RESEARCH PAPER

Nanocomposites for Packaging Applications: Synthesis, Characterization, Thermal and Microbial Degradation of Its Residues for Plant Growth

Zahra Abbasi[*1], Hossein Motamedi[2], Zinat Zirrahi[3], Mehdi Taghavi[4], Abdolhadi Farrokhnia[4], Ermia Aghaie[5] and Yashar Behnamian[6]

1. Faculty of Science, Ilam University, P.O.Box 69315516, Ilam, Iran.
2. Department of Biology, Faculty of Science, Biotechnology and Biological Science Research Center, Shahid Chamran University of Ahvaz, Ahvaz, Iran.
3. Department of Biology, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran.
4. Chemistry Department, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran.
5. School of Engineering, University of British Columbia - Okanagan, 1137 Alumni Avenue, Kelowna, V1V 1V7, Canada.
6. Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G1H9, Canada.

ABSTRACT
Environmental pollution, caused by traditional plastic packaging, has recently become more severe due to non-biodegradable nature of petroleum-based plastics. The present research studies the preparation of polyvinyl alcohol (PVOH)/Starch (ST)/Humic Acid (HA) contained sodium montmorillonite clay (MMT) as a plastic packaging method. It also investigates biodegradability of films in terms of microbial and thermal degradation and their residual effect on plant growth. For doing so, the research utilizes Broido Technique to obtain the activation energy of the films' thermal degradation. The influence of HA/MMT ratio on the surface morphology and physical characteristics has also been assessed, using the Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscope (SEM), and thermogravimetric analysis (TA). After 12 days of microbial degradation, the total remaining solids are 32.12 wt% (PVOH/ST/HA (3%)/MMT (1%)); 48.17 wt% (PVOH/ST/HA (3%)/MMT (3%)), and 58.82 wt% (PVOH/ST/HA (1%)/MMT (3%)). The research shows that the highest activation energy for PVOH/ST/HA (3%)/MMT (3%) is 75 kJ/mol.
Keywords: Microbial degradation; Broido method; Thermogravimetric; Thermal degradation

INTRODUCTION

Plastic materials are one of the most popular and indispensable materials, which is basically due to their flexibility, toughness, excellent barrier, and physical properties. Due to the superior properties of polymeric materials including, high stability, ease of fabrication, mechanical and thermal properties, they have gained significant attention from researchers (Katherine, 2008; Aiqin, 2014). They are unique in chemical composition, mechanical, and

* Corresponding author: Z. Abbasi, Faculty of Science, Ilam University, P.O.Box 69315516, Ilam. Iran. Tel. Number: 00989188422775, E-mail: Zahra.abbasi886@gmail.com

physical properties (Lawrimore et al. 2016). The use of synthetic polymeric materials has triggered substantial environmental issues. Solid waste from these materials is a significant contributor to environmental pollution as it requires thousands of years to degrade (Taghizadeh et al., 2012). The environmental pollution resulted from traditional plastic packaging has become more serious due to the non-biodegradable nature of petroleum-based plastics. Therefore, there is a necessity to acquire new packaging materials (Ding et al., 2020). The physical and chemical characteristics of nanoparticles are essential for their activity, ability, biodistribution and protection. Therefore, characterizations of nanomaterials are essential to estimate the uses of the extended particles (Chen, 2020).

Another essential is the recyclability of polymer nanocomposite materials. Plastic waste is a global problem, and the doubling of global plastic production over the next decade is expected to have a significant adverse effect on the environment due to its lack of environmental degradability (GreenFacts, 2020).

Many plastics are blends of plastic components such as polymers and additives to improve the characteristics of the ultimate product. In this respect, various studies have been conducted to design new packaging to reduce the residence time using renewable sources and biodegradable materials. Forward with biodegradability, other properties must be considered and performed (Guo-Xiang, 2008; Michal, 2010; Boyle et al., 2019). It is crucial to develop to develop some biodegradable materials to reduce environmental pollution, providing convenience for daily life (Emamhadi et al., 2020). With the development of modern biotechnology, biodegradable films as eco-friendly materials have become the topic of many projects and research studies (da Silva, 2019; Fonseca-García et al., 2021; Wu et al., 2017; Imen, 2017). Some studies (Yachuan, 2014; Lawrimore, 2016; Ju, 2019; Mei, 2020) demonstrated the potential of the organo-clays for starch-based polymer nanocomposites to be used for improving the mechanical characteristics over the unfilled formulations. Table 1 describes some of the studies performed and the improvement of the properties of composite with fillers.

Table 1. Bio-nanocomposites for food packaging applications

Polymers	Filler Type	Improved Features	References
GEO/PP	SiO$_2$	antimicrobial	(Ellahi et al., 2020)
PLA	SiO$_2$	decrease in oxygen permeability	(Sepulveda et al., 2020)
Gelatin–Chitosan	SiO$_2$	barrier and mechanical	(Batra et al., 2020)
Poly (vinyl alcohol-co-ethylene)	MMT	thermal and mechanical	(Seethamraju et al., 2013)
LDPE	ZnO	antimicrobial	(Rojas et al., 2019)
PLA	Nano-magnesium oxide	antibacterial	(Swaroop et al., 2018)
PA/PE	Cloisite 30B and Dellite 43B	barrier and mechanical	(Garofalo et al., 2018)
Gelatin/ Starch	Nano-Cellulose	tensile strength	(Noorbakhsh-Soltani et al., 2018)

GEO= gum essential oil of Pistacia atlantica tree, PP= Polypropylene, PE= Polyethylene, PA= Polyamide, PLA= Polylactic acid, LDPE= low-density polyethylene

In this study, polyvinyl alcohol (PVOH)/ Starch (ST)/ Humic acid (HA)/ montmorillonite (MMT) blend films were prepared using the solution casting technique. The biodegradability of these films was assessed based on treatment with Bacillus subtilis through burial in soil.

This work aimed to assess the influence of the montmorillonite clay and humic acid content on the thermal and microbial degradation of prepared film. The outcome of these films in soli plays a vital role in soil fertility and plant nutrition.

MATERIALS AND METHODS

Starch (ST), polyvinyl alcohol (PVOH) with Mn= 72,000 and glycerol (Mn= 92/10, 78% purity) were obtained from Merck Chemicals Co. The sodium montmorillonite was purchased from Nanocor Inc. The sodium montmorillonite had a d_{001}-spacing of 12.5 Å cation exchange capacity (CEC) of 145 mequiv/100 g, and an aspect ratio of 200-400. The humic acid was purchased from Sigma-Aldrich. In this study, the *Bacillus subtilis* (ATCC 6633) was selected as a bacterial species. This bacterium was cultured in nutrient broth (Merck, Germany) and incubated for 24 h at 37 $^{\circ}$C (Pinkee, 2012; Nowak, 2011; Iman, 2017). The Fourier transform infrared (FT-IR) spectra of the polymer blends were obtained at room temperature using a Perkin Elmer spectrophotometer with 4 cm^{-1} resolutions. The surface topography of the films prior and after the biodegradation was evaluated using a scanning electron microscope (SEM, XL30 model, Netherland). Before the SEM analysis, the samples were coated with pure gold with a thickness of 100 A˚. Thermal analysis (TA) is used to evaluate the properties of materials as they change with temperature. The thermal analysis was carried out using a Simultaneous Thermal Analyzer STA 503 at a heating rate of 10 °C/min under the Ar atmosphere, from ambient temperature to 1200 °C using 10.25 mg of specimen in the Al_2O_3 crucibles.

15 mL of distilled water was measured and then mixed with the montmorillonite (MMT) for 24 h at ambient temperature. The clay ratios were 1% and 3% (w/w), relative to dry blend. The films were prepared using the casting method (Taghizadeh and Sabouri, 2013). First, 2 gr of PVOH was dissolved in 50 mL of distilled water at 70 °C, and then 2 gr of starch was dissolved in 15 mL of distilled water. Afterward, in order to obtain a clear solution, the glycerol (4 mL/100 g starch) was mixed with 20 mL of boiling water. Then, the blends of PVOH/Starch/HA/MMT were prepared by adding dropwise the PVOH and starch aqueous solution and the HA (1 and 3 w/w) to the MMT dispersion, and stirred for 4 h at 70 °C. In order to prepare the composite films, a required amount of dispersion was casted on a Teflon plate, and then the water was allowed to evaporate at the ambient temperature. Then, the PVOH/Starch/HA/MMT 50/50/3% (w/w) /3% (w/w), 50/50/1% (w/w)/3% (w/w) and 50/50/3% (w/w)/1% (w/w), containing small amounts of glycerol for plasticizers were examined.

The bacterial degradation of films was studied following the Kathirasan method (Kathiresan 2004). The films were cut into small pieces (5 cm × 3 cm) with about 0.1 g weight and were buried at a depth of 3 cm in the soil. Two different pots (1L) were filled with soil. The specimens were cut into 5 cm × 3 cm pieces and buried in the soil. The microbial degradation of the samples was evaluated every 12 days. Each sample was removed carefully from the soil and washed with distilled water to separate the soil from the film. Then it was dried under vacuum until the weight remained u. The degree of degradation, DD (%), was calculated using Equation 1

$$DD\% = \frac{W_I - W_F}{W_I} \times 100 \tag{1}$$

Where W_F is the dry weight and W_I is the initial weight of films. The effect of this soil on the bean growth was investigated, as well.

Dynamic TGA methods can evaluate the chemical and physical processes that occurred during the polymer degradation. In the kinetic techniques (Pallab, 2017); E_a is the apparent activation energy (kJ/mol), A is the pre-exponential factor (min^{-1}), n is the apparent order of reaction, T is the temperature (K), R is the universal gas constant (8.3136 J/K.mol), α is the degree of conversion, k is the rate constant (s^{-1}), t is the time (min), and β is the heating rate ($^{\circ}$C/min). The basic rate equation (Equation 2) is typically used in kinetic studies.

$$da/dt = k. f(a) \tag{2}$$

Equation 2 presents the conversion rate, dα/dt, at a constant temperature versus the reactant concentration loss and rate constant. In the TGA analysis, the conversion [α (t)] is defined as the ratio of the mass loss at time t to the total mass loss, corresponding to a particular stage of degradation.

$$\alpha(t)=[W_0-W_t]/[W_0-W_\infty] \tag{3}$$

Where W_0 is the initial mass of the specimen, W_t is the sample mass at time t, and w_∞ is the sample mass at infinite time. In the polymer degradation process, the conversion rate is proportional to the material concentration that should react.

$$f(\alpha)=(1-\alpha)^n \tag{4}$$

Combining these equations and the empirical Arrhenius expression provides the Equation 5.

$$Da/dt =A.(1-a)^n .\exp(-E_a/RT) \tag{5}$$

Introducing the heating rate, β into Equation (5):

$$da/(1-a)^n =A/\beta.\exp(-Ea / RT).dT \tag{6}$$

This is the fundamental expression of analytical techniques to obtain the kinetic parameters based on the TGA experimental data.

RESULTS AND DISCUSSION

Figure 1 demonstrates the effect of the broth culture of *Bacillus subtilis* on the nanocomposite film (PVOH-ST-HA3-MMT3). Therefore, it seems the film has been degraded following the microbial inoculation.
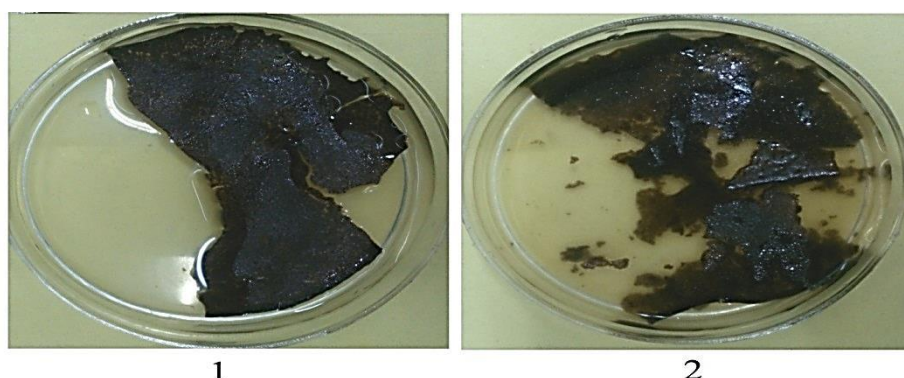
Fig 1. Effect of *B. subtilis* on film (PVOH-ST-HA (3%)-MMT (3%), (1) after 10 min., and (2) after 12 h.

The soil burial test was assessed by evaluating the film weight loss over time. Figure 2 reveals the weight loss of the three films in the soil.
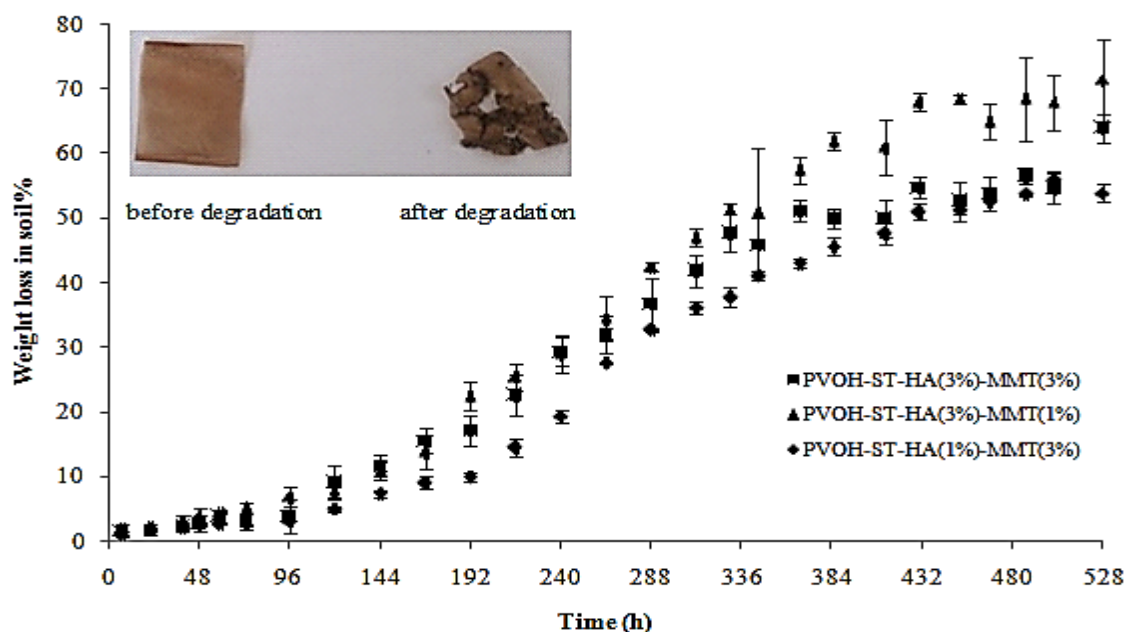

Fig 2. Weight loss (%) of the three films in soil. Values are mean± standard deviation (n=3).

As shown in Figure 2, the biodegradability raised up to 57% as the burial time increased in the soil. During 12 h it was observed that all of the films in soil and compost degraded. The total amounts of the remained solids after 12 days were 32.12 wt% PVOH/ST/HA (3%)/MMT (1%), 48.17 wt% PVOH/ST/HA (3%)/MMT (3%), and 58.82 wt% PVOH/ST/HA (1%)/MMT (3%). The MMT's hydroxyl groups are capable of forming a strong hydrogen bond with the hydroxyl groups on the PVOH, ST and the hydroxyl and carboxyl groups on HA.
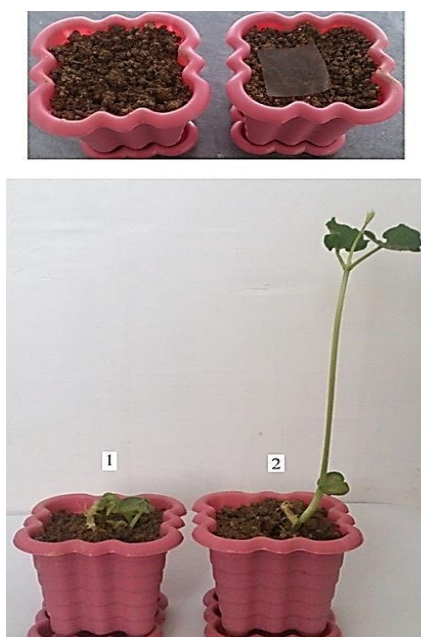
Fig 3. Growth of bean after 7 days, (1): Without fertilization with degraded PVOH-ST-HA (3%)-MMT (3%) film and (2): following in present film fertilization with degraded PVOH-ST-HA (3%)-MMT (3%) film.

Therefore, the molecules interactions, the biopolymer matrix cohesiveness, and biodegradation will improve. Figure 3 shows the effect of the PVOH-ST-HA (3%)-MMT (3%) film degradation on soil fertility and plant nutrition.

The structural analysis is a key parameter for identifying the structural changes that occurs during the degradation which is the cause of the weight loss. Figure 4 illustrates the FT-IR spectrum of the undegraded and degraded nanocomposites in the presence of the *Bacillus subtilis*. In this research study, we evaluated the absorption pattern in eight main regions including, stretching vibration of the O–H group and N–H stretching between 3455 and 3230 cm^{-1}, stretching vibration of the C=O at about 1726 cm^{-1}, stretching vibration of the C=C at about 1638 cm^{-1}, stretching vibration of the C–O at about 1237 cm^{-1}, stretching vibration of the C–H at about 2945 cm^{-1}, stretching vibration of the COO^{-} group between 1500 and 1600 cm^{-1} and for HA two peaks were observed in this region (around 2925 and around 2854 cm^{-1}). The aforementioned absorption peaks are ascribed, respectively, to the asymmetrical and symmetrical stretching of methylene (-CH$_2$-) groups which are the properties of the aliphatic and constrained cyclic hydrocarbons. FT-IR is so sensitive to the local molecular environment and it has been extensively utilized to evaluate the macromolecules' interactions during the PVOH/ST/HA/MMT degradation. The absorbances at 1166 cm^{-1} and 1026 cm^{-1} are highly sensitive to the conformational changes occurred through the degradation processes, demonstrating a short-range order and helicity variations when the crystallinity and molecular orientation are disappeared (Giannakas, 2020). The peak intensity at 1166 cm^{-1} and 1026 cm^{-1} was reduced after the microbial degradation. This indicated the action of *Bacillus subtilis* in cleaving the glycosidic linkages of starch. The FT-IR spectra of the residue showed that the absorbance at 1044 cm^{-1} and 1650 cm^{-1} are due to vibration of Si-O and aromatic structure created the barrier influence of the mineral clay, respectively. The absorption peak at the range of 1055-1150 cm^{-1} that corresponded to the (C–O–C) is a shoulder in the spectra of the undegraded films. This also is a well-defined band in the degraded ones, demonstrating the crosslinking of the PVOH. The films' spectra showed the typical bands below 1500 cm^{-1}, where the glucose molecules vibrations dominate (Gómez-Aldapa et al., 2020).
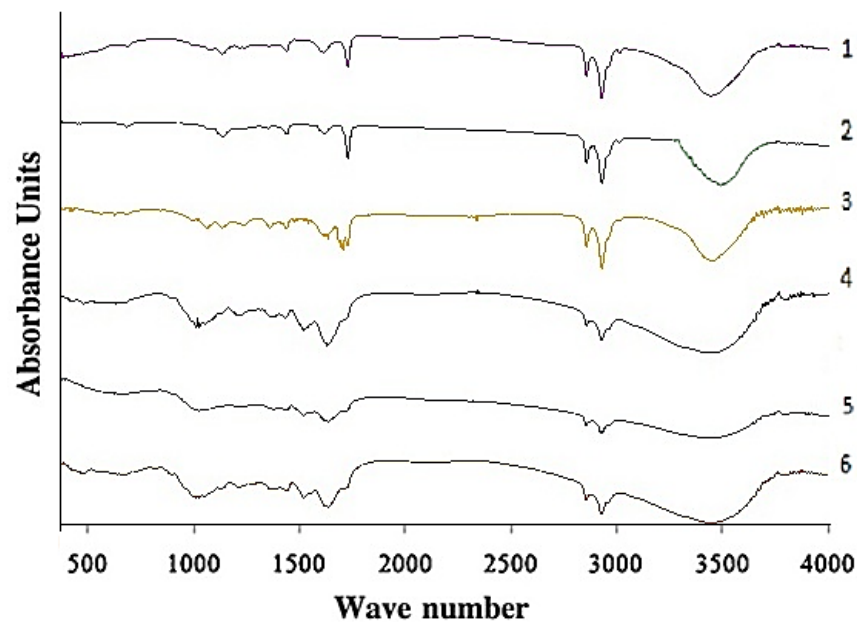
Fig 4. FT-IR spectra of nanocomposite films: (1) PVOH/ST/HA (3%)/MMT (3%) undegraded; (2) PVOH/ST/HA (1%)/MMT (3%) undegraded; (3) PVOH/ST/HA (3%)/MMT (1%) undegraded; (4) PVOH/ST/HA (3%)/MMT (3%) degraded; (5) PVOH/ST/HA (1%)/MMT (3%) degraded; (6) PVOH/ST/HA (3%)/MMT (1%) degraded.

Figure 5 compares the changes on the surface of the PVOH/ST/HA/MMT films control before and after the degradation. By comparing the SEM images in Figure 5 (a)-(f), it can be clearly seen that, that porosity, heterogeneity, and roughness of the specimens were reduced as a function of content MMT and increased as a function of content HA between the control (smooth) and more degraded samples (528 h) being rougher. In addition, it was found that the PVOH/ST/HA (3%)/MMT (1%) had the highest degradation and PVOH/ST/HA (1%)/MMT (3%) the lowest degradation.
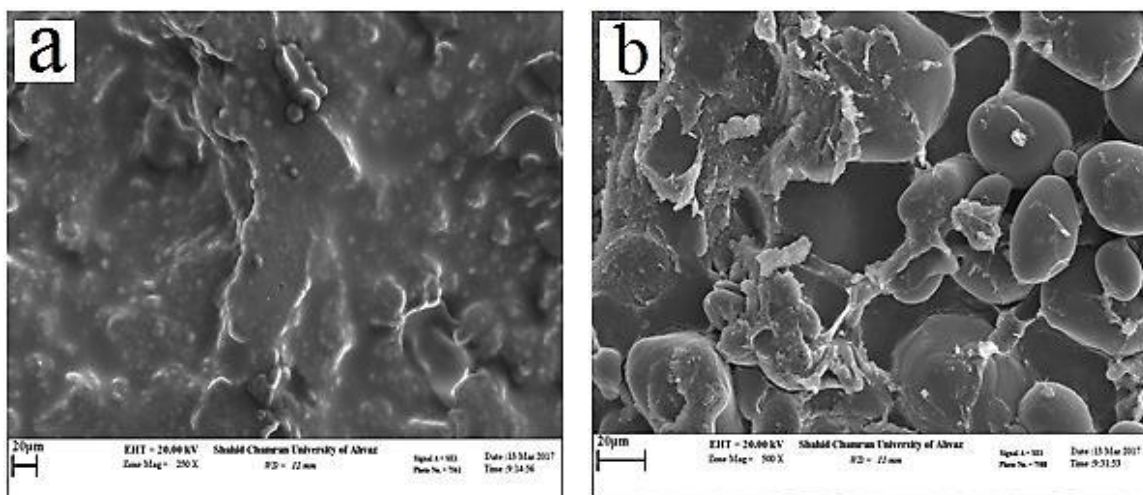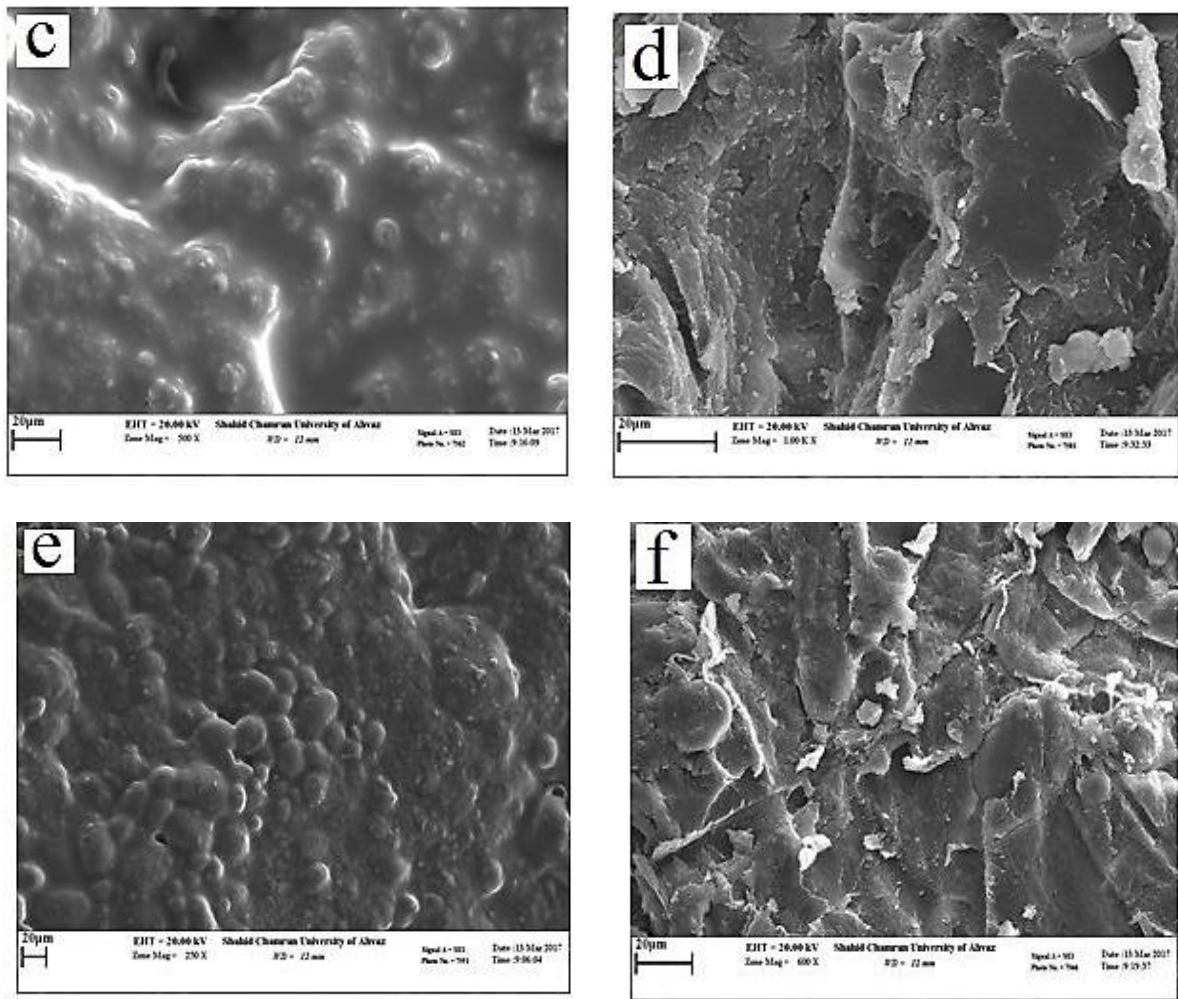
Fig 5. Scanning electron micrographs of PVOH/ST/HA/MMT degradable films in 12 days of microbial degradation due to the action of *Bacillus subtilis*: (a) PVOH/ST/HA (3%)/MMT (1%) undegraded; (b) PVOH/ST/HA (3%)/MMT (1%) degraded; (c) PVOH/ST/HA (3%)/MMT (3%) undegraded; (d) PVOH/ST/HA (3%)/MMT (3%) degraded; (e) PVOH/ST/HA (1%)/MMT (3%) undegraded; (f) PVOH/ST/HA (1%)/MMT (3%) degraded.

The derivative thermogravimetry (DTG) and thermogravimetric analysis (TGA) can be utilized to assess the thermal stability and degradation extent in polymeric materials. TGA, DTA and DTG curves for PVOH/ST/HA (3%)/MMT (3%), PVOH/ST/HA (1%)/MMT (3%) and PVOH/ST/HA (3%)/MMT (1%) blend at the heating rate of 10 $^{°}$C/min are demonstrated in Figure 6. As seen, the nanocomposites depicted a fourth-step degradation pattern. Since the samples have a small amount of adsorbed water, the first stages of degradation (up to around 190 °C) show the water evaporation and volatilization of the easily degraded components including glycerol. The main mass loss occurred in the step two (at the range of 220-380 °C), where weight loss was mainly the characteristic degradation of a polymer structure (HA, MMT and starch decomposition and water elimination of PVOH) (Zhao, 2006). The step two was found to be the main degradation process, so this range of temperature was chosen for the kinetic evaluation, followed by a lower mass loss in the step three (at the range of 400-430 °C). Zhou *et al*. (Zhou et al., 2009) evaluated the thermal stability of MMT and reported that the onset decomposition temperature of the resultant organically modified layered silicates was at around 180 °C and the thermal decomposition of organic substances between silicate layers was found to be at the range of 200-500 °C. In the fourth step (from about 900 to 1100

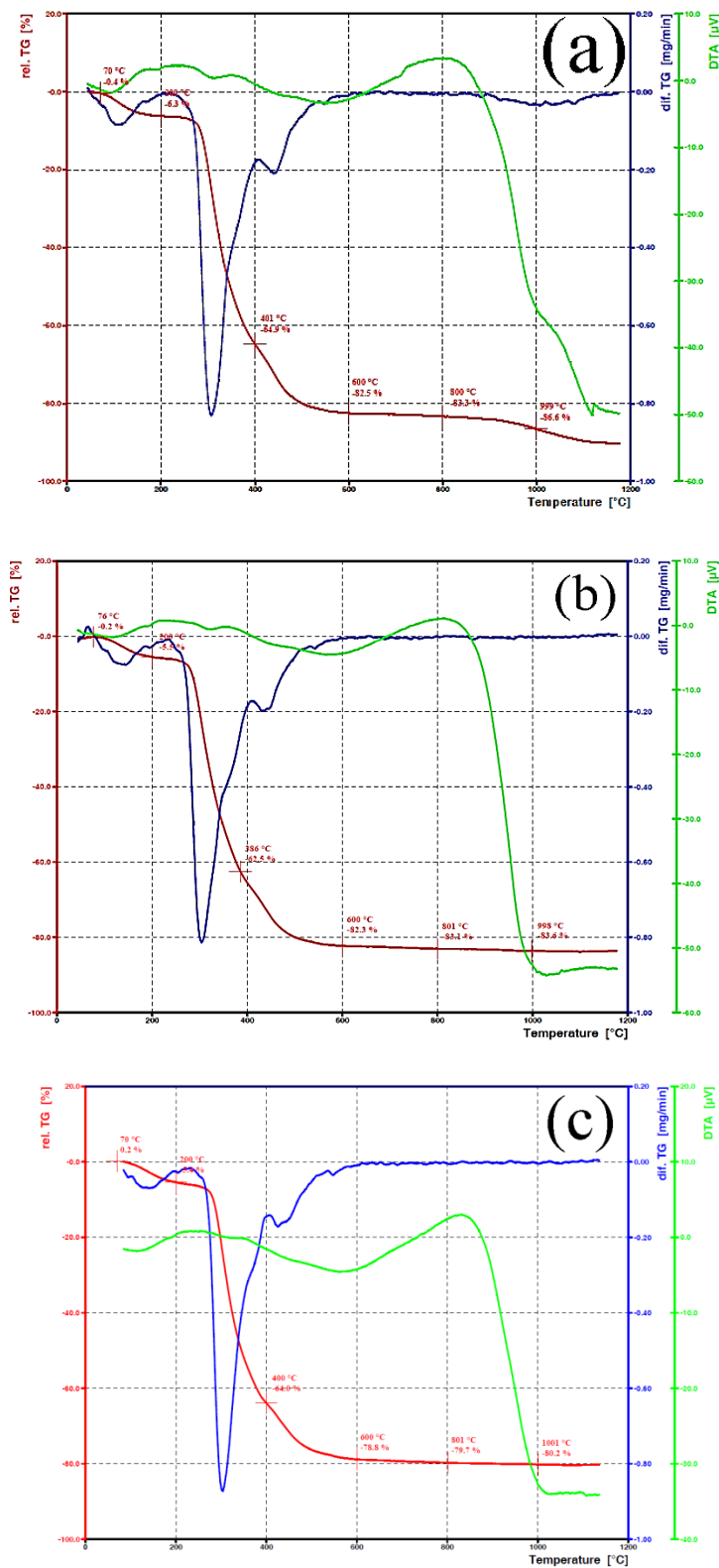°C) further heating broke down the polymer's backbone and HA (cracking of PVOH/ST and broken structure HA).

Fig 6. The TGA, DTA and DTG curves for nanocomposites at heating rate 10 ^{0}C/min.: (a) PVOH/ST/HA (1%)/MMT (3%); (b) PVOH/ST/HA (3%)/MMT (1%); (c) PVOH/ST/HA (3%)/MMT (3%).

The polymers' thermal degradation is molecular deterioration resulted from the overheating. At increased temperatures, the components of the long-chain backbone of the polymer may break (chain scission), reacting with each other to alter the properties of the polymer.

TGA is an appropriate technique to assess the polymeric systems' thermal stability. Table 2 presents the thermal analysis data extracted from the TGA thermograms. For the thermal degradation processes, the Ea, activation energy was investigated using the Broido equation (Equation 7).

$$-\log[-\log(1-\alpha)] = \frac{E_a}{2.303\,R} \cdot \left(\frac{1}{T}\right) + C \tag{7}$$

Where α is the fractional mass loss, E_a is the apparent activation energy (kJ/mol), T is the temperature (K), C is a constant, and R is the universal gas constant (8.3136 J/K.mol). The thermal degradation rate is dependent upon the conversion (α). The degradation rate (as a function of conversion) is obtained from the experimental data (Figure 7).
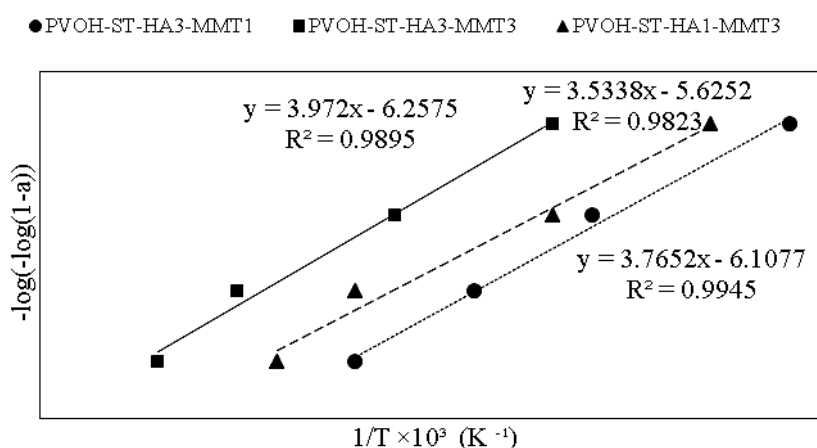

Fig 7. Application of Broido method to films with different conversion 0.3-0.6.

Table 3 presents the activation energy (E) values for all the blends obtained using Equation 7. The activation energy of the PVOH-ST-HA (3%)-MMT (3%) blend is higher than that of the PVOH-ST-HA (1%)-MMT (3%) and PVOH-ST-HA (3%)-MMT (1%), so the MMT significantly improved the films' thermal stability.

Table 2. Thermal data obtained from TGA thermograms, positions of the mass loss of all processes (exception first peak) in all the studied nanocomposites.

Sample	PVOH-ST-HA (1%)-MMT (3%)	PVOH-ST-HA (3%)-MMT (1%)	PVOH-ST-HA (3%)-MMT (3%)
Second peak (^{0}C)	200	200	201
Third peak (^{0}C)	401	386	400
Fourth peak (^{0}C)	600	600	600
Fifth peak (^{0}C)	800	801	801
Sixth peak (^{0}C)	999	998	1001

The lowest Ea value was for the PVOH-ST-HA (3%)-MMT (1%) composite compared with that of the other composites. This might be because of the lower energy needed to remove the volatile components and low-molecular weight materials in the low MMT.

Table 3 The activation energy (E) values of all the blends.

Method	Broido
Sample	E(kJ/mol), (250-400 $^{\circ}$C)
PVOH-ST-HA(1%)-MMT(3%)	72
PVOH-ST-HA(3%)-MMT(1%)	68
PVOH-ST-HA(3%)-MMT(3%)	75

CONCLUSION

This research study discussed the effects of HA and MMT on the biodegradability and thermal degradation of the PVOH/ST/HA/MMT nanocomposites. The influence of the HA content on the biodegradability of the tested films was assessed by obtaining the weight loss of samples buried to the soil until 12 days. The weight loss of the films was increased by enhancing the HA content and decreased with increasing the MMT. The exposure time into soil indicated the starting of the degradation process. The combination of polyvinyl alcohol, starch, montmorillonite and humic acid can be used as a plastic packaging, increasing the concentration of the plant growth present in the humic acid and in soil fertility. Thermal stability of the blends that treated with MMT was fund to be higher compared to the one treated with HA.

GRANT SUPPORT DETAILS

The present research did not receive any financial support.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

REFERENCE

Aiqin, D., Jie, X., Qian, L., Dan, L. and Po, H. (2014). Rheological and thermal behavior of PVA/starch blends modified by acrylic acid. Polym Eng Sci., 54(10); 2449-2454.

Batra, M., and Mitra, J. (2020). Enhancing the properties of gelatin–chitosan bionanocomposite films by incorporation of silica nanoparticles. J. Process Eng., 43; 13329.

Boyle, K.K., Kuo, F.C., Horcajada, J. P., Hughes, H., Cavagnaro, L. and Marculescu, C. (2019). General assembly, treatment, antimicrobials: proceedings of international consensus on orthopedic infections. J. Arthroplasty., 34; 225–237.

Chen, L., Ao, F., Ge, X., and Shen, W. (2020). Food-grade Pickering emulsions: preparation, stabilization and applications. Molecules., 25;3202.

da Silva, T. F., Menezes, F., Montagna, L. S., Lemes, A. P., and Passador, F. R. (2019). Effect of lignin as accelerator of the biodegradation process of poly (lactic acid)/lignin composites. Mater. Sci. Eng. B., 251;114441.

Ding, L., Li, X., Hu, L., Zhang, Y., and Mao, Z. (2020). A naked-eye detection polyvinyl alcohol/cellulose-based pH sensor for intelligent packaging. Carbohydr. Polym., 233;115859

Ellahi, H., Khalili Sadrabad, E., Hekmati moghaddam, S., Jebali, A.; Sarmast, E. and Akrami Mohajeri, F. (2020). Application of essential oil of Pistacia atlantica Gum, polypropylene and silica nanoparticles as a new milk packaging. Food Sci. Nutr., 8; 4037–4043.

Emamhadi, M. A., Sarafraz, M., Akbari, M., Fakhri, Y., Linh, N. and Khaneghah, A. (2020). Nanomaterials for food packaging applications: a systematic review. Food Chem. Toxicol., 146;111825.

Fonseca-García, A., Jiménez-Regalado, E. J. and Aguirre-Loredo, R. Y. (2021). Preparation of a novel biodegradable packaging film based on corn starch-chitosan and poloxamers. Carbohydr. Polym., 251;117009.

Garofalo, E., Scarfato, P., Di Maio, L., and Incarnato, L. (2018). Tuning of co-extrusion processing conditions and film layout to optimize the performances of PA/PE multilayer nanocomposite films for food packaging. Polym. Compos., 39; 3157–3167.

Giannakas, A., Stathopoulou, P., Tsiamis, G., and Salmas, C. (2020). The effect of different preparation methods on the development of chitosan/thyme oil/montmorillonite nanocomposite active packaging films. J. Food Process. Preserv., 44;14327.

Gómez-Aldapa, C. A., Velazquez, G., Gutierrez, M. C., Rangel-Vargas, E., Castro-Rosas, J. and Aguirre-Loredo, R. Y. (2020). Effect of polyvinyl alcohol on the physicochemical properties of biodegradable starch films. Mater. Chem. Phys., 239;122027.

Green Facts (2020). Available online at: https://www.greenfacts.org/en/digests/food-lifestyle.htm.

Guo-Xiang, Z., Ping, Q. J. and Liang-Zou, X. (2008). Extruded Starch/PVA Composites: Water Resistance, Thermal Properties, and Morphology. J. Elastomers Plas., 40(4); 303–316.

Hongwei, Y., Yuan, C., Qun, F. and Zhikun, L. (2015). Effects of Treatment Temperature on Properties of Starch-based Adhesives. BioResource., 10;3520-3530.

Imen, T., Naourez, K., Sirine, B., Slima, M., Triki, S., Bardaa, H., Mnif, R. **and** Ben, S. (2017). Evaluation of dermal wound healing activity and in vitro antibacterial and antioxidant activities of a new exopolysaccharide produced by Lactobacillus sp. Ca$_6$. Inter. J. Bio. Macro., 103;194-201.

Ju, J., Chen, X., Xie, Y., Yu, H., Guo, Y. and Cheng, Y. (2019). Application of essential oil as a sustained release preparation in food packaging. Trends Food Sci. Technol., 92; 22–32.

Kathiresan., K. (2004). Polythene and plastic degrading microbes from mangrove soil. Rev Biol. Trop., 51;629–633.

Katherine, M. D., Dieu, D., Eustathios, P. and Long, Yu. (2008). Key interactions in biodegradable thermoplastic starch/poly (vinyl alcohol)/montmorillonite micro- and nanocomposites. Comp. Sci. Tech., 68(6);1453-1462.

Lawrimore, W.B., Paliwal, B., Chandler, M. Q., Johnson, K. and Horstemeyer, M. F. (2016). Hierarchical multiscale modeling of Polyvinyl Alcohol/Montmorillonite nanocomposites. Polym., 99;386–398.

Mei, L., and Wang, Q. (2020). Advances in using nanotechnology structuring approaches for improving food packaging. Annu. Rev. Food Sci. Technol., 11; 339–364.

Michal, I., Oľga, H., Barbora, B. and Jiří, K. (2010). FT-IR study of gamma-radiation induced degradation of polyvinyl alcohol (PVA) and PVA/humic acids blends. J. Rad. Nucl. Chem., 283; 9–13.

Noorbakhsh-Soltani, S.M., Zerafat, M.M. and Sabbaghi, S. (2018). A comparative study of gelatin and starch-based nano-composite films modified by nano-cellulose and chitosan for food packaging applications. Carbohydr. Polym., 189;48–55.

Nowak, B., Pająk, J., Łabużek, S., Rymarz, G. and Talik, E. (2011). Biodegradation of poly (ethylene terephthalate) modified with polyester "Bionolle" by Penicillium funiculosum. Polimery., 56;35-44.

Pallab, D. and Pankaj, T. (2017). Thermal degradation kinetics of plastics and model selection. Thermochimica Acta., 654;191-202.

Pinkee, P., Jyoti, P., Saikia, B. and Kumar, K. (2012). Bio-plastic (P-3HB-co-3HV) from Bacillus

circulans (MTCC 8167) and its biodegradation. Colloids and Surfaces B: Biointerfaces., 92(1);30-34.

Rojas, K., Canales, D., Amigo, N., Montoille, L., Cament, A., Rivas, L.M., Gil-Castell, O. Reyes, P., Ulloa, M.T. and Ribes-Greus, A. (2019). Effective antimicrobial materials based on low-density polyethylene (LDPE) with zinc oxide (ZnO) nanoparticles. Compos. Part B Eng., 172;173–178.

Seethamraju, S., Ramamurthy, P.C. and Madras, G. (2013). Flexible poly (vinyl alcohol-co-ethylene)/modified MMT moisture barrier composite for encapsulating organic devices. RSC Adv., 3;12831–12838

Sepulveda, J., Villegas, C., Torres, A., Vargas, E., Rodriguez, F., Baltazar, S., Prada, A., Rojas, A., Romero, J. and Faba, S. (2020). Effect of functionalized silica nanoparticles on the mass transfer process in active PLA nanocomposite films obtained by supercritical impregnation for sustainable food packaging. J. Supercrit. Fluids., 161;104844.

Swaroop, C. and Shukla, M. (2018). Nano-magnesium oxide reinforced polylactic acid biofilms for food packaging applications. Int. J. Biol. Macromol., 113;729–736

Taghizadeh, M. T., Abbasi, Z. and Nasrollahzade, Z. (2012). Study of enzymatic degradation and water absorption of nanocomposites starch/polyvinyl alcohol and sodium montmorillonite clay, J.Taiwan Inst. Chem. Eng., 43(1); 120–124.

Wu, Z., Wu, J., Peng, T., Li, Y., Lin, D., Xing, B., Li, C., Yang, Y., Yang, L., Zhang, L., Ma, R., Wu, W., Lv, X., Dai, J. and Han, G. (2017). Preparation and Application of Starch/Polyvinyl Alcohol/Citric Acid Ternary Blend Antimicrobial Functional Food Packaging Films, Polymers., 9(3);102.

Yachuan, Z., Curtis, R. and Qiang, L. (2014). Thermoplastic starch processing and characteristics-a review. Crit Rev Food Sci Nutr., 54(10); 1353-1370.

Zhao, G., Liu, Y., Fang, C., Zhang, M., Zhou, C. and Chen, Z. (2006). Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly (vinyl alcohol) blend film. Polym. Degrad. Stab., 91(4);703-711.

Zhou, X. Y., Cui, Y. F., Jia, D. M. and Xie, D. (2009). Effect of a complex plasticizer on the structure and properties of the thermoplastic PVA/ starch blends. Polym.-Plast. Technol. Eng., 48;489–495.