



Effect of Acrylic Acid on The Mechanical Properties of PVA/ Starch Blend Films



El-Sayed Negim^{*1,2}, B. Bakytzhanuly³, P.I. Urkimbayeva³, L. Bekbayeva³, M.B.H. Othman⁴, M.N. Mohamad Ibrahim⁴, G.A. Mun³

¹Laboratory of Advanced Materials and Technology, Kazakh-British Technical University, 59 Tole bi St., 050000, Almaty, Kazakhstan

²National Research Centre, Polymer & Pigment Department, 33 El Bohouth St., Dokki, Giza 12622, Egypt

³Department of Chemistry & Technology of Organic Materials, Polymers and Natural Compounds, al Faraby Kazakh National University, 71, al-Faraby av., 050040, Almaty, Kazakhstan

⁴School of Chemical Science, Universiti Sains Malaysia, 11800 Penang, Malaysia

GRAFTING polymers based on acrylic acid (AA) with blend copolymer were synthesized with different ratio of AA (0.125, 0.25 and 0.5% by mass of blend copolymer) using ammonium persulfate as an initiator. The blend copolymer (PVA/S) was prepared by blending poly(vinyl alcohol) (PVA) with starch (S) in ratio (1: 1 wt.%), in presence of glacial acetic acid as a catalyst. The obtained polymers (PVA/S/AA) were characterized by FT-IR, TGA, DTG, SEM and mechanical test. The results showed that the mechanical properties of blend films are strongly dependent on the AA. Moreover, an increase in the ratio of AA in grafted polymers, increase thermal stability, tensile strength and elongation at break.

Keywords: PVA, Starch, Blend, Grafting, Mechanical

Introduction

Polyvinyl alcohol (PVA) is a biodegradable polymer and has been widely used in numerous applications as adhesive, paper, emulsifier, pharmaceutical, textile and in biomedical application [1-4]. PVA can be blended with other polymers including starch, chitosan, cellulose and polyethylene glycol [5-8]. Physico-mechanical properties of PVA play an important role in the industrial applications of PVA. There are many factors affecting the physico-mechanical properties of PVA including crosslinker, catalyst, solvent and temperatures. Solvents are used during preparation to improve freeze/thawed of PVA gels [5-7]. Formaldehyde, glutaraldehyde, acetaldehyde, tetra ethyl ortho silicate and other monoaldehydes are some of crosslinking agents used to crosslink PVA [9]. Mansur et al., [10] prepared PVA/poly (ethylene glycol) blend by

dissolving the polymer in aqueous solution in presence of 1.0 M HCl, followed by addition of glutaraldehyde as a crosslinker. PVA/PEG blends materials were successfully produced with GA crosslinking in the nanometer-scale network. Mamdouh et al., [11] investigated the preparation conditions of PVA/PEG including the ratio of PVA to PEG, solvent concentration, and temperature. An increase in the amount of solvent resulted in a decrease in the crystallinity of the resulting of PVA/PEG blend films.

Javanbakht et al. [12] studied the physico-mechanical properties of PVA/PEG blend treated with photo-initiated chemical vapor deposition. Contact angle measurements showed that both polymers increase in surface hydrophobicity after photo treatment. Further, the improved hydrophobicity facilitated dispersion into non-polar solvents.

*Corresponding author: elashmawi5@yahoo.com

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Mechanical properties of the PVA/chitosan blend crosslinked by glutaraldehyde were investigated via stress-strain tensile test. An increase in the chitosan content of blend, the swelling index and toughness decreased [8]. However, the plastic deformation, elongation at break and degree of crystallinity decreased by increasing ratio of chitosan in the blends. Moreover, the addition of chitosan enhanced rigidity and resistance fracture of the blend films [13-15].

The effect of composition and humidity on the properties of the PVA/starch blends were studied. The PVA/ starch blends were prepared with different compositions by melt process. Mechanical properties of blend films decreased with increasing content of starch and humidity. However, at 50% starch content, the flexibility of the blend films was still high with tensile strength of 9 MPa [6]. Negim *et al* [5] improved biodegradability of PVA/ starch blend films by using glacial acetic acid as a crosslinking agent. In addition, the effect of blend ratio and molecular weight of PVA on physico-mechanical properties of the blend films were studied. the results showed that crosslinking agent, blend ratio and molecular weight of PVA were highly effective in improving physico-mechanical properties of polymer blends.

In the present work, grafting of acrylic acid on blend copolymer in the presence of ammonium persulfate as initiator was prepared. The effect of acrylic acid on the physico-mechanical properties of the blend films was investigated.

Experimental Method

Materials

Poly (vinyl alcohol) (PVA) with a molecular weight 72000 g/mol was supplied by Fluka, Switzerland. Corn starch (S) was obtained from Changchun Jincheng Corn Development Co., Ltd., Da Cheng Gropu (China). Glacial acetic acid was purchased from Merck (Germany). Acrylic acid (AA) and ammonium persulfate was purchased from Aldrich (USA). All of these chemical were used without purification.

Synthesis of blend copolymer

Solutions of PVA/S blend (1 : 1 wt.%) have been prepared as previously described [5]. The mix proportion of PVA and S in the blend copolymer was 1: 1. The obtained blend solution has a viscosity of 350 cps.

Synthesis of grafting polymer

PVA/S (1:1 wt. %) blend solution was charged into a 500 mL three-necked flask. The free radical initiator (ammonium persulfate) was added to the flask during mechanical stirring at 800 rpm. The AA monomer was added at various concentrations (0.125, 0.25 and 0.5 % by the mass of the blend copolymer) drop by drop for 30 minutes during the stirring process at 65 oC using an automatically controlled water bath under nitrogen atmosphere. After that, the reaction was allowed to proceed for another 2 hrs at 65 °C, followed by another 1 hr at 80 oC.

Preparation of PVA/ S/ AA films

PVA/S/AA blend films were prepared by casting their aqueous solutions onto flat glass surfaces and allowing them to dry at room temperature for 7 days, and then in an aerated oven at 60 °C, for 12 h to completely eliminate water [16-20]. Then, the films were washed thoroughly with distilled water and followed by acetone in order to eliminate the residual glacial acetic acid and AA. Finally, the films were dried and stored in a desiccator at room temperature for further characterization and measurements.

Tests

FT-IR analyses for the prepared polymers were carried out using Perkin Elmer FTIR (300E, JASCO type, Japan). Thermogravimetric analysis (TGA) was recorded on a TGA/SDTA851e, METTLER TOLEDO. The measurements were carried out between 30 °C and 900 °C at a heating rate of 10 °C min⁻¹. The tensile properties of the blend films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. The microstructure of the hydrophilic polymers was investigated by scanning electron microscopy (SEM) recorded on a Carl-Zeiss SMT, Oberkochen.

Results and Discussion

FT-IR Spectra

FTIR spectra of pure PVA film, PVA/S blend, and PVA/S/AA are presented in Figure 1a-c. Figure 1a showed the most peaks associated with poly (vinyl alcohol). C–H broad alkyl stretching band at 2939 cm⁻¹ and 3274 cm⁻¹ for free alcohol (–OH stretching band). The peaks appeared between 1730 and 1680 cm⁻¹ for the C=O and C–O stretching vibration are related to the residual acetate groups in PVA [21-23].

Absorption peaks at 1141 and 1086 cm^{-1} are related to $-\text{C}-\text{O}$ stretching bond and $\text{C}-\text{O}-\text{H}$ bending vibration, were used for assisting semi-crystalline of PVA to form some domains depending on different process parameters [10, 24, 25]. The intensity of the OH peaks extended and became less broad as shown in Figure 1b due to the hydrogen bonding resulting from blending of PVA with S. In addition, a new band was observed at 1016 cm^{-1} related to $\text{C}-\text{O}-\text{C}$ (stretching vibration) of the glucose unite in the starch and confirms the blending between PVA and St. FTIR spectrum of PVA/S/AA is shown in Figure 1c. It can be seen the appearance of a new peak at 1712 cm^{-1} due to the carbonyl group of AA. Also, the intensity of OH reduced and became broader due to the grafting of AA on the blend copolymer PVA/S.

Thermogravimetric analysis (TGA)

Thermal properties of PVA/S and PVA/S/AA blend films were investigated by TGA/DGT technique to study the effect of acrylic acid as a crosslinker on thermal stability of PVA-S-AA biodegradable film. Figure 2 and Table 1 showed the thermogravimetric curves and some thermal properties of PVA-S-AA film series under a nitrogen atmosphere

The TG traces revealed three stages of thermal

decomposition for PVA-St-AA film series. The first stage of decomposition (T1) for the PVA-S-AA series significantly started at 40 $^{\circ}\text{C}$ and came to an end at about 180–230 $^{\circ}\text{C}$ with the maximum weight loss around 125 $^{\circ}\text{C}$ which corresponding to the removal of water. Besides, the major gases that are evolved during degradation such as hydrocarbons, CO_2 , CO , and H_2O . The presence of AA in PVA-S film has shown the degradation temperature at this stage shifted to a lower temperature, decreased by 40 $^{\circ}\text{C}$. This means, the acceleration of the degradation at a lower temperature was contributed by AA.

The second stage of decomposition (T2) for the PVA-S-AA series started around 200 $^{\circ}\text{C}$, corresponding to the decomposition of the PVA-S-AA main chain. Noted, this stage is a major contribution Thermal decomposition of PVA-S-AA film series. However, the degradation temperature at this stage shifted to a lower temperature. This due to the presence of AA will reduce the percentage of PVA-S chains in PVA-S-AA which attribute to reducing the existing bond strength of PVA-S. This is also supported by the reduction of the area under the curve on this stage. As the side groups are broken from the main chain at this stage, CO_2 , and H_2O are also produced during the second stage of decomposition as the

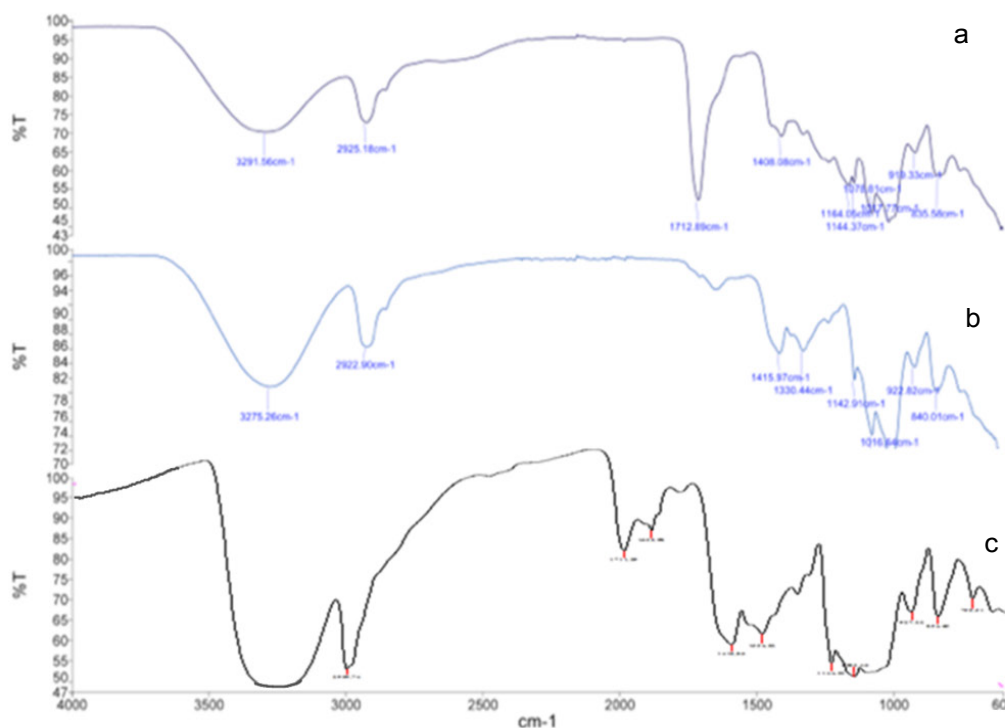


Fig. 1. FTIR spectra of (a) Pure PVA; (b) PVA/S (1/1) and (c) PVA/S/AA.

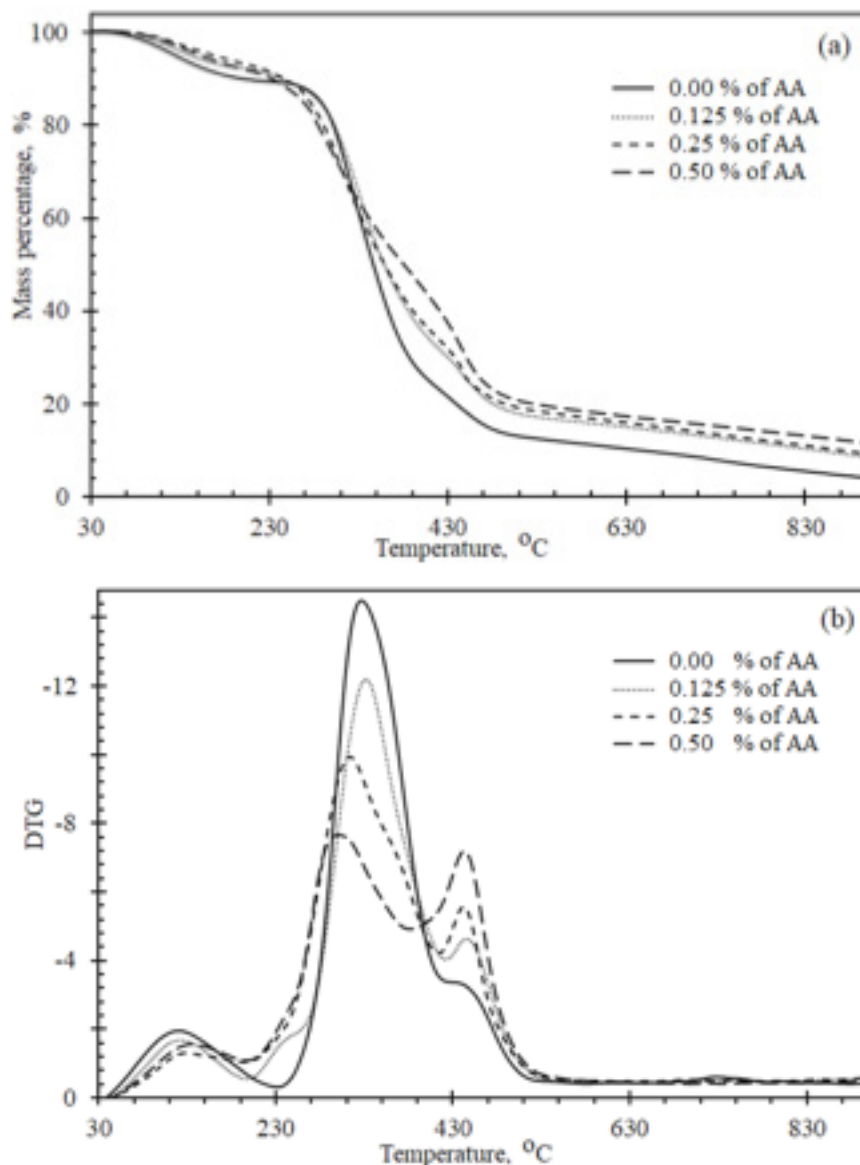


Fig. 2. Thermal decomposition of PVA-S-AA film series in N_2 atmosphere (a) Mass percentage (b) derivative thermogravimetric analysis, DTG.

main chain start to be broken down. However, H_2O is evolved at all temperatures from around 100 $^{\circ}C$ to very high temperatures, which indicates the ability of PVA-S to retain the moisture is better than PVA-S-AA molecule.

The third stage of decomposition (T3) for the PVA-S-AA series occurred around 440 $^{\circ}C$. At this stage, instead increase DTG intensity the presence of AA in PVA-S-AA film does not indicate any significant changes to thermal stability (shifting to left or right). At this stage, a maximum rate of mass loss (ΔT_2) showed a significant increase in value which indicates that the contribution of the

decomposition stability as thermodynamically. The CO_2 , CO , and H_2O are evolved during the third stage of decomposition. The evolution of gas may be due to breaking the crosslinked structure instead of the linear structure.

There was 8.5 % of residue once the degradation was completed at 900 $^{\circ}C$ as 0.125 % AA had reinforced in PVA-S-AA film series. The residue appears to increase once the AA content were increased. Apparently, the present of AA in PVA-S-AA showing a slight increase in thermal stability due to the resulting ΔT_2 and

TABLE 1. Thermal properties of PVA-S-AA film series in nitrogen atmosphere.

Sample Designation	T _{5%} ^a °C	T ₁ °C	T ₂ °C	T ₃ ^b °C	T _{2onset} ^c	T _{2end} ^d	ΔT ₂ ^e	Residue ^f %
1:1	126	121	328	442	233	536	303	4.1
1:1:0.125	143	123	333	444	197	557	360	8.5
1:1:0.25	169	130	315	443	196	560	364	9.3
1:1:0.50	154	136	301	443	198	567	368	11.6

^a Temperature corresponding to percentage of mass loss, 5%,

^b Temperature of maximum rate of mass loss,

^c Onset temperature of degradation,

^d Endset temperature of degradation,

^e ΔT = T_{end} - T_{onset},

^f wt. % residue at 900 °C

residue. This suggests that instead of reducing the PVA-S in PVA-S-AA film, AA acting as a crosslinker or copolymerized in the PVA-St-AA and both improving the thermal stability properties of PVA-S-AA film.

Mechanical properties

The effect of grafting of AA with different concentrations (0.125, 0.25, 0.5 %) on the mechanical properties of PVA/S blend films is shown in Figures 3 and 4. An increase was observed in tensile strength from 27 MPa (0.0 AA) to 42 MPa (0.5% AA) when AA grafted on PVA/S as shown in Figure 3. Also, the tensile strength of grafted films increased from 34 MPa to 42 MPa with increasing the concentration of AA in the grafted films from 0.125% to 0.5 %. The increase in tensile strength with grafting AA on blend films is due to network cross-linking between AA and blend copolymer (PVA/S). Carboxyl group of AA acted as a cross-linker agent among polymer backbone chain of PVA and S. At the highest concentration of AA, cross-linking become more and gave the highest mechanical properties. Similar results based on blend films prepared with different ratios of starch/ PVA/ citric acid have been reported [26-28]. The grafting of AA on the blend films enhances the mechanical properties of blend films and increases their elongation at break. However, elongation at break of blend films increased from 87% to 239% when concentration of AA grafted on blend films increased up to 0.5 % as shown in the Figure 4. Blend films grafted with 0.5% AA gave the highest elongation at break (239%), while blend films grafted with 0.125% gave elongation at break (127 %) [5].

Scanning electron microscopy (SEM)

The SEM micrographs of pure PVA film, PVA/S with AA (0.125, 0.25 and 0.5%) at 1000 magnification are shown in Figure 5a-e. The surface morphologies show differences between PVA and PVA/S after addition of different concentrations of AA. Figure 5a showed the spaces between the nodulus are quite small. Obviously, the surface morphology of PVA/ S undulant and coarse surface due to undissolved starch particles as shown in Figure 5b. However, as the concentration of acrylic acid is increased, the spaces between the nodulus become apart. Figure 5b showed the largest space between nodulus for the PVA/S with AA 0.5% compared to others. In Figure 5c, PVA/S with AA 0.25% showed less spaces between the nodulus compared to Figure 5b but wider space area of nodulus than Figure 4d (PVA/S with AA 0.125%). Larger space could be due to better cross-link of the polymers [29]. Thus, the conditions for the production of films with a high content of starch with the introduction of acrylic acid (AA) in the films are optimized. The presence of a carbonyl group of acrylic acid in the film mixture was detected by IR spectroscopy.

Conclusions

PVA/Starch blend films grafted with acrylic acid (AA) at different concentrations (0.125, 0.25, 0.50 % by the mass of PVA/S) were prepared. The obtained blend films were characterized in terms of their chemical composition, thermal properties, microstructure, morphology, and mechanical properties. Based on the experimental results, the following conclusions can be summarized as follow:

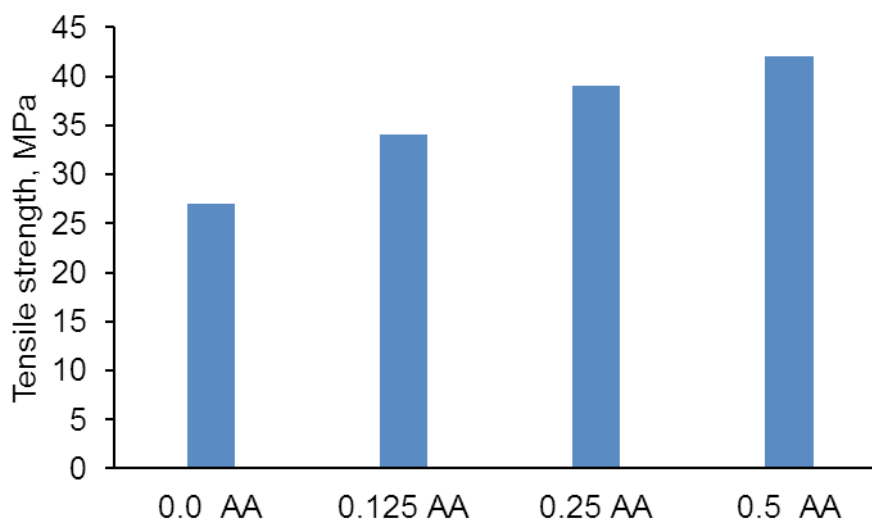


Fig.3. Effect of AA concentrations on tensile strength of the PVA/S/AA blend films.

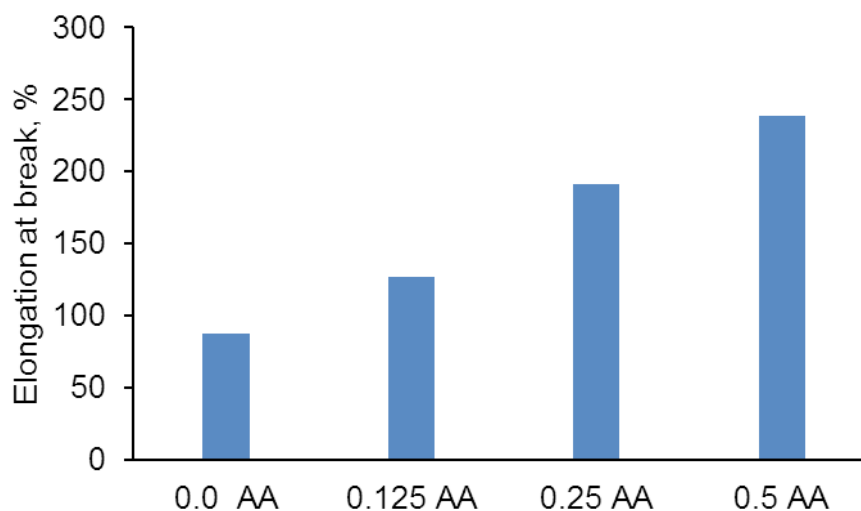


Fig. 4. Effect of AA concentrations on elongation at break of the PVA/S/AA blend films.

1. TGA and DTG measurements revealed that grafting PVA/S blend films with AA increased thermal stability of PVA/S/AA films, especially those grafted with 0.5 wt. % AA.
2. Elongation at break and tensile strength of the blend films increase with increasing the content of AA in the PVA/S/AA blend films.
3. SEM of the PVA/S/0.5% AA blend film showed larger space of nodulus than others that could be attributed to the high crosslink density in this blend film.
4. Optimized conditions for the production

of films based on PVA and high content S with incorporating AA into the films as a crosslinking agent were PVA/S (1/ 1 wt. %) and 0.5 wt.% AA (based on total weight PVA/S blend).

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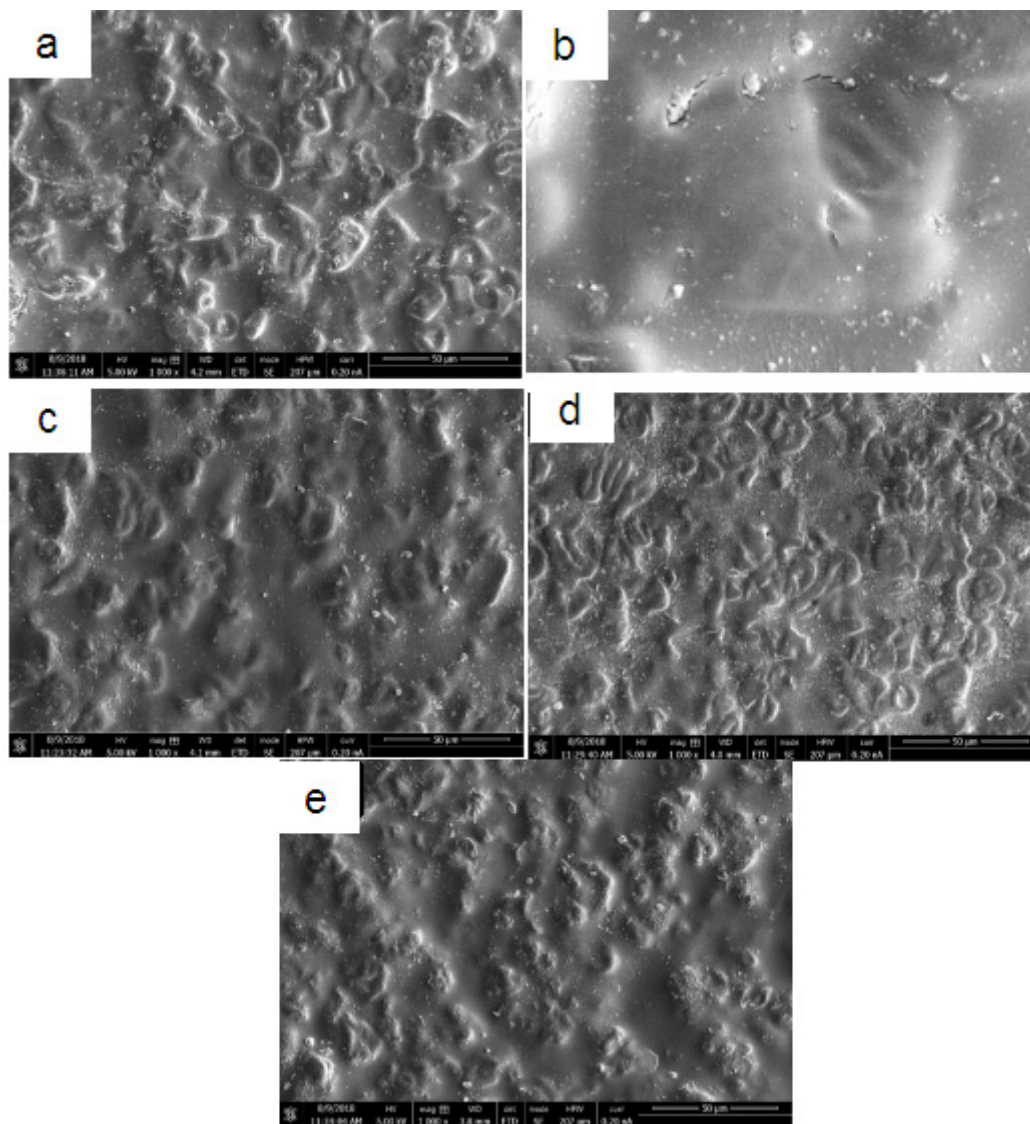


Fig. 5. SEM image of (a) Pure PVA; (b) PVA/S (c) PVA/S/0.5% AA; (d) PVA/S/ 0.25% AA and (e) PVA/S/ 0.125% AA.

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