SiO$_2$ particles effect on the mechanical properties of the starch/PVA blends

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Abstract

The present work studies the mechanical properties of SiO$_2$ µPs, and NPs in St/PVA blends. The samples were prepared by casting method as PVA, St/PVA blends at different concentrations (30, 40, 50, and 60 %). DSC and TGA tests were carried out to the samples evolved. The result showed a single glass transition temperature ($T_g$) for all St /PVA blends that was attributed to the good miscibility of the blends involved. It was found that ($T_g$) decrease with starch ratio increase. It was seen that (PVA) of ($T_g$=105 °C); The glass transition temperature which was decrease with starch ratio that was attributed to glass transition relaxation process due to micro-Brownian motion of the main chain back bond. The endothermic peak at 200 °C was attributed to melting point of (PVA). Thermal properties of PVA; and St/PVA blends at different concentration (30, 40, 50, and 60 %) were evaluated by thermo gravimetric analysis (TGA). The analyses were carried out from 20 to 600 °C at 10 °C/min heating rate in air oxygen atmosphere. The weight loss stages depended on polymer system. The starch addition causing shifting in the second degradation temperature to the higher temperature; which result in overlapping between the two main degradation steps, these result was attributed to the St/ PVA blend compatibility. The mechanical properties results showed a decrease in ultimate strength with starch ratio increase. The ultimate strength of (PVA) was (47 MPa), whereas the ultimate strength of 60 %St/PVA was (11 MPa) and for 30 %St/PVA was the highest ultimate strength of blends involved (26 MPa). SiO$_2$µPs (753.7 nm), and NPs (263.1 nm) were added at different concentrations (1.5, 2, and 2.5 %). 1.5% SiO$_2$µPs, and NPs of the best ultimate strength (69 MPa), (86 MPa) respectively then it was decreased by SiO$_2$µPs, and NPs increase. Optical microscope of the samples involved was investigated. It was concluded the prepared samples were suggested to be used as packaging materials for agriculture application and its ultimate strength could be controlled by SiO$_2$µPs, and NPs addition.

Key words

PVA, corn starch, SiO$_2$, mechanical properties.

Article info

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Starch /PVA على الخواص الميكانيكية لخلائط SiO$_2$

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The drop in the petroleum resources and an exponential growth in the usage of non-biodegradable plastic films cause a great danger to the environment. The composites and polymer blends were development to be biodegradation. Reinforcement of polymer matrices by nano fillers has been studied broadly in the last two decades. SiO\(_2\) particles are white amorphous powder have various linkage of hydroxyl groups on their surface and unsaturated residual bond. Nano and micro SiO\(_2\) particulate fillers enhanced the mechanical properties, that attributed to the increase in the contact surface area introduced by the fine particles; and increased the transferred stress. Polyvinyl alcohol (PVA) is a linear artificial polymer formed by partial or full hydrolysis of (polyvinyl acetate) to eliminate the acetate groups. it is a polymer consists of many hydroxyl groups, with very good properties, such as poor permeability, water soluble, good water absorption capability, and used in various industrial and agricultural applications [1-4]. Starch is a semi-crystalline polymer stocked in granules as corn, rice, and potato. It is composed of amylose and amyllopectin. The amounts of amylose and amyllopectin depend on the source of plant. Corn starch granules generally consist of (70 %) amylopectin and (30 %) amylose [5, 6]. Zainab et al investigated the polymer blend and polymer nano composite that based on (PVA) and studies the Structural properties, barrier properties (The permeability of blends depends on many factors such as the surrounding relative humidity, temperature, film thickness, water and plasticizer contents in addition to the nature of blend components), mechanical, and thermal properties, as well as biodegradation of these material [7]. HanGuo et al found that SiO\(_2\) addition improve the mechanical properties, decreased the degradation as well as in compatibility and Miscibility [8]. Chao et al reported that were increase in tensile strength, amorphous phase and tear strength with SiO\(_2\) addition.
[9]. In this work, St/PVA blends were modifying by adding SiO$_2$ particles to study its effects on the mechanical properties of the blend.

**Experimental**

The materials used in this research are a white powder of poly vinyl alcohol (PVA), from Barcelona Espana (Didactic). A white powder of corn starch (St) from spain (panreac) with purity (99.9 %), a white powder of SiO$_2$ µPs (753.7 nm), NPs (263.1 nm) from china, distilled water with purity (100%) to dissolve the PVA, And a beige powder of alpha amylose source (Aspergillus oryzae) from England. (10 g) of purified polymer (PVA) was dissolved in (100 ml) of distilled water in water bath. The solution was mixed by using magnetic stirrer. The stirring process was done for 1 hour, raising the temperature gradually from room temperature (20) °C to (90) °C and then cooling the solution gradually to room temperature with stirring. The solution was poured on glass plate for curing for 24 hour, after that it can removed by using tong or needle. For preparing St/PVA blend films, the (PVA) was dissolved as previous step and starch was added in different ratio (30, 40, 50, and 60 %) at (90) °C, and then cooling the solution to the room temperature with stirring, till get homogeneous solution. The solution was poured on glass plate to curing for 48 hour. For prepared SiO$_2$/St/PVA films, the solution of (30:70) St/PVA ratio was mixed with silicon dioxide (SiO$_2$) powder at (90) °C and then cooling to room temperature for 2 hour with stirring, till get homogeneous solution. The solution was poured on glass plate to curing for 48 hour. For prepared SiO$_2$/St/PVA films, the solution of (30:70) St/PVA ratio was mixed with silicon dioxide (SiO$_2$) powder at (90) °C and then cooling to room temperature for 2 hour. The silicon dioxide was added in two particle size micro particle (SiO$_2$ µPs), and nano particle (SiO$_2$ NPs) in different ratios (1.5, 2, and 2.5), to study the effect of particle size on the blend. Differential scanning calorimetry (DSC) was performed using a STA PT 1000 from Linseis Germany. The weights were within (16-21) mg cut in circle plates, packed in platinum pans and sited in the DSC cell. The heating rate was (10) °C/min, the resulting curve represents the relationship between temperature (°C) in x-axis and HDSC (heat flow) (µV) in y-axis. Thermo gravimetric analysis (TGA) was performed using a STA PT 1000 from Linseis Germany. The samples were carried out from 65 to 600 °C at a heating rate of (10) °C/min, in air. The weight of the sample was between (16- 21) mg. The given data represents the relationship between temperature (°C) in x-axis and Rel-mass change (%) in y-axis. Tension test is used to determine the mechanical properties of the samples. It is broadly used to get main design data on the material strength. It is a suitable test to measure the material requirement. The main parameters that establish the stress-strain curves are the yield strength, elastic modulus, ultimate strength, and $F_{\text{max}}$. The samples were characterize by tensile machine of (LARYEE-50 KN, China), to determine the ultimate tensile strength (UTS), elongation (%), and young modulus (E). The samples were cut according to standard (ASTM D-638). The speed of cross head was (5 mm/min). The test was done at room temperature. Optical microscopes are widely used for sample examination because of their low price, simple sample preparation and ease of use. It is used to study cracks, air bubbles and deformation in samples. The morphology of PVA, St/PVA blend, and µPs, and NPs SiO$_2$/St/PVA films were studied using Optical microscope of Carl Zeiss Company, with magnification X100 (100 times magnified).
Results and discussion

1. Differential Scanning Calorimetry (DSC)

Figs. 1 to 6 show the biodegradation reaction occurred during glass transition temperature ($T_g$) and melting temperature ($T_m$)[10]. It was found decrease in ($T_g$) with starch ratio increase, whereas increase in melting point ($T_m$). The result proved one glass transition temperature ($T_g$) for all St/PVA blends that was attributed to the good miscibility of the blends involved. The miscibility was due to the hydrogen bonds between the (PVA) and (Starch). This miscibility was associated with hydrogen bonds between the hydroxyl groups (OH) of (PVA) and (Starch). The ($T_g$) and ($T_m$) values were listed in Table 1. It was seen that ($T_g$) and ($T_m$) values were plasticizer contents dependent. It was found that decrease ($T_g$) with starch ratio increase which is in a good agreement with (Shafik, and Esraa) [10-13]. The role of starch was ($T_g$) decrease that was in a good agreement with [Fahmide] [14]. Poly vinyl alcohol is composed of crystalline and amorphous phases, the result in quite a complex behavior when the polymer is heated. From the previous Fig. 2., it was found that (PVA) glass transition temperature ($T_g$ =105 °C); which attributed to the glass transition ($T_g$) relaxation process due to micro-Brownian motion of the main chain back bond [13]. The endothermic peak at 200 °C was attributed to melting point of (PVA) which is in a good agreement with (Esraa and Elisabita) [13-15].

![DSC of pure starch](image_url)
Fig. 2: DSC of pure PVA.

Fig. 3: DSC of 30% St/PVA.
Fig. 4: DSC of 40 %St/PVA.

Fig. 5: DSC of 50 %St/PVA.
Table 1: Shows $T_g$ and $T_m$ values.

| Polymer system   | $T_g$ °C | $T_m$ °C |
|------------------|----------|----------|
| Starch           | 85       | 270      |
| PVA              | 105      | 200      |
| 30% St/PVA       | 90       | 205      |
| 40% St/PVA       | 70       | 230      |
| 50% St/PVA       | 65       | 250      |
| 60% St/PVA       | 55       | 250      |

2. Thermo Gravimetric Analyses (TGA)

Thermal properties of PVA; and St /PVA blends at different concentration (30, 40, 50, and 60%) were evaluated by thermo gravimetric analysis (TGA). The analyses were carried out form 20 to 600 °C at 10 °C/min heating rate in air oxygen atmosphere. Fig. 7 to 12 summarizes the (TGA) results of the samples involved. The number of stage is polymer system dependent. Table 2 shows the weight loss stages of (PVA) occurred primarily in three stages. The first one was within range of (210-373.02 °C); the second one was within (373.02-460 °C); and the third was (460-592.3); which were corresponded in weight loss of (40.68, 33.7279, and 15.917 %), respectively. The first loss was due to the evaporation of residual moisture; the second loss, which corresponded to the side chain decomposition of PVA, and the third correspond to the main chain of PVA [12]. The result showed that the onset temperature of degradation reaction of PVA was significantly reduced by starch addition [15]. The degradation of blend started at lower temperatures was attributed to the degradation of interface of St/PVA. The starch addition caused some degree of
overlapping between the two main degradation steps, causing a shift of the second degradation temperature to the higher temperature; that was attributed to the compatibility of Starch; with PVA; where in thermally resistant cyclic hemiacetal in starch imparts thermal stability to the St/PVA blend [16]. When starch was added of different concentration, the stability of blend lowered down compared to the pure PVA. It was concluded that starch addition to the (PVA) reduced the thermal stability of PVA [17]. For (30 % St/PVA); the disappearance of the second and third stages was due to the decrease in the volatilization of starch [18].

![TGA pure PVA](image)

**Fig. 7: TGA pure PVA.**

![TGA pure starch](image)

**Fig. 8: TGA pure starch.**
Fig. 9: TGA 30 %St/PVA.

Fig. 10: TGA 40 %St/PVA.

Fig. 11: TGA 50 %St/PVA.
Table 2: Thermal decomposition data of the St/PVA blend film.

| Polymer system | First stage | Second stage | Third stage | IDT °C | PDT max |
|----------------|-------------|--------------|-------------|--------|----------|
|                | T           | Weight loss% | T           | Weight loss% | T       | Weight loss% |
| PVA            | 210-373.023 | 40.6808      | 373.02-460  | 33.7290      | 460-592.3 | 15.917       | 373.02       | 460 |
| Starch         | 20-264.716  | 10.9282      | 264.716-396.474 | 66.122 | 396.474-594.983 | 15.6185 | 264.716       | 495 |
| 30%St/PVA      | 205-592.641 | 94.5336      | /           | /             | /       | /             | 205          | 592.64 |
| 40%St/PVA      | 60-205.304  | 4.79074      | 205.304-393.385 | 55.6454      | 393.385-594.496 | 34.1735 | 205.304       | 395 |
| 50%St/PVA      | 95-235.172  | 5.40246      | 235.172-386.356 | 54.6296      | 386.356-532.848 | 33.423 | 23.517       | 390 |
| 60%St/PVA      | 62-229.736  | 3.19236      | 229.736-406.605 | 56.9563      | 406.605-539.796 | 27.8864 | 229.736       | 406.65 |

3. Mechanical properties

Fig. 13 shows stress-strain curve for (PVA) and St/PVA blended at different concentrations (30, 40, 50, and 60 %). The result showed a decrease in ultimate strength with starch ratio increase Fig. 14 which is in a good agreement with Fahmide and Esraa [13, 19]. These results were attributed to decrease in hydroxyl group by starch addition hydroxyl group give good mechanical properties to polymer system. Starch also possess hydroxyl group (OH), which were reduced during (actylation process). The hydroxyl group decreased caused ultimate strength decreased; that was a good agreement with Fahmide and Qingjie [14, 20]. The starch addition to (PVA) caused a fall in tensile strength; that was due to the decrease in hard segment contents and hydrogen bonding density in the films; this was in a good agreement with...
Fig. 15 and 16 show the stress-strain curve of 30% St/PVA after SiO$_2$ µPs, and NPs addition at different concentration (1.5, 2, and 2.5%). The result proved that the tensile strength of the (PVA) was (47 MPa) which was higher than St/PVA film at different ratio. Whereas there was a significant increase in tensile strength by SiO$_2$ (µPs, and NPs); which is attributed to the formation of intermolecular bonds between (SiO$_2$-PVA) and (SiO$_2$-Starch), 1.5% SiO$_2$ (µPs, and NPs) of the higher tensile strength value. It was (75 MPa) for 1.5% SiO$_2$ (µPs) addition and (86 MPa) for 1.5% SiO$_2$ (NPs) addition Fig. 15 and 16. The tensile strength decrease due to saturation of intermolecular bonding at high concentration of SiO$_2$ µPs, and NPs Fig. 17a and 17b; which is in a good agreement with [21]. It was found that tensile strength at nano SiO$_2$ particles addition was higher than that of micro SiO$_2$ particles addition Fig. 18; that was attributed to the fact of large particles and dispersion-strengthened composites are the two sub-classification of particle-reinforced composite. The distinction between these is based upon reinforcement or, strengthening mechanism. The term "large" or "micro" is used to indicate the particle-matrix interaction cannot be treated on the atomic or molecular level; rather, continuum mechanics is used. For most of these composites, the particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to retain movement of matrix Phase in the vicinity of each particle. In essence, the matrix transfers some of the applied stress to the particles which bear a fraction of the load. The degree of reinforcement or improvement of mechanical behavior depends on the strong bonding at matrix-particle interface. For dispersion-strengthened composite, particle diameters within the range of (10-100 nm). The matrix interaction strengthened on the atomic or molecular level. The mechanism of strengthening is similar to that for precipitation hardening. Whereas the matrix bears the major portion of an applied load, the small dispersion particles hinder or impede the motion of dislocation. The plastic deformation is restricted such that yield and tensile strength improved [21]. Figs. 19-23 show the elongation of samples involved, it was seen decrease in elongation with starch, and SiO$_2$ µPs, and NPs addition: whereas significant increase in young modules Fig. 24-26. This may lead to efficient load transfer between the matrix and filler, causing enhancement in mechanical properties [12].
Fig. 14: Ultimate strength of St/PVA blend film.

Fig. 15: Stress-strain curve of micro SiO$_2$/St/PVA blend film.

Fig. 16: Stress-strain curve of nano SiO$_2$/St/PVA blend film.
Fig. 17a: Ultimate strength of micro SiO$_2$ / St/PVA blend film.

Fig. 17b: Ultimate strength of nano SiO$_2$ / St/PVA blend film.

Fig. 18: Ultimate tensile strength of SiO$_2$ /St/PVA film.
Fig. 19: Elongation of St/PVA blend film.

Fig 20: Elongation of micro SiO$_2$ /St/PVA blend film.

Fig. 21: Elongation of nano SiO$_2$ /St/PVA blend film.

Fig. 22: Elongation of SiO$_2$ /St/PVA film.
Fig. 23: Young modulus of St/PVA blend film.

Fig. 24: Young modulus of micro SiO$_2$/St/PVA blend film.

Fig. 25: Young modulus of nano SiO$_2$/St/PVA blend film.
These results was enhanced with optical micrographs, Figs. 27 to 29 show the optical micrographs of (PVA), (Starch), and St/PVA blends at different concentration (30-60%) before and after SiO$_2$ µPs, and NPs addition at different concentration (1.5, 2, and 2.5%). the results proved that the blend compatibility increased with starch ratio and SiO$_2$ NPs concentration, but decreased with SiO$_2$ µPs addition. That was in a good agreement with [23]. By starch addition; the dispersed phase (starch) would be miscible in (PVA); as a results of that the blends would be miscible blends and of homogenous morphology; it was attributed to the (PVA) characteristic (hydrophilic); that property caused hydrogen linking increase and result in an adhesion strength between the starch chain. This results in a good agreement with Azahari [24]. It was seen the porous increased with (PVA) ratio increased that was attributed to the blend miscibility that was in a good agreement with Esraa [13]. As shown in Fig.29 for NPs SiO$_2$/St/PVA at different concentration; that the (SiO$_2$) NPs films were smooth and compact that suggested the miscibility and compatibility of samples involved increased. Because the surface of NPs SiO$_2$ had plenty of unsaturated residual bonds, and different hydroxyl group bonding stats; it was ease to form a strong hydrogen bond with starch and (PVA). The Strong chemical bond (C-O-Si) was also formed in NPs SiO$_2$ /St/PVA hybrid materials, such that the strong interfacial binding force took place in NPs SiO$_2$ and St/PVA, and the films surface showed compact and smooth ultra structure [8].
Fig. 27: The optical micrographs of (PVA), (starch), and (St/PVA) blend films.

Fig. 28: The optical micrographs of (micro SiO$_2$/St/PVA) films.

Fig. 29: The optical micrographs of (nano SiO$_2$/St/PVA) films.

Conclusion
In this work, the results showed a single glass transition temperature ($T_g$) for all St/PVA blends that was attributed to the good miscibility of the blends involved. The ultimate strength of (PVA) was (47MPa), whereas the ultimate strength of
60%St/PVA was (11 MPa) and for 30%St/PVA was the highest ultimate strength of blends involved (26 MPa). 1.5% SiO$_2$µPs, and NPs of the best ultimate strength (69 MPa), (86 MPa) respectively then it was decreased by SiO$_2$µPs, and NPs increase. Optical microscope result proved that porous increase with (PVA) ratio increase that was attributed to the blend miscibility. For NPs SiO$_2$/St/PVA at different concentration: the (SiO$_2$) NPs films were smooth and compact that suggested the miscibility and compatibility of samples involved increased. It was concluded that the samples involved could be used as packaging materials for agriculture application and its degradation could be controlled by SiO$_2$µPs, and NPs addition.

References
[1] T. Hayashi, Prog. Polym. Sci., 19 (1994) 663-702.
[2] K. Sandhu, N. Singh, N. Malhi, Food Chem., 89 (2005) 541-548.
[3] T. Ouchi, S. Ichimura, Y. Ohya, Polymer, 47 (2006) 429-434.
[4] Z. Konsula, M. Liakopoulou-Kyriakides, Process Biochem., 39 (2004) 1745-1749.
[5] C.S. Pereira, A.M. Cunha, R.L. Reis, B. Vazquez, J.S. Roman, J. Mater. Sci. Mater. Med. 9 (1998) 825-830.
[6] N. Teramoto, T. Motoyama, R. Yosomiya, M. Shibata, European Polym. J., 39 (2003) 255-261.
[7] W. A. Zainab, D. Yu, J. D. Ian, B. Salim, Polymer-Plastics Technology and Engineering (2016) 1-38.
[8] HanGuo xiong, shangWen Tang, HuaLi Tang, PengZou carbohydrate, Polymers, 71 (2008) 263-268.
[9] Chao Wang, Jingwei Wei, Bingxiang Xia, Xian Chen, Bobing He, Journal of Applied Science J. Appl. Polym. Sci. (2012) 1-7.
[10] S. S. Shafik, J. M. Kawakib, I. K. Mohanad, International Journal of Materials Science and Applications, 3, 2 (2014) 25-28.
[11] B. Sreedhar, M. Safram, D. K. Chattopadhyay, R. P. A. Syamala R. D.V. Mohan, 96, (2005) 1313-1322.
[12] E.S.M. Negim, R. Raichan, Y. Gulzhakhan, U. Perizat, P. Saltanat, K. Daulet, K. Jamal, M. Grigory, W. Craig, International Journal of Basic and Applied Sciences, 3, 3 (2014) 263-273.
[13] J.M. Esraa, “Preparation of different polymer blends of (PVA) matrix as biodegradable packing materials and study its properties; Msc-thesis, University of Technology, Applied Science Materials Science, (2016).
[14] P. Fahmida, A. K. Mubarak, A. H. M. Saadat, M. H. K. Anwar, M. M. Jahid, M. A. Islam, M. A. Gafur, Journal of Polymers and the Environment, 19, Issue 4, (2011) 1013-1022.
[15] E. T Elisabela, E. P. Mona, R. Maria, P. Ovidiu, Romanian Biotechnological Letters, 20, 2 (2015) 10306-10315.
[16] Jobin Jose, Mamdouh A. Al-Harthi, Mariam Al-Ali AlMa’adeed, Jolly Bhadra Dakua, Sadhan K. De, Journal of Applied Polymer Science (2015) 1-8.
[17] Susmita Dey Sadhu, Anshuman Soni, Meenakshi Garg, J. Nanomedic Nanotechnol., 002 (2015) 1-5.
[18] Yuxin Liu, Xianzhong Mo, Jinying Pang, and Fang Yang”, Journal of Applied Polymer Science (2016) 1-9.
[19] P. Fahmida, R Arifur, M. M. I. Jahid, A. K. Mubarak, A. H. M. Saadat, Advanced Materials Research, 123-125 (2010) 351-354.
[20] S. Qingjie, N. Chong, D. Lei, J. Na X. Liu, School of Food Science and Engineering, Qingdao
Agricultural University, 66, Issue 9-10 (2014) 788-794.
[21] P.C, Sangeetaa, A-K. Jana, International Journal of Research in Mechanical Engineering and Technology IJMET, 3, 3 (2013) 36-40.
[22] W. D. Callister. Jr, “Fundamental material science and engineering; cdEth John wilye (2002).

[23] N. A. Azahari, N. Othman, H. Ismail, Journal of Physical Science, 22, 2 (2011) 15-31.
[24] Mohammad Taghi Taghizadeh, Narges Sabouri, Babak Chanbarzadeh, Springer Plus, Springer open Journal, 2, 376 (2013) 1-8.