

Role of Nano-Sized TiO₂ on Mechanical and Thermal Behavior of Starch/Poly (vinyl alcohol) Blend Films*

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(Received: 30 Nov. 2012 and Accepted: 27 Dec. 2012)

Abstract:

A novel Starch/Poly (vinyl alcohol)/nano-Titanium dioxide (ST/PVA/nano-TiO₂) biodegradable nanocomposite film was prepared by homogeneously dispersed TiO₂ nanoparticles in different ratios of starch/PVA-based materials, via a solution casting method. Glycerol was used as plasticizer. The mechanical and thermal properties of films were studied using tensile and perforation strength tests and thermogravimetric analysis (TGA). In order to determine the effective parameters on mechanical properties of prepared films, a general full factorial experimental design approach was used. ST/PVA/TiO₂ nanocomposites were also characterized by scanning electron microscopy (SEM). The results of mechanical analysis showed that ST/PVA films with higher content of PVA had much better mechanical properties. In thermal analysis it was found that addition of TiO₂ nanoparticles have considerable effects on the thermal stability of the films. This enhancement of thermal stability can be attributed to an improvement in the interfacial adhesion and compatibility between the nano- TiO₂ and matrix, due to the treating effect of plasticizer and film forming process. SEM micrographs, taken from the fracture surface of samples, illustrated a quite uniformly dispersion of TiO₂ nanoparticles in the matrix. Moreover, addition of PVA to the composition of film made it softer and more flexible.

Keywords: Nanocomposite, Biodegradable, Nano-TiO₂, Mechanical properties, Thermogravimetric analysis.

1. INTRODUCTION

The main types of plastics that are currently used widespread throughout the world are derived from non-renewable petroleum resources. Because of vast applications, the disposal of waste plastics creates serious problem of environmental pollution. For this reason, the development of biodegradable films has been regarded as more environmentally friendly materials for packaging. They have the potential to replace the synthetic conventional non-biodegradable

polymers. Among biopolymers, starch has received considerable attention in many applications because of its biodegradability, availability and low cost. However, the poor mechanical properties and hydrophilic nature of starch prevent its use in widespread applications; hence its modification is necessary. Blending with other biodegradable synthetic polymeric materials is a common method to improve mechanical properties and reduce water sensitivity of starch. Starch/Poly (vinyl alcohol) blend films are one of the most popular biodegradable polymers, and are widely used in

* This paper is selected from 4th International Congress on Nanoscience and Nanotechnology (ICNN 2012)

packaging applications. Jayasekara et al., [1], blended the PVA with starch and glycerol to form polymer films. They modified the surface of the films by treatment with chitosan and observed improvements in some properties. Zhai et al., [2], showed that the properties of starch-based plastic sheets such as flexibility and wet strength was improved further by incorporating PVA into starch-based sheets under ionizing radiation. Ray et al., [3], prepared starch/ PVA films plasticized with glycerol and characterized for their physicomechanical and morphological properties. Zhou et al., [4], found that the surface modification, considerably reduced the surface hydrophilic character of the thermoplastic starch/PVA films, enhanced the film's water resistance and also increased tensile strength and Young's modulus but decreased elongation at break of the films. PVA is a biodegradable synthetic polymer which has the advantages of good film formation, strong adhesiveness, high thermal and mechanical properties and it may be the only synthesized polymer whose backbone mainly composed of c-c bond, that is absolutely biodegradable [5]. Nevertheless, the mechanical properties and water resistance of the starch/PVA film are still lower than those of other polymers made from petroleum. Many studies have indicated that nano-materials can improve the performance of polymeric materials such as plastics. Avella et al., [6], prepared starch/clay films. They observed a good intercalation of the polymeric phase into clay interlayer galleries, together with an increase of mechanical parameters, such as modulus and tensile strength. Tang et al., [7], developed several starch/ poly (vinyl alcohol) /nano-silicon dioxide biodegradable blend films and discovered the mechanism for improving the properties of a starch-based biodegradable film using nano-SiO₂. Dean et al., [8], prepared thermoplastic starch/poly (vinyl alcohol) montmorillonite (Na-MMT) micro- and nanocomposites and observed improvements in properties of films. Yoon et al., [9], found that the mechanical properties and water resistance of starch/PVA composite films were improved up to 70–400% by the addition of nano-sized poly (methyl methacrylate-co-acrylamide). In this work, the starch/PVA blend film was prepared by a casting method, and nano-TiO₂ was used to improve the properties of starch/PVA blend films.

Titanium dioxide is a nontoxic material and has been applied in environmental treatments such as water and air disinfection because of its unique properties such as strong photocatalytic activity and chemical stability [10]. TiO₂ which promotes peroxidation of the polyunsaturated phospholipids of microbial cell membranes is widely used as a photocatalytic disinfecting and self-cleaning material for surface and coatings industry [11]. A kind of photodegradable polystyrene-TiO₂ nanocomposite film was synthesized by Zan et al., [12]. They showed that PS/TiO₂ nanocomposite films could be efficiently photocatalytically degraded under UV illumination in air. They observed that big cavities were formed not only on the surface, but also inside the films. The film structure was destroyed and the chalking phenomenon took place, whereas only small cavities and cracks were observed on the surface of the pure polystyrene film. This indicates that TiO₂ nanoparticles will greatly enhance the photocatalytic degradation of the polystyrene material. Chawengkijwanich and Hayata et al., [13], developed a TiO₂ powder-coated packaging film and verified its ability to reduce *E. coli* contamination on the surface of solid food products.

To the best of our knowledge, any research concentrated on thermal and mechanical properties of biodegradable ST/PVA polymers modified by nano-TiO₂ have not yet been reported. The starch/PVA blend films were prepared by a casting method, and different contents of nano-TiO₂ were used to improve the properties of prepared films. The main objective of this paper is to investigate the mechanical and thermal properties of resulted nanocomposites. Starch commonly exists in the form of granules with about 15–45% crystallinity. To produce thermoplastic starch (TPS) without granular structure, plasticizers have to be incorporated, because they can form hydrogen bonds with starch, replacing the strong intra- and intermolecular hydrogen bonds in starch, resulting in plasticization [14]. Generally, polyols are used as plasticizers for TPS. After some studies glycerol was selected as plasticizer for corn starch to prepare thermoplastic starch. The amount of plasticizer should be high enough to obtain a suitable flexible film. Our initial tests showed that 30 wt. % glycerol gives good mechanical and thermal properties in prepared films.

2. MATERIALS AND METHODS

2.1. Materials

Corn starch (ST) was provided by Sigma-Aldrich (amylose content 27%) and poly (vinyl alcohol) (PVA) by Merck (molecular weight 72000 g/mole). Nano-TiO₂ powder (anatase-phase crystal structure with average particle size of about 25 nm) was supplied by Nanolin, Germany. Glycerol (GLY) (99% purity from Merck) was employed as plasticizer. The distilled and deionized water was used in experiments.

2.2. Preparation of the films

Blended Starch/PVA gels were prepared by thermal gelatinization of mixture suspensions on a magnetic stirrer using different starch and PVA concentrations. Some of films were filled with TiO₂ nanoparticles according to the corresponding run of experiments. The levels of each component were selected after preliminary tests. At first, aqueous ST/PVA solutions were prepared by dissolving PVA in 60 mL distilled water at 80 for about 6 h. After complete dissolving of PVA, starch was mixed and after that, glycerol at a 30 wt. % ratio based on total dry weight of starch and poly (vinyl alcohol) was added. This mixture was stirred for about 120 min until 40 mL volume of solution was left.(water should be adequately

available in order to facilitate the PVA dissolving and starch gelatinization completely, but at the end, the amount of water should be minimized in order to get a less sticky and easy drying). The TiO₂ nanoparticles were dispersed in the matrix using a bath sonicator for one hour. These solutions were then poured onto glass petri dishes, placed on a leveled flat surface and dried under atmosphere conditions. The fully dried films were peeled away from the glass plates and stored at 20°C. The series of starch/PVA/nano-TiO₂ formulations along with plasticized corn starch and PVA, which were prepared for this study, are summarized in Table1.

2.3. Film characterization

2.3.1. Moisture content

Moisture content of samples was determined measuring weight loss of films, upon drying in an oven at 105 C. Samples were analyzed at least twice and results were expressed as percent of moisture content of samples. Percentage of moisture was calculated based on the original weight of specimen as follows:

$$moisture(\%) = \left[\frac{w_1 - w_2}{w_1} \right] \times 100 \quad (1)$$

Where:

w_1 = Original weight of specimen

w_2 = Weight of specimen after oven drying

Table 1: Composition of experimental samples

Sample	Starch (Wt. %)	Polyvinyl alcohol (PVA) (Wt. %)	Glycerol (wt. %) (based on total dry weight of starch and PVA)	TiO ₂ nanoparticle (wt. %) (based on total dry weight of starch and PVA)
Set 1	60	40	30	0
Set 2	60	40	30	2.5
Set 3	60	40	30	5
Set 4	50	50	30	0
Set 5	50	50	30	2.5
Set 6	50	50	30	5
Set 7	40	60	30	0
Set 8	40	60	30	2.5
Set 9	40	60	30	5
Set 10	100	0	30	0
Set 11	0	100	30	0

2.3.2. Thickness measurements

Thickness of the films was determined using a digital micrometer (Mitutoyo, Japan) at 10 random positions of the film and the mean value was reported and used in the calculations of the mechanical properties.

2.3.3. Mechanical tests

Tensile and perforation strength tests were performed using a universal tensile machine model Zwick/Z250 system (Germany). Tensile tests were performed according to the ASTM D882(2004), [15], method; films were cut into 120×30 mm strips, with the gauge length (i.e., the distance between the two clamps) set at 50 mm, and the tensile rate (cross head speed) was kept 3 mm/min. Stress (MPa) as a function of strain (%) and maximum force at break (N), tensile strength (calculated by dividing maximum force by film cross-section in MPa) and E- modulus (Young's modulus, slope of stress-strain curve, N/mm²) were reported by the system software. Moreover, elongation at break of the films (deformation divided by initial length and multiplying by 100, %) were measured. In perforation test, samples with diameters of 120 mm were fixed on the holder with a hole of 40 mm diameter. A 2 KN load cell with perforation rate of 3 mm/min was perpendicularly moved to the film surface until the probe passed through the film. The curves of force (N) as a function of displacement (mm) and the tolerated maximum force against perforation were automatically recorded by the system software.

2.3.4. Scanning Electron Microscopy (SEM)

The morphology, nano-particle dispersion and rupture mechanism of films were studied by scanning electron microscopy (SEM). Analysis were performed using an electron microscope model LEO 1450 VP (Germany) equipped with EDX model 7353 (UK), with a nominal resolution of 133 EV, and an acceleration voltage of 35 kV. All images were taken with an operating voltage at 10 kV and 250, 1000, 2000, 5000, 10000 and 15000 magnifications. All the specimens were sputter-coated with gold-cadmium alloy in a sputter coater model CS 7620 in 2 min.

2.3.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) techniques, used to characterize the thermal stability of prepared films, using thermal analysis instrument (Shimadzu, Japan). Film samples were cut into small flakes weighing about 6-7 mg, the temperature range was from 20 to 1000°C at heating rate of 10°C/min under nitrogen atmosphere.

2.4. Statistical analysis

A general full factorial design was used for analyzing resulted data and determining the influence of the two independent variables (PVA and nano-TiO₂ concentrations), at three levels (40, 50, 60 wt. % for PVA and 0, 2.5 and 5 wt. % for nano-TiO₂) on mechanical properties of starch film. The factors and their levels have been selected according to preliminary tests. Design expert software version 8 was used for analysis of variance (ANOVA). The significance level used was 0.05.

3. RESULTS AND DISCUSSION

3.1. Moisture and thickness measurements

Moisture content of samples was from 0.12 to 0.15 wt. % based on the original weight of specimen and their average thickness was about 200µm.

3.2. Mechanical properties of the films

As packaging materials may be subjected to various kinds of stress during use, determination of mechanical properties is necessary. The interaction between different components has an important role in different properties of the films, especially in mechanical properties. Different quantities of starch and PVA, and consequently different extents of H-bonding in the films, besides of their various interactions with the plasticizer and TiO₂ nanoparticles, lead to different mechanical behavior of samples. Also, it should be noticed that homogeneous matrix of films is a good indicator of their structural integrity, and consequently good mechanical properties; so a complete mixing and using of sonication for adequate dispersion of nanoparticles in the based polymers is necessary.

On the other hand, the thermoplastic starch (TPS) is obtained after disruption and plasticization of starch macromolecules by heating in the presence of water and plasticizers such as glycerol. The previous studies also have shown that addition of plasticizer is necessary to improve biopolymer film properties, specially the mechanical ones. Furthermore, the effect of plasticizer on mechanical behavior of plasticized films depends on its concentration. Films with lower plasticizer content have rigid and brittle structure and are not flexible enough for film formation [10]. In this work, after doing wide tests on effective content of glycerol on the mechanical properties of films, a 30 wt. % concentration, based on total dry weight of starch and PVA, was considered.

The dependency of tensile and perforation strength, E- modulus, toughness and elongation at break of the films on the PVA and nano-TiO₂ content of the ST/PVA/TiO₂ nanocomposites were studied.

The dependence of the elongation at break (E.B. %) on the PVA and nano-TiO₂ content of the films is shown in Figure (1a). The elongation at break of the blend films increases along with an increase in more flexible PVA molecules. This result is similar to what proposed by Dean et al., [8], in starch/PVA/montmorillonite nanocomposite. The maximum amount of elongation at break for the films containing 40% PVA is 198.34 %, rather than that of films with 50 % PVA which is 244.48%. The magnitude promotes up to 366.7 % when PVA content reaches to 60 %. Tensile and perforation

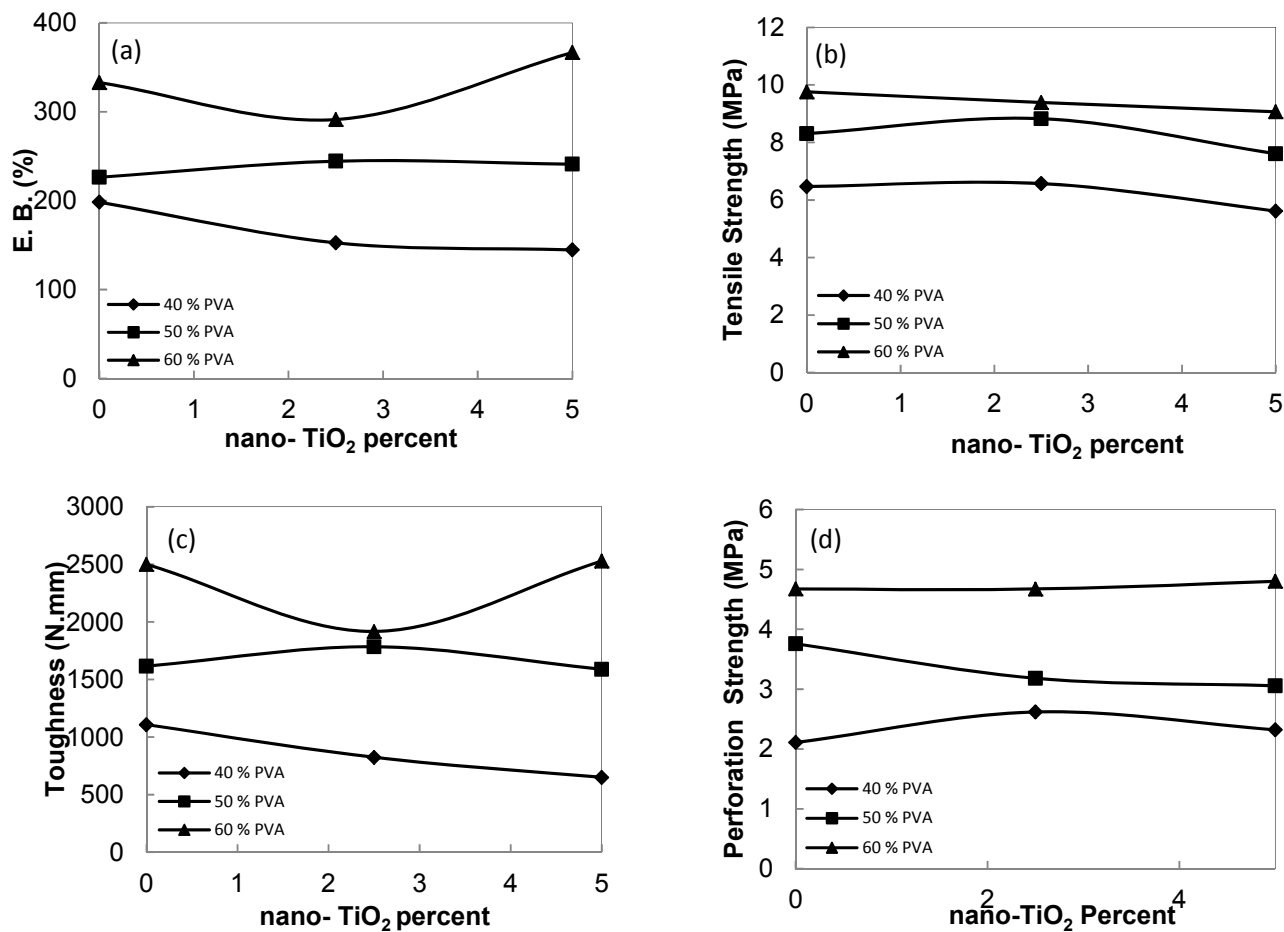


Figure 1: Effect of nano-TiO₂ content on: (a) elongation at break (E. B.) (b) tensile strength (c) toughness (d) perforation strength

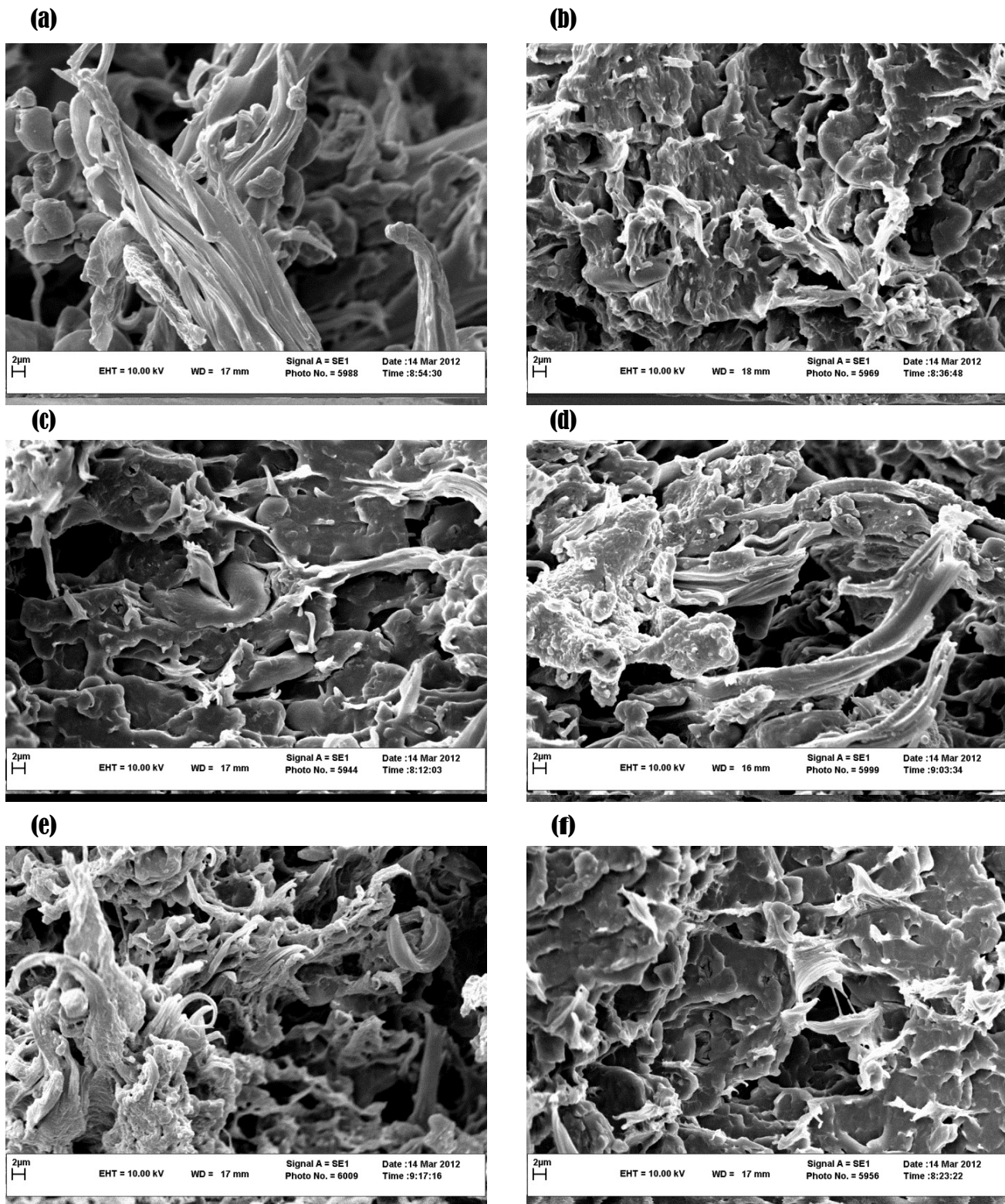


Figure 2: SEM images of fracture surface of films formulated as: (a) ST/PVA (60:40) composite film, (b) ST/PVA/TiO₂ (60 :40:2.5) nanocomposite film, (c) ST/PVA/TiO₂ (60 :40: 5) nanocomposite film, (d) ST/PVA (40:60) composite film, (e) ST/PVA/TiO₂ (40 :60:2.5) nanocomposite film, (f) ST/PVA/TiO₂ (40 :60: 5) nanocomposite film.

strength of films also increase slowly along with an increase in PVA content (Figures 1b, d). The tensile strength of packaging film must be more than 3.5 MPa, according to conventional standards [17]. Thus, the value of over 6 MPa for ST/PVA/TiO₂ nanocomposites is an appropriate value for its use as a disposable packaging film. Moreover, as it is seen in Figure (1c), toughness of the films has improved by addition of PVA. Toughness is defined as the ability of a material to absorb energy before fracture. Statistical analysis, also shows that the influence of PVA content on mechanical properties of the films is significant ($P < 0.05$). We attribute these results to good mechanical properties of PVA and its suitable interaction with starch, in presence of glycerol in the matrix.

ST/PVA film with 40:60 ratio containing 5 wt.% TiO₂ has the best toughness and elongation at break at about 2529.5 and 366.7 compare to the same film without TiO₂ nanoparticles which is 2501.1 and 332.9 indicating an improvement equal to 1.14 and 10.16% respectively in the presence of TiO₂. However statistical analysis of mechanical results shows that the addition of nano-TiO₂ has not a significant effect on mechanical properties of the films ($P > 0.05$). With respect to this matter that TiO₂ hasn't any negative influence on mechanical properties of the ST/PVA film, it will be possible to use it for improving other valuable properties such as antibacterial, degradability, thermal and so on.

3.3. SEM analysis of films

The SEM micrographs of the cross section of some blend films are shown in Figures 2a to 2f. The nanoparticle will reinforce the polymer if it is dispersed properly. Using of ultrasonic mixing has led to quite uniform dispersion of TiO₂ nanoparticles inside the starch/PVA matrix. SEM micrographs, taken from the fracture surface of samples, illustrate that starch granules are completely disrupted and a continuous phase is obtained, also EDX analysis of samples showed the presence of Titanium, Oxygen and Carbon elements. Micrographs of the fracture surface of sets 1, 2 and 3 are shown in Figures 2a, b and c. As it is seen, there is a hard breakdown in samples with 60 wt. % starch and these samples have approximately flat and brittle fracture surface;

whereas in samples 6, 7 and 9 that contain lower content of starch (40 wt. %) a quite soft breakdown is happened (Figures 2d, e and f) and stretched fibers in film texture are observable. In fact, the addition of PVA to the composition of film makes it softer and more flexible.

3.4. Thermal analysis

Thermogravimetric analysis was performed to examine the thermal stability of pure corn starch, pure PVA, and plasticized starch (100 wt.% starch + 30 wt.% glycerol), plasticized PVA (100 wt.% polyvinyl alcohol + 30 wt.% glycerol), ST/PVA composite and ST/PVA/TiO₂ nanocomposite films. The thermal stability of a polymeric material depends on the inherent characteristics of the constituents as well as on the molecular interactions between the different macromolecules [18]. The thermal stability of the prepared films is affected by starch to PVA ratio and TiO₂ nanoparticles content. The various proportions of starch/PVA and TiO₂ content, so different extent of H-bonding between the molecules and incorporation of TiO₂ nanoparticles have influenced the thermal degradation behavior of the samples. Ray, *et al.*, [18], also obtained the same results that indicated intercomponent H-bonding between starch, Poly (vinyl alcohol) and glycerol enhances the thermal stability of the films.

Compared with the organic materials, the inorganic materials have better thermal stability, due to their configuration characteristics. Therefore, the introduction of inorganic particles would greatly improve the thermal stability of organic polymer materials [19].

Weight loss and the rate of degradation of sets 1 to 11 along with pure corn starch and PVA are shown by TGA and Derivative Thermo Gravimetry (DTG) curves in figures 3 to 6. A considerable shift in the height and position of the peaks depending on the proportion of different constituents in films is observable.

Figure 3 shows weight loss of pure corn starch and PVA powders and the curves related to set 10 and 11 films are shown in Figure 4. As it is seen, pure starch and its plasticized film (set 10), have a lower thermal stability relative to PVA and its film. Pure

starch shows a sharp and strong peak at 311.89°C, indicating a very high degradation rate, while pure PVA shows a comparatively low intensity peaks indicating lower rate of degradation. Comparison of their plasticized films shows the same result.

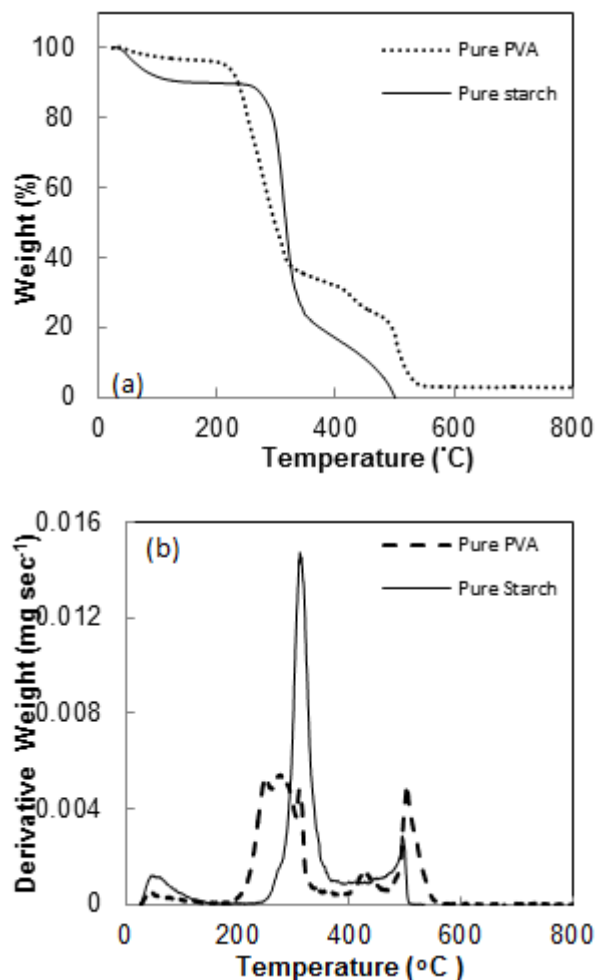


Figure 3: TGA and DTG thermograms of pure PVA and Starch powder

Weight loss and the rate of degradation of sets 1 to 3 along with plasticized corn starch and PVA films (sets 10 and 11) are shown in Figures (4a, b). It can be seen that, decomposition temperature of plasticized corn starch and PVA films improves considerably in blend films of starch / PVA in presence of glycerol and nano -TiO₂. Thus the thermal degradation temperature of the blend films is higher than that of plasticized starch and PVA.

The reason is related to new H-bonding between the molecules of starch, PVA and glycerol and incorporation of TiO₂ nanoparticles. Thermal degradation of the plasticized starch (sets 10) is occurred in approximately two-step degradation process (Figure 4a).

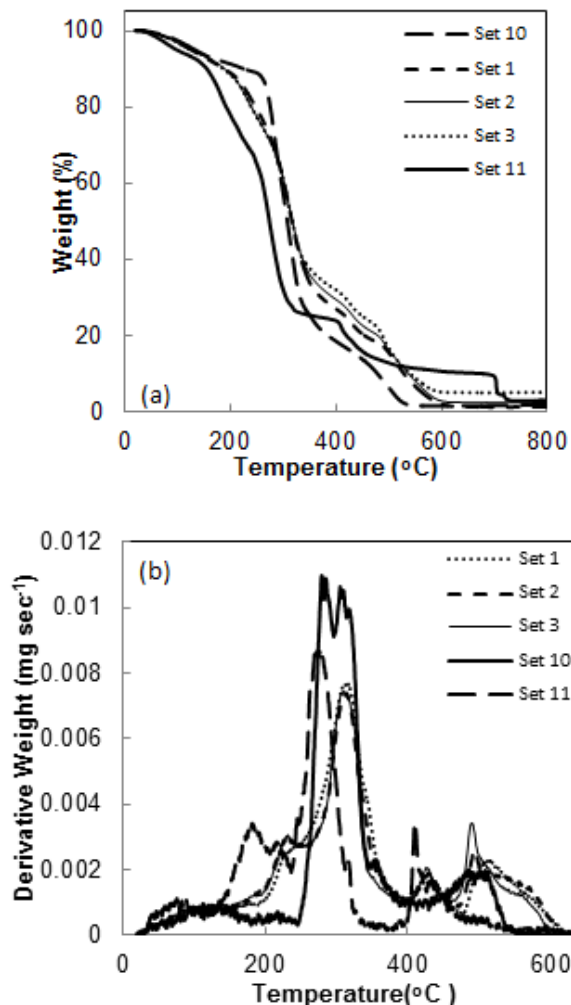


Figure 4: TGA and DTG thermograms of ST/PVA (60:40) based films along with plasticized starch and PVA films

It has a very slight degradation rate below 230°C, above this temperature, degradation process takes place very rapidly until 344°C, after this point, degradation continues with lower rate to less than 520°C. This result is also confirmed by the presence of two peaks (in 279.38 and 484.31°C) in DTG curve (Figure 4b). In addition, as it is seen

in Figures (4a, b), plasticized PVA (set 11) has a five stage degradation process and therefore has five peaks (in 181.58, 270.94, 410.07, 703.76 and 720.38°C). It can be seen that position and intensity of peaks in starch/PVA blend films (sets 1, 2 and 3) is considerably different relative to plasticized starch and PVA films (sets 10 and 11), as the main peak of blend films takes place in higher temperatures with lower intensities.

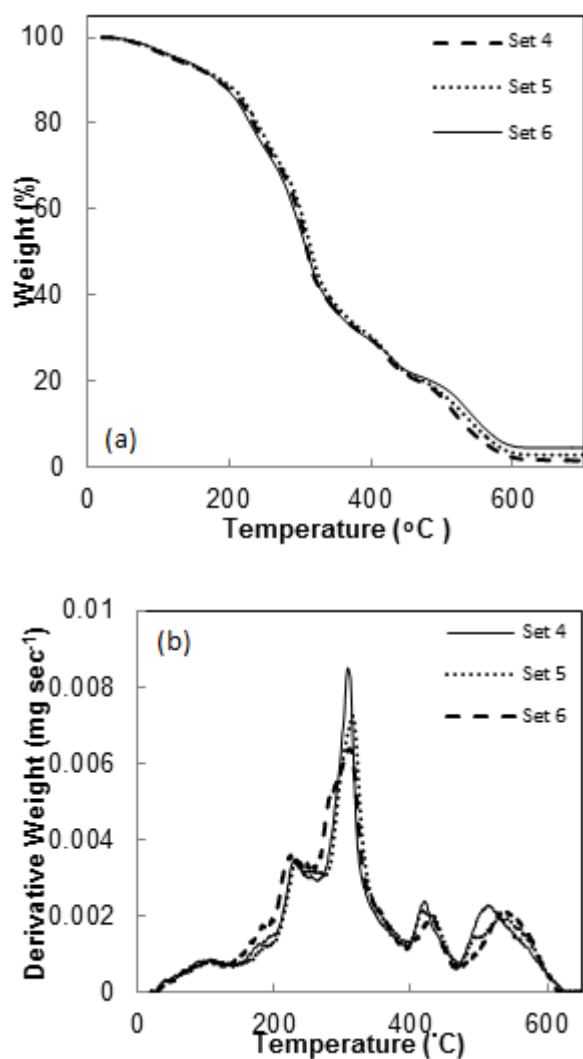


Figure 5: TGA and DTG thermograms of ST/PVA (50:50) based films

Figure 5 shows a comparison between sets 4, 5 and 6. Three samples have the same proportion of starch and PVA, but amount of TiO₂ nanoparticles

is varied in three levels of 0, 2.5 and 5 wt. %. As it is seen, there is not a considerable shift in the peak positions, but the rate of degradation decreased with addition of TiO₂ nanoparticles. The reason is related to adequate incorporation of nano-TiO₂ particles with matrix molecules Ray et al., [18], had obtained the same results for starch/poly (vinyl alcohol) and bentonite clay films.

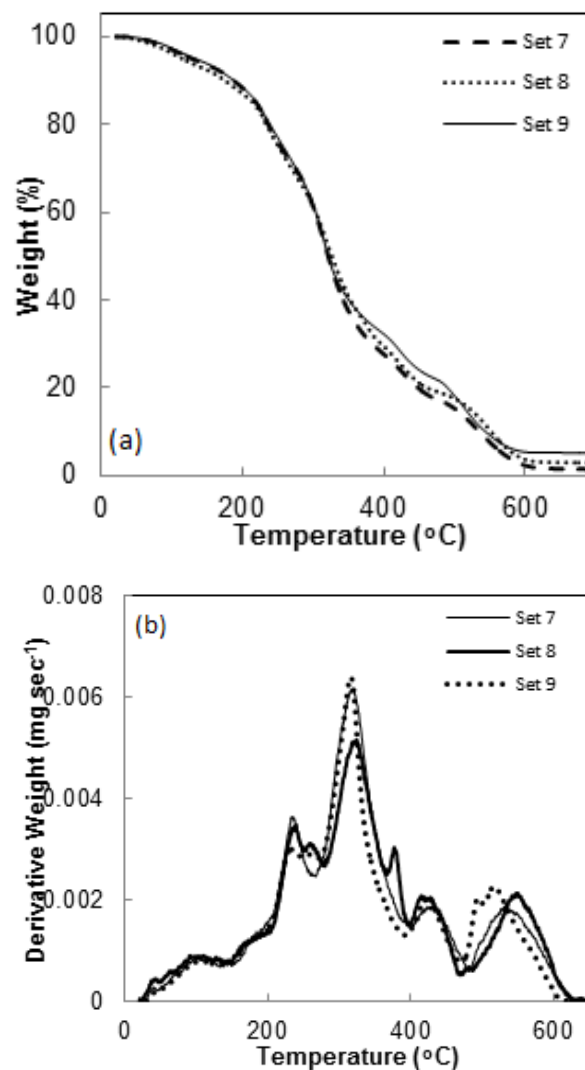


Figure 6: TGA and DTG thermograms of ST/PVA (40:60) based films

A comparison between sets 7, 8 and 9, is shown in Figure 6. It can be seen that, in 40:60 proportion of starch and PVA, the film containing 2.5 wt. %

of TiO₂ nanoparticles (set 8) indicates a lower degradation rate and has a better thermal stability relative to sets 7 and 9.

The resulted data shows that the addition of PVA in the matrix increases the degradation temperature of composites; also the addition of TiO₂ nanoparticles to ST/PVA improves its degradation temperature. It can be seen from the Figs. 4 to 6 that for all composites, temperature of main peak is higher than plasticized starch and PVA ones.

Decomposition temperatures at 10, 50 and 90 % mass loss ($T_{d(-10)}$, $T_{d(-50)}$ and $T_{d(-90)}$), for sets 1 to 11, are summarized in table 2. As it is seen, in all of blend films, decomposition temperatures at 10, 50 and 90 % mass loss improves by addition of TiO₂ nanoparticles. Dai et al., [19], obtained similar results for thermoplastic starch and montmorillonite nanoparticles. For entire prepared films, decomposition temperatures show a considerable increase by addition of TiO₂ nanoparticles to 2.5 wt. %, but in some samples a decrease in decomposition temperatures for addition of TiO₂ nanoparticles from 2.5 wt. % to 5 wt. % TiO₂ is observed. Sets 7, 8 and 9 all have the same matrix (40% starch and 60% PVA) while sets 8 and 9 have additional 2.5 and 5 wt. % nano -TiO₂ particles loadings respectively. As it is seen, Decomposition temperatures at 10% mass loss ($T_{d(-10)}$) increases from 186.72 °C in set 7 (without TiO₂ nanoparticles) to 193.62°C in set 8 (with 2.5 wt. % TiO₂ nanoparticles), and reaches to 217.41°C in set 9 (with 5 wt. % TiO₂ nanoparticles). Also it is observable that, when the nano - TiO₂ content varies from 2.5 to 5%, the $T_{d(-50)}$ and $T_{d(-90)}$

of the film decrease, but they are still much higher than that of the set 7 (containing any nanoparticles). Comparison between decomposition temperatures of sets 10 and 11 in table 2, shows that plasticized PVA (set 11), in despite of its lower $T_{d(-10)}$ and $T_{d(-50)}$ compared to plasticized starch (set 10), have a much more $T_{d(-90)}$ and lower degradation rate, indicating its higher thermal stability.

Totally, the curves of Figures 3 to 6 confirm that the thermal degradation began to occur only after the materials have absorbed certain amounts of heat energy. The heat initiated the degradation processes and the breaking down of the matrix structure by causing molecular chain ruptures. Moreover, the addition of nano-TiO₂ improves the thermal resistance of starch/PVA based composites.

4. CONCLUSIONS

In this work, mechanical and thermal properties of biodegradable starch/polyvinyl alcohol/TiO₂ nanocomposite films were studied. All the films were obtained by solution casting method. Nanocomposite films were prepared by homogeneously dispersing TiO₂ nanoparticles in different ratios of starch/PVA mixtures. Concentration of glycerol was fixed at 30 wt. %, based on total dry weight of starch and PVA. The results showed that the addition of PVA in film structure, will improve its thermal, mechanical and morphological properties significantly. Along with the addition of PVA chains, which are more flexible than the starch molecules, film rigidity

Table 2: Decomposition temperatures at 10, 50 and 90 % mass loss of films

Sample	$T_{d(-10)}$	$T_{d(-50)}$	$T_{d(-90)}$
Set 1	187.56	316.31	528.55
Set 2	205.83	319.04	538.85
Set 3	218.45	320.78	544.37
Set 4	183.67	310.67	531.79
Set 5	207.63	318.40	546.57
Set 6	209.64	314.92	558.36
Set 7	186.72	321.14	535.48
Set 8	193.62	328.97	553.40
Set 9	217.41	325.96	547.75
Set 10	224.88	307.71	478.25
Set 11	155.20	273.83	671.52

was decreased and its elongation was increased. Statistical analysis of obtained experimental data showed that, mechanical properties of the films were not enhanced by addition of nano-TiO₂ significantly. However, Set 9 sample was found to have the best tensile and perforation strength, toughness, and elongation at break compare to other samples. Thermogravimetric analysis of prepared films indicated that, thermal stability of ST/PVA/nano-TiO₂ nanocomposites was improved by addition of PVA and TiO₂ nanoparticles.

ACKNOWLEDGMENTS

We are grateful to Iran Nanotechnology Initiative council for partial financial support and to Chemical Engineering Research and Mechanical laboratories of Ferdowsi University of Mashhad for their helps in performing thermal and mechanical experiments.

REFERENCES

1. R. Jayasekara, I. Harding, I. Bowater, G.B.Y. Christie and G.T. Lonergan: *Polym. Test*, Vol. 23, (2004), pp. 17-27.
2. M. Zhai, F. Yoshii and T. Kume: *Carbohydr. Polym.* Vol. 52, (2003), pp. 311-317.
3. D. Ray, P. Roy, S. Sengupta, S.P. Sengupta, A. K. Mohanty and M. Misra: *J. Polym. Environ.*, Vol. 17, (2009), pp. 56-63.
4. J. Zhou, Y. Ma, L. Ren, J. Tong, Z. Liu and L. Xie: *Carbohydr. Polym.* Vol. 76, (2009), pp. 632-638.
5. Y. H. Yun and S. D. Yoon: *Poly. Bull.*, Vol. 64, (2010), pp. 553-568.
6. M. Avella, J.J. De Vlieger, M.E. Errico, S. Fischer, P. Vacca and M.G. Volpe: *Food Chem.*, Vol. 93, (2005), pp. 467-474.
7. Sh. Tang, P. Zou, H. Xiong and H. Tang: *Carbohydr. Polym.*, Vol. 72, (2008), pp. 521-526.
8. K.M. Dean, M.D. Do, E. Petinakis and L. Yu: *Compos. Sci. Technol.*, Vol. 68, (2008), pp. 1453-1462.
9. S. D. Yoon, M. H. Park, H. S. Byun: *Carbohydr. Polym.*, Vol. 87, (2012), pp. 676- 686.
10. Sh. Ansari Amin, M. Pazouki and A. Hosseinnia: *Powder Technol.*, Vol. 196, (2009), pp. 241-245.
11. A. Fujishima, T.N. Rao and D.A. Tryk: *J. Photochem. Photobiol. , C: Photochemistry Reviews*1, Vol. 1, (2000), pp. 1-21.
12. L. Zan, L. Tian, Z. Liu and Z. Peng: *Appl. Catal., A*, Vol. 264, (2004), pp. 237-242.
13. C. Chawengkijwanich and Y. Hayata: *Int. J. food microbial.*, Vol. 123, (2008), pp. 288-292.
14. Y. Chung, S. Ansari, L. Estevez, S. Hayrapetyan, E.P. Giannelis and H. Lai: *Carbohydr. Polym.*, Vol. 79, (2010), pp. 391-396.
15. ASTM, American Society for Testing and Materials, D882-01. *Annual Book of ASTM*, Philadelphia, PA, (2004).
16. O.V. Lopez, M.A. Garcia and N.E. Zaritzky: *Carbohydr. Polym.*, Vol. 73, (2008), pp. 573-581.
17. K. Majdzadeh Ardakani, A. H. Navarchian and F. Sadeghi: *Carbohydr. Polym.*, Vol. 79, (2010), pp. 547-554.
18. D. Ray, P. Roy, S. Sengupta, S. P. Sengupta, A. K. Mohanty and M. Misra: *J. Polym. Environ.*, Vol. 17, (2009), pp. 49-55.
19. H. Dai, P.R. Chang, F. Geng, J. Yu and X. Ma: *J. Polym. Environ.*, Vol. 17, (2009), pp. 225-232.

