC-MMT sample enjoyed the desirable and optimal features described for both previous systems in terms of microstructure. Fig. 1 (d, e and f) indicated distribution of nanocellulose and montmorillonite and its composition in ethylene vinyl acetate polymer matrix. As can be seen in the Figure, EVA-NFC and EVA-MMT films showed a non-homogeneous distribution and the accumulation of nanocellulose and montmorillonite within the polymer matrix. It means that the nanoparticles were not able to expand and distribute within the polymer matrix under the operational conditions mentioned in the experimental section of the study. This was due to the difference in the hydrophilicity of nanoparticles and polymers. The ethylene vinyl acetate polymer had relatively hydrophobic chains, but montmorillonite and cellulose nanoparticles had highly hydrophilic groups on their surface, and thus no favorable interactions occurred between the chains and nanoparticles. This problem was more severe in the ethylene vinyl acetate film which contained both cellulose and montmoril-
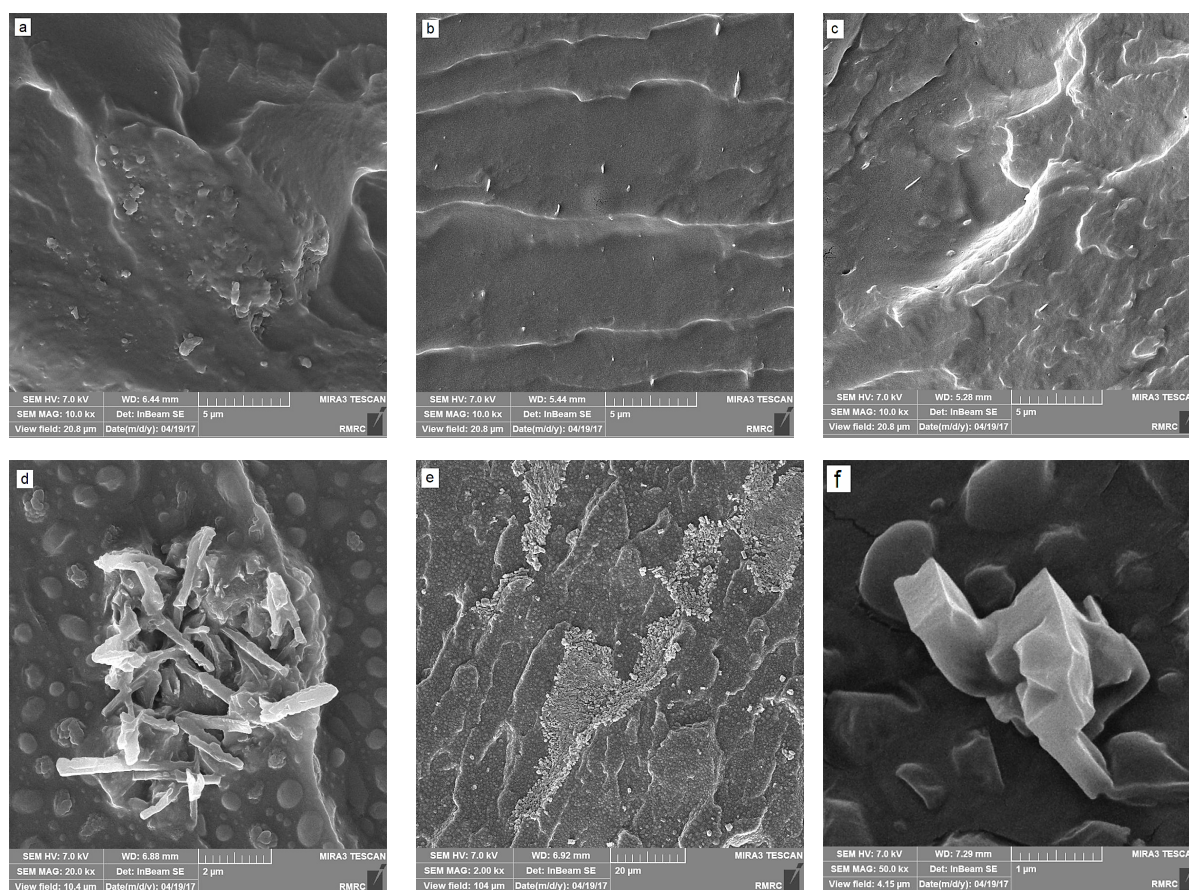
Fig. 1. Scanning Electron Microscopy Images of Nanocomposite Films a) PVA-NC b) PVA-MMT c) PVA-NFC-MMT d) EVA-NFC e) EVA-MMT f) EVA-NFC-MMT

lonite nanoparticles at the same time. Fig. 1(f) shows the presence of single nanocellulosic structures, the agglomerate nanocellulose, and montmorillonite nanoparticle structures. In such condition, the produced nanocomposite film lacked the proper quality and transparency and could not be used as a polymer nanocomposite in food packaging. By adding a small amount of modified copolymer by maleic anhydride, the distribution of nanoparticles and transparency of the produced films were apparently changed. Fig. 1 shows the molecular structure of ethylene-vinyl acetate copolymer modified by maleic anhydride. As can be seen, by addition of maleic anhydride to the structure, the amount of hydrophilic groups was increased on the polymer chain, resulting in an increase in the interaction between the polymer chains and the hydrophilic surface of the nanoparticles. In other words, the addition of a compatibilizer would lead to compatibility between the copolymer chains and nanoparticles; on the one hand, the compatibilizer was bonded to the nanoparticles, and on the other hand it was coupled with the polymer, and thereby caused compatibility of the chain with nanoparticles. This contributed to the improvement of nanoparticle distribution within the polymer matrix. To better illustrate the distribution of nanoparticles, energy dispersive X ray spectroscopy (EDX) analysis was performed.

Fig. 2 (a, b, c and d) shows the distribution of aluminum, silicon and carbon elements in PVA-MMT, PVA-NFC-MMT, EVA-MMT and EVA-NFC-MMT nanocomposite films. It should be noted that in the EDX maps, the aluminum, silicon and carbon elements were shown in blue, red and gray, respectively. Silicon and aluminum elements represented the presence of clay nanoparticles in polymer matrix. As shown in Fig. 2, PVA-NFC-MMT and EVA-NFC-MMT nanocomposite films had a more homogenous elemental distribution compared to PVA-MMT and
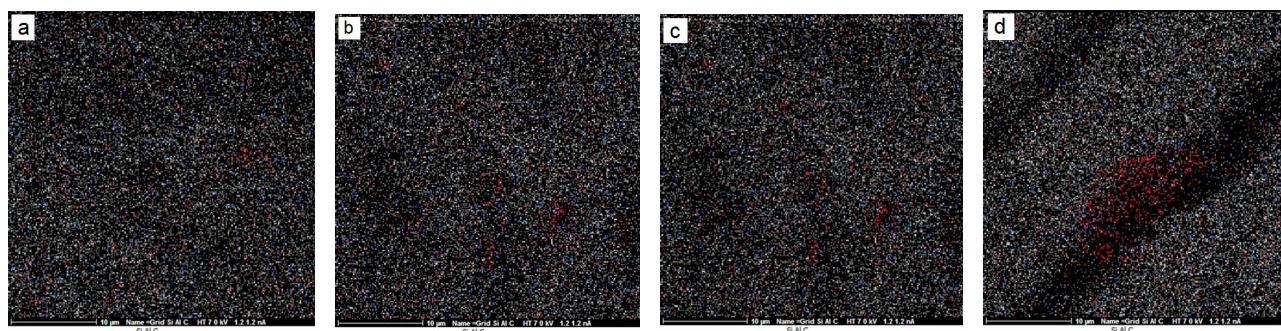
Fig. 2. EDX maps to illustrate the nanoparticles distribution in nanocomposite samples a) PVA-MMT b) PVA-NFC-MMT c) EVA-MMT d) EVA-NFC-MMT

EVA-MMT, indicating excellent interaction of nano-cellulose, montmorillonite and polymer matrix.

Fig. 3 (a-f) shows the EDX spectrums of nanocomposite samples to investigate the presence of elements in polyvinyl alcohol/ethylene vinyl acetate-based nanocomposite films. Considering the changes in the atomic percent of the elements in PVA-MMT and EVA-MMT nanocomposite films, it could be shown that montmorillonite nanoparticles contained two parts of silicon oxide and aluminum oxide in silica and alumina phases, which increased the atomic percent of oxygen, silicon and aluminum relative to EVA-NFC and PVA-NFC samples. Changes in atomic percent of elements in PVA-MMT and EVA-MMT films,

compared to PVA-NFC-MMT and EVA-NFC-MMT showed a better elemental distribution in PVA-MMT and EVA-MMT samples.

Differential Scanning Calorimetry (DSC)
Figs. 4a and b show DSC curves of PVA and EVA films and PVA-NFC-MMT and EVA-NFC-MMT nanocomposites. As seen in the curve above, after the addition of montmorillonite nanoparticles to polyvinyl alcohol film, glass transition temperature of copolymer was increased from 84°C to 96°C and its melting temperature was also increased from 204°C to 207°C. Moreover, the degree of crystallinity for copolymers was increased by about 15%. As shown
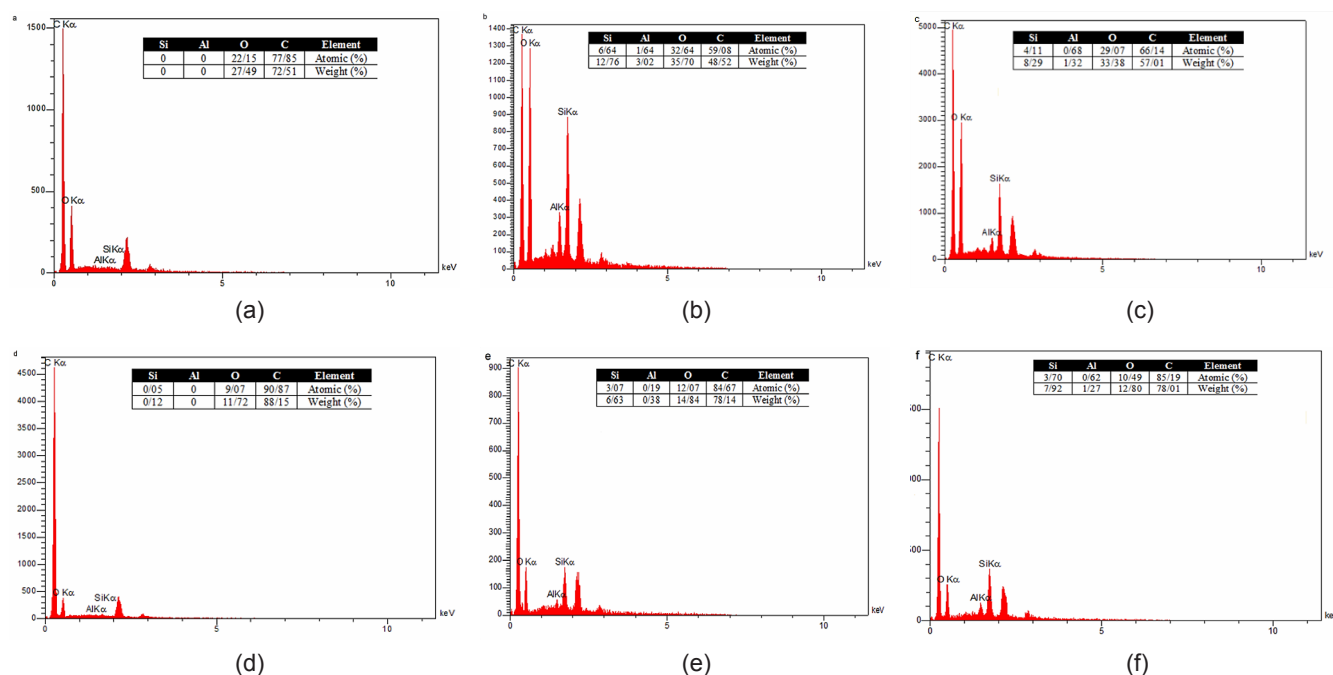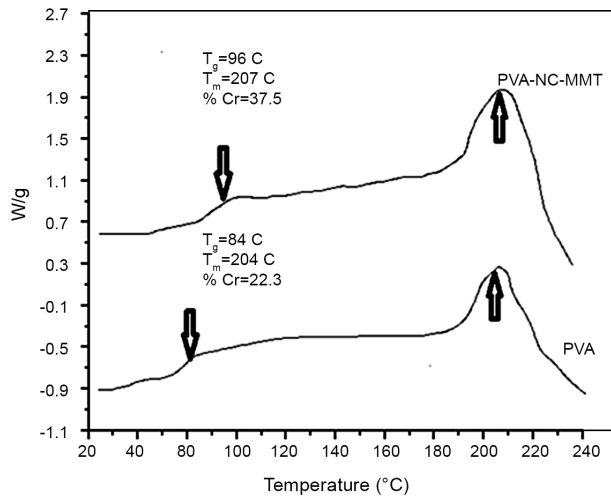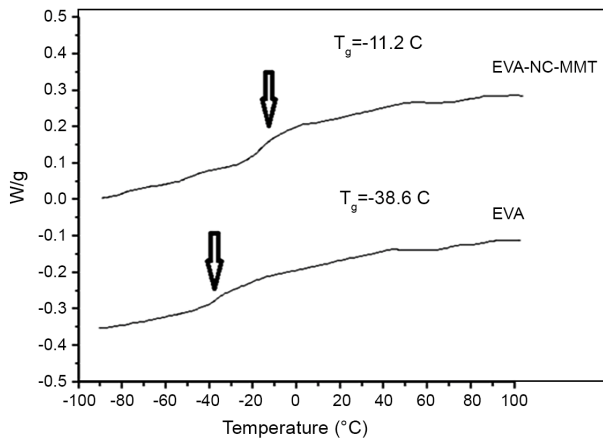

Fig. 3. EDX spectrums to illustrate the presence of elements in nanocomposite films: a) PVA-NFC, b) PVA-MMT, c) PVA-NFC-MMT, d) EVA-NC, e) EVA-MMT and f) EVA-NFC-MMT

(a)

(b)

Fig. 4. DSC curves of nanocomposite films: a) pure PVA and PVA-NFC-MMT b) pure EVA and EVA-NFC-MMT

in Fig. 4b, the EVA film showed the same behavior as PVM-NFC-MMT film after the addition of montmorillonite nanoparticles, so that glass transition temperature of copolymer was increased from -38.6°C to -11.2°C. In fact, by placing polymeric chains in the vicinity of nanoparticles and subsequently the interaction between chains with the surface of the montmorillonite plates and filling of the empty spaces and free volume among chains, movements and rotation of chains were more restricted, thereby leading to an increase in glass transition temperature of the copolymer contained in the nanocomposite film relative to that of raw copolymer. Indeed, new surfaces were formed for nucleation and growth of polymer crystals by adding nanoparticles during the cooling process. These new surfaces and the increased probability of

nucleation on these heterogeneous nuclei could be attributed to the increased degree of crystallinity of the sample containing nanoparticles. Moreover, the slight increases in the melting temperature could be attributed to the enlargement of crystals, which may be justified by an increase in crystallinity percentages of the samples.

The increase in glass transition temperature, melting temperature and degree of crystallinity is a good advantage for polymeric nanocomposite films used in food packaging. Indeed, because of the slower movement of the chains and filling of empty spaces between them and nanoparticles as well as new crystals, the paths for penetration of air molecule into the molecular pores of the polymeric film got more curvilinear, more restrictive and inflexible, which in turn played a very positive role in reducing the permeability of a polymeric nanocomposite film used in packaging. The increase in glass transition temperature and degree of crystallinity was directly related to the reduced permeability and the increased strength of polymer films.

Mechanical Properties

A biodegradable film should be resistant to the natural stresses arisen from transportation and protect the packaged food against external factors (Elsabee and Abdou, 2013). Therefore, the mechanical properties of food packaging film including its strength and durability are of great importance. The mechanical properties of PVA and EVA films and their nanocomposite films containing nanocellulose and montmorillonite were investigated and their stress-strain graph was shown in Fig 5. Generally, tensile strength of pure PVA and EVA films was less than that of nanocomposite films. The increase in the tensile strength of the PVA-NFC-MMT and EVA-NFC-MMT nanocomposite films may be due to the adhesion between rigid nanocellulose chains and the polymer, the homogeneous distribution of the montmorillonite nanoplates in the polymer matrix, and the penetration of polymer chains between its plates (Sarwar *et al.*, 2018). On the other hand, simultaneous presence of nanocellulose and montmorillonite reduced the increased length at rupture point of PVA and EVA films. The increased crystallinity and the reduced mobility of the molecular chains due to the bonding between the polymer and the nanometer-
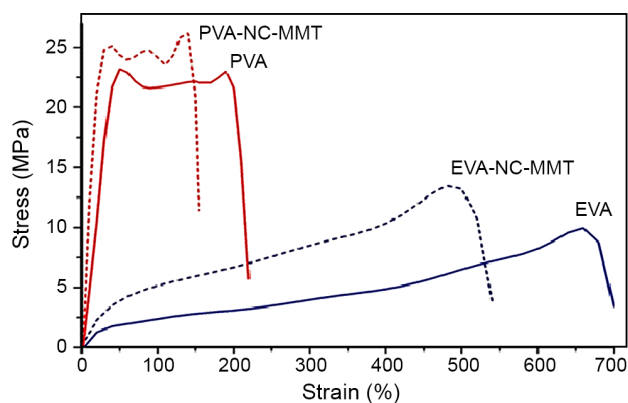
Fig. 5. Stress-strain curves of pure PVA, PVA-NFC-MMT and pure EVA, EVA-NFC-MMT

Fig. 6. Weight-loss profile of: pure PVA and EVA films, PVA-NFC-MMT and EVA-NFC-MMT nanocomposite films.

sized fillers may cause a decrease in strain at break-point (Sarwar *et al.*, 2018; Mittal *et al.*, 2016). It was also been proven by the results of the DSC analysis.

Oxygen Permeability

Oxidative changes due to exposure to oxygen are another cause of corruption and the reduced quality, especially in fatty foods. For this reason, oxygen permeability rate is another important feature that should be considered when choosing the suitable polymer for food packaging (Almasi *et al.*, 2013). The degree of oxygen permeability in nanocomposite films depends on the physical properties and molecular weight of the reinforcing materials as well as changes in chemical structure of film due to the chemical interactions and oxygen adsorption (Cárdenas *et al.*, 2009). The results from the oxygen permeability of pure polyvinyl alcohol and ethylene vinyl acetate films and their resulting nanocomposite films in a relative humidity of 60% were shown that the oxygen permeability in polyvinyl alcohol and ethylene vinyl acetate raw samples was 28.5 and 760 cc/m^2.day.atm, respectively, which was decreased to 3.7 and 114cc/m^2.day.atm after simultaneous addition of nanocellulose and montmorillonite. This indicated that permeability of PVA and EVA film would decrease significantly after addition of 2 w% of nanocellulose and montmorillonite. The results from the oxygen permeability test showed that cellulose nanofiber and montmorillonite nanoplate may have a positive effect on the increased coherence between the polymer fibers and the reduced free space between them. As a result, a lower amount of oxygen could penetrate and pass through the polymer matrix. More-
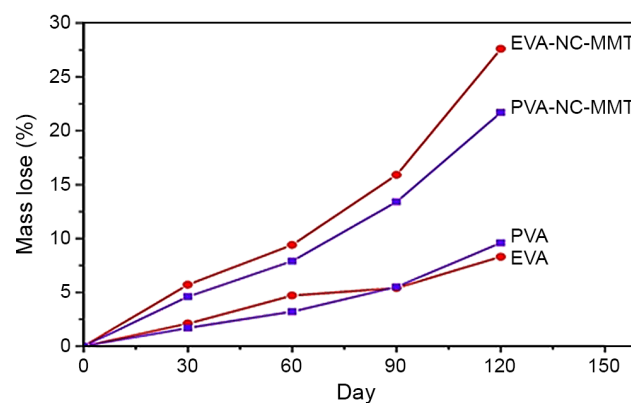
over, Cellulose nanofibrils and montmorillonite nanoplate created a tortuous path by forming a disorderly network that resulted in a decrease in the penetration and movement of oxygen within the spaces between the polymer networks (Huang *et al.*, 2017).

Biodegradability Test

The biodegradability process consisted of three steps: (1) the growth of microorganisms on the polymer matrix surface; (2) the continued growth of microorganisms using the polymer matrix components; and (3) the initial and final degradation of the polymer (Sonia and Dasan, 2013). In the present study, the biodegradability rate of raw PVA and EVA films and PVA-NFC-MMT and EVA-NFC-MMT nanocomposite films were determined under soil burial conditions. Fig. 6 displays the amount of weight loss of film samples during 120 days. As can be seen in the Figure, weight loss percentage was increased in all samples over time. Raw PVA and EVA films lost less than 2% of their weight after 30 days, while PVA-NFC-MMT and EVA-NFC-MMT samples lost 4% and 6% of their weight respectively. Pure PVA and EVA films' resistance to microorganisms could be attributed to the hydrophobic nature of these polymers. On the other hand, the amount of weight loss in raw samples of PVA and EVA was increased to 8 and 7%, and that of polyvinyl alcohol and ethylene vinyl acetate was increased to 22 and 27% after 120 days. In fact, the microorganisms in the soil helped to degradation of films through their growth and the use of the enzymatic and acidic by-products generated by their metabolism (Roy *et al.*, 2012). The increased degradation of PVA-NFC-MMT

and EVA-NFC-MMT nanocomposite films was due to the hydrophilic nature of nanocellulose and montmorillonite, which allowed microorganisms such as bacteria and fungi to enter into polymer matrix in order to access water as a culture medium. In this condition, the level of exposure, hydrophilicity and permeability, and so degradation of films would be increased (Tharanathan, 2003).

CONCLUSIONS

Due to high level and high length of fiber, cellulose nanofibrils and montmorillonite were simultaneously used as nanometer-sized reinforcing material in the polymer matrix of PVA and EVA- based films. Scanning Electron Microscopy showed the uniform dispersion of nanocellulose and montmorillonite nanoplates in PVA and EVA polymer matrix. The results of DSC showed an increase in the glass transition temperature and the degree of crystallinity of films containing nanocellulose and montmorillonite. Oxygen permeability was significantly reduced in the presence of nanometric fillers which created a tortuous path that restricted penetration of oxygen into polymer matrix. Having been placed within polymeric chains and bonded with them, nanocellulose and montmorillonite contributed to the increased mechanical strength of film and the decreased length at rupture point. Based on the biodegradability test, biodegradability of PVA-NC-MMT and EVA-NFC-MMT films was significantly increased after 120 days, compared to that of raw samples. Finally, it may be concluded that addition of cellulose nanofibrils and montmorillonite did not decrease transparency of PVA and EVA films, on the contrary, it helped improve the mechanical properties, reduce oxygen permeability and increase biodegradability. Consequently, cellulose nanofibrils and montmorillonite could be used in food packaging by enhancing their above-mentioned properties.

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