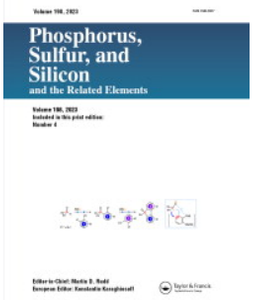

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Nano SiO_2 doping effect on physicochemical properties of PVA-starch bionanocomposite films

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ABSTRACT

In this study, starch-PVA based composite films combined with nano SiO_2 were prepared by a solvent casting technique. Different amounts of nano SiO_2 additives were added to starch-PVA films and the results were evaluated. Accordingly, in starch-PVA films containing nano SiO_2 added in the ratio of 1%, 3%, and 5% by mass, nano SiO_2 was homogeneously distributed on the surface of the composite films. However, loss of elasticity was observed in films from containing 3% nano SiO_2 onwards. The unique properties of nanocomposite films obtained with small amounts of nanomaterial reinforcement have been demonstrated. Composite films have been characterized by Fourier-transform infrared spectroscopy, UV–Vis spectrophotometry, and field emission scanning electron microscopy. Fogging tests were compared. Less nano SiO_2 additive in the samples showed the best anti-fogging behavior. This study aims to demonstrate the potential use of starch-PVA nanocomposite films with unique properties in food packaging applications. The surface of starch/PVA films is strengthened by the deposition of SiO_2 nanoparticles.

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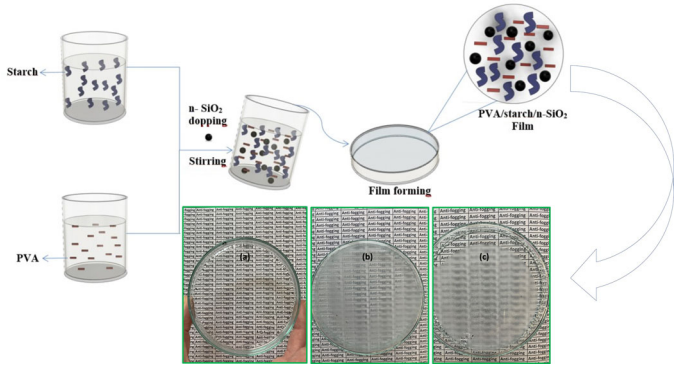
KEYWORDS
Food packaging; polyvinyl alcohol; starch; nano-SiO_2; solvent-casting; anti-fogging

GRAPHICAL ABSTRACT



Introduction

Today, the increasing consumption of ready-to-eat foods creates the need for the development of smart food packaging materials such as petroleum-based polymers and bio-based plastics.[1] Various polymers have been used in many applications in food packaging materials. It has been found that the use of polymer alone has some limitations. These limitations include low mechanical and thermal stability and weak anti-bacterial properties.[2] Poly vinyl alcohol (PVA) is a film-formable polymer with flexible and adhesive properties. Nanotechnological initiatives in materials that have used in the food packaging industry are beneficial in the widespread for using of smart materials with nano additives. Environmental problems caused by non-biodegradable, petroleum-based packaging materials, and their negative effects on human health have triggered the development of biopolymer-based nanocomposite films. Our study is an example of green chemistry, as each material used in this study has biodegradable, nontoxic, and bioactive properties. Thus, it enables the use of nanocomposite films developed as packaging material[3] for food preservation, easy use, preservation, and long-term storage.[1] In this way, these materials can be made more attractive in conventional systems.[4] However, packaging is a procedure that protects food from external pollutants.[5] Packaging materials prepared by traditional methods[6] do not control the interaction of the nutrients in the products with the packaging. Oxygen, moisture and light are the most sensitive elements of these interactions.[7] Bionanocomposite films, usually made by proteins, polysaccharides, lipids, and different biopolymers, contribute to reducing the use of petroleum-based plastics as renewable and biodegradable packaging material.[8–10] Due to its tendency to composite formation, high hydrophilicity, excellent composite stability and excellent film forming ability, PVA is suitable for use in food packaging

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films.[11–13] PVA has strong bond interaction properties with the presence of a great number of hydroxyl groups that trigger the formation of hydrogen bonds.[14] With the declaration made by EFSA in 2005, it has been proven that PVA can easily be used as a coating material for some foods without causing health problems.[15] PVA is one of the smart food packaging material.[16] Smart food packaging materials are also preferred for long-term storage of products without deterioration.[17–19] The pH difference between the foods and the visual colorimetric changes of the packaging have become traceable with this method.[19,20] In addition, color changes can be observed due to the change in temperature during storage and the diffusion rate of the dyes in the package at various temperatures.[21,22] Spoilage of food due to microbial contamination is also a serious problem for food safety.[23] Therefore, there is high interest in a new and functional food packaging materials that inhibit microbial growth.[24] Many non-synthetic biopolymers, such as pectin,[25] starch,[26] konjac glucomannan,[27] and chitosan,[19] have been widely selected in food packaging by virtue of their low toxicity, biodegradability and biocompatibility.[19] Starch is widely used in food packaging because of its low cost and film forming ability.[28–30] However, the lack of mechanical strength and sufficient water resistance is a problem that needs to be overcome with starch-based films. To avoid this problem, starch can be chemically crosslinked with sodium trimetaphosphate (STMP).[31] In addition, the water resistance property of starch can be improved by using it as a mixture with hydrophobic polymers such as poly-vinylalcohol (PVA).[32] Starch has received a great deal of attention in this field at both academic and industrial levels. Although starch is widely used as a food packaging material, its weak mechanical and thermal properties are among its most important disadvantages.[4] To overcome the weak properties of starch, it can be blended with polymers such as PVA, PLA, and lignin.[33] It has been reported in previous studies that PVA has excellent compatibility with starch.[34] While PVA improves the weaknesses of starch, it has less mechanical strength due to its moisture retention property. Silicon is a strong metalloid found in abundance in the earth's crust.[5] Silicon dioxide nanoparticles are fused with petroleum-based or natural polymers to increase mechanical and thermal strength.[35,36] SiO_2 nanoparticles are widely used in plastics, elastics, and other materials in stable form, in light of their small molecular size, tremendous surface area, and reactivity of surface hydroxyl groups.[37–39] In this study, mechanical strength was achieved by adding SiO_2 nanoparticles into the starch/PVA blend as a nano-reinforcement material using the solvent casting technique. The individual superior properties of the polymer and starch were preserved and combined in a single material with the solvent casting technique.

Results and discussion

Fourier-transform infrared spectroscopy (FT-IR) analysis

The functional groups of PVA, starch, and SiO_2 was given in Figure 1 and Table 1. PVA had the characteristic broad peak at 3275 cm^{-1} that corresponds –OH stretching vibration.[40,41] The band at 2917 cm^{-1} and 2906 cm^{-1} was evidence of the presence of alkyl groups. The strong C–H bending peaks at 1422 cm^{-1} and 1325 cm^{-1} region were seen. The most intense sharp peak at 1090 cm^{-1} belonged to –OH stretching and it indicated the acetyl group on the PVA backbone.[42] Starch was characterized with the broad-band at 3288 cm^{-1}, medium band at 2924 cm^{-1}, and weak band at 1333 cm^{-1} by O–H stretching, C–H stretching and C–H bending, respectively.[43] The adsorption band at 1637 cm^{-1} was showed intermolecular H-bond involving the carboxyl group.[44] The strong and sharp peak was attributed to O–H bending in starch structure. Si–O–Si asymmetric stretching and bending vibrations were seen in the spectrum of SiO_2 cm^{-1} at 1067 and 453 cm^{-1}.[45,46] The weak peak at 3370 cm^{-1} signified surface –OH group where the bending of –OH groups adsorbed water molecules.[47]

FT-IR spectra of PVA:starch film and PVA film were given in Figure 2 (left). The PVA film conserved the groups that the PVA polymer in powder form contains such as alkyl (CH_3–) (2917 cm^{-1} and 2906 cm^{-1}) and acetyl groups (1090 cm^{-1}). When starch was added to PVA film, the peaks belonging to the C = O stretching of powdered starch also became more distinct that located at between 1500 and 1845 cm^{-1}. As can be seen from the spectra, when starch is added to PVA film, both PVA and starch preserve their characteristic properties in the composite film. The results of FT-IR analysis performed in order to specify the SiO_2 nanoparticles in PVA-starch films were given in Figure 2 (right). The intensity of the peak seen in ~3260 cm^{-1} region which indicated the –OH stretching decreased with the addition of SiO_2 nanoparticles to PVA-starch films. The peak, that showed the C = O groups in the starch structure and seen at 1709 cm^{-1}, lost their intensity as the amount of SiO_2 nanoparticles increased. In addition to this, the peak intensity in the 1332 cm^{-1} region belonging to the C–H groups in the PVA structure also decreased when SiO_2 amount increased in the film. The intensity of the Si–O–Si asymmetric stretching peak (1067 cm^{-1}), which was the characteristic for SiO_2 nanoparticles, was highest in 5% SiO_2 containing film; as the amount of SiO_2 decreased, its intensity decreased. This result may be due to the interaction between nano material and polymer chain.

Scanning electron microscope (SEM) analysis

In order to examine the morphological properties of nano-composite films, SEM images of the materials used in film

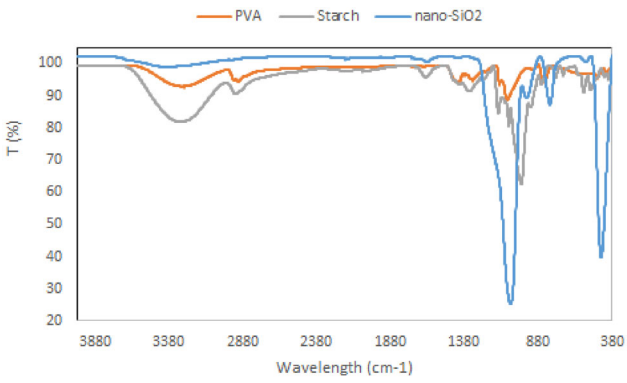

Figure 1. FT-IR spectra of PVA, starch, and nano SiO_2.

Table 1. FT-IR tables of PVA, starch and SiO_2.

Wavenumber (cm^{-1})	Chemical group	Possible compounds	Identification		
			PVA	Starch	SiO_2
3200–3900	O–H stretching	Water, alcohol, phenols	Broad	Broad	Weak
2840–3000	C–H	Alkyl groups	Medium	Medium	None
1500–1845	C = O stretching	Ketones, aldehydes, carboxylic acids, esters	Low	Medium	None
1325–1500	C–H bending	Alkanes	Strong	Weak	None
950–1300	C–O stretching O–H bending	Primary, secondary and tertiary alcohols, esters, ethers, R–OH	Strong sharp	Strong sharp	None
846	C–C		Strong	None	None
~1067	Si–O–Si asymmetric stretching	SiO_2	None	None	Strong sharp
~453	Si–O–Si bending	SiO_2	None	None	Strong sharp

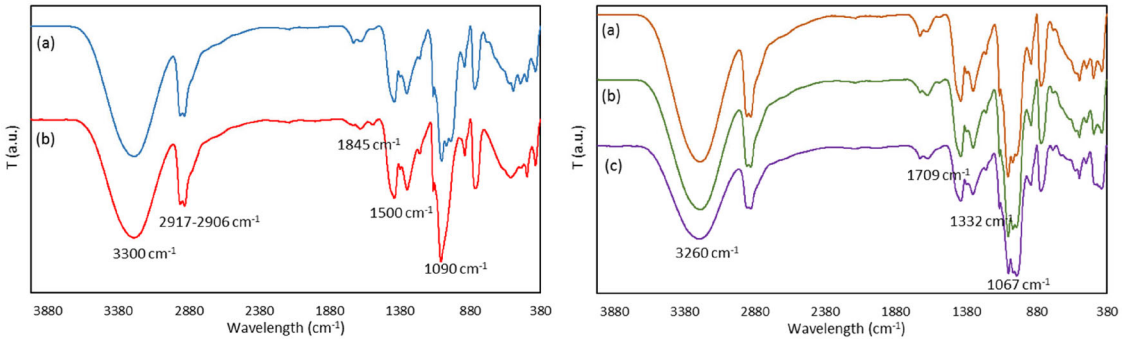

Figure 2. (left) FT-IR spectra of (a) PVA:starch film (b) PVA film; (right) FTIR spectrums of SiO_2 doped PVA:starch film (a) 1% SiO_2, (b) 3% SiO_2, and (c) 5% SiO_2.

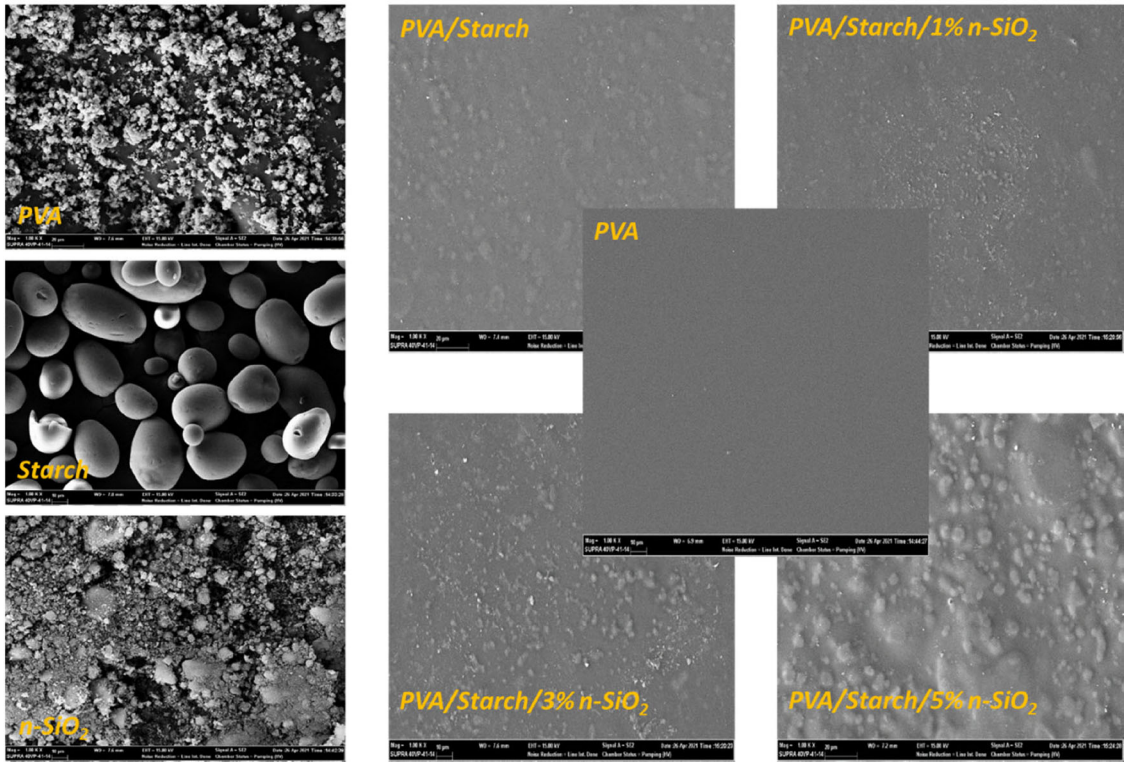

Figure 3. The morphological images of raw materials PVA, starch and nano SiO_2 (left column); SEM images of PVA, PVA/starch and 1%, 3%, and 5% nano SiO_2 doped PVA/starch nanocomposite films (right column).

production were taken. Looking at the left column of Figure 3, SEM images of PVA, starch, and nano SiO_2 powders (from top to bottom) are seen, respectively. Although PVA powders have a leafy structure, starch and nano SiO_2 consist of micro and nanospheres (Figure 3).[48] Synthesized films for use in food packaging are smooth, homogeneously doped and elastic structures are obtained without the use of cross-linkers (Figure 3 right column). Film forming of PVA is seen in the center of the right column. According to the SEM image of the PVA-starch blend obtained with starch in order to provide stronger mechanical strength, it is seen that the starch is homogeneously distributed in the smooth PVA

on the surface substrate. In order to provide stronger mechanical strength, the SEM image of the PVA-starch blend is seen homogeneously distributed in the smooth PVA on the substrate. By adding nano SiO_2 as a reinforcement material to the PVA-starch blend, the films have been functionalized. SEM images of PVA-starch films containing 1%, 3%, and 5% nano SiO_2 by mass, respectively, are given in Figure 3, right column. The homogeneous distribution of nano SiO_2 added at each ratio on the PVA-starch surface is clearly seen. On the other hand, agglomerated structures were seen on the surface of PVA-starch containing 5% nano SiO_2.

Elemental map images show that Si distribution on starch-PVA composite films in Figure S1 (supplemental materials). The distributions were given by the red dot belong to the element Si in nano SiO_2. As expected, the distribution of Si on the film surfaces increased as the percentage by mass increased.

Table S1 (supplemental materials) shows the table of EDX spectrum results of nano SiO_2 dispersed on the starch-PVA composite film surface. Accordingly, Si on the surfaces was found to be 1.53%wt. in 5% doping, which is the highest ratio of addition. At the map results of the films, the most dispersed Si amount on the surface belongs to the PVA/Starch/5% n-SiO_2 nanocomposite film. Also, in 1% nano SiO_2 doping, the amount of Si on the surface could not be detected because of with low amount of nanomaterial reinforcements in nanocomposites.

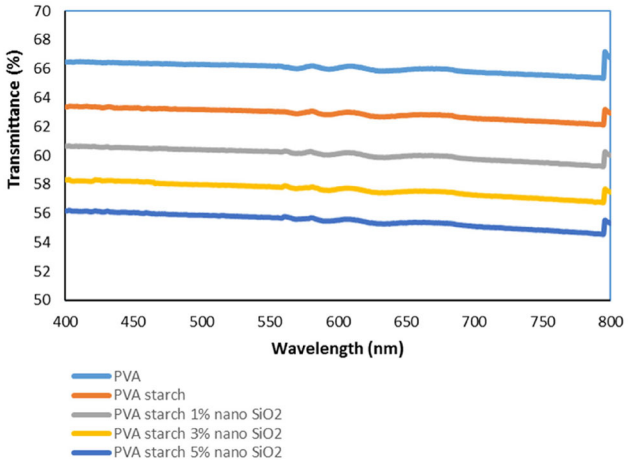

Figure 4. UV spectrum of nanocomposite films.

UV analysis

%T measurements of nanocomposite films were tested by UV analysis. In Figure 4, spectroscopic comparison of PVA, PVA-starch, and nano SiO_2 doped PVA-starch films is given. According to this result, it is the PVA film with the highest UV transmission with 66%. The UV transmission of the film obtained with the PVA-starch mixture is 63%. As SiO_2 was added, the UV–Vis permeability of the films decreased in the 400–800 nm wavelength range.[4] The least permeable film is PVA-starch composite film with approximately 56% with 5% nano SiO_2 doped PVA/starch solution.

Anti-fogging tests

Anti-fogging behavior tests can be performed in two different ways. The first of these; fogging in coated and uncoated petri dishes placed over a beaker with hot water. The second is the fogging test observed after the coated and uncoated petri dishes are kept in the freezer for a while.[49] In Figure 5, the first one of the tests was chosen and applied in a simple way. There is a PVA film coating on the "a" petri dish. As can be seen, there was no condensation on the film after the hot water vapor treatment. The anti-fogging behavior of an uncoated glass petri dish is indicated by "c." The "*Anti-fogging*" text below is unreadable. It has been proven that PVA coated packaging materials will not fog up under hot-cold effects. It was observed that the starch-PVA film-coated petri dish denoted with "b" fogged more than the PVA-coated film.

Anti-fogging tests were performed for PVA, starch-PVA, and uncoated glass petri dishes (Figure 5). The images in which starch-PVA films doped with different amounts of nano SiO_2 are compared with uncoated petri dishes are given in Figure 6. According to the results of Figure 6, although the films obtained are homogeneous, they appear

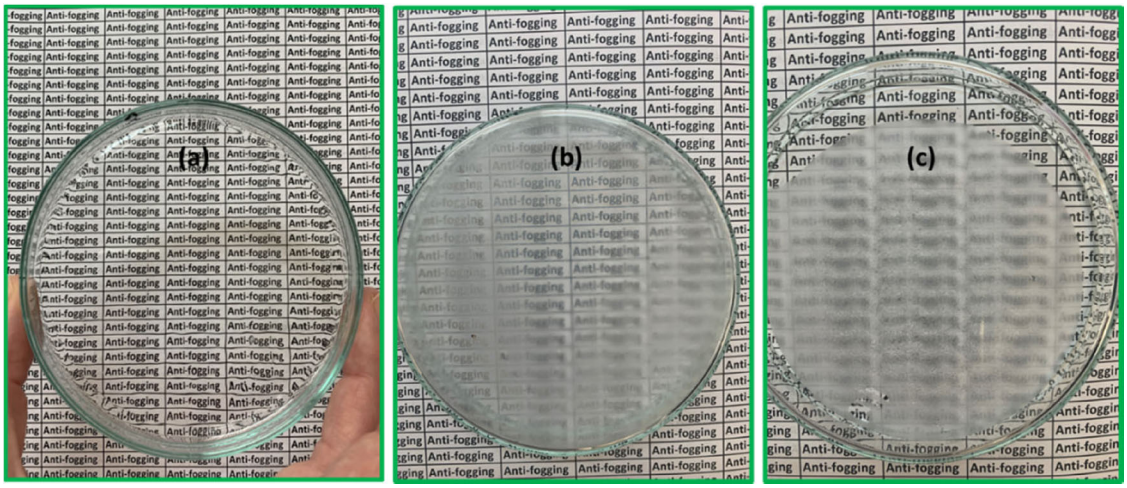

Figure 5. Anti-fogging behavior of (a) PVA film; (b) starch-PVA film; and (c) glass petri dish without film coating after hot water treatment.

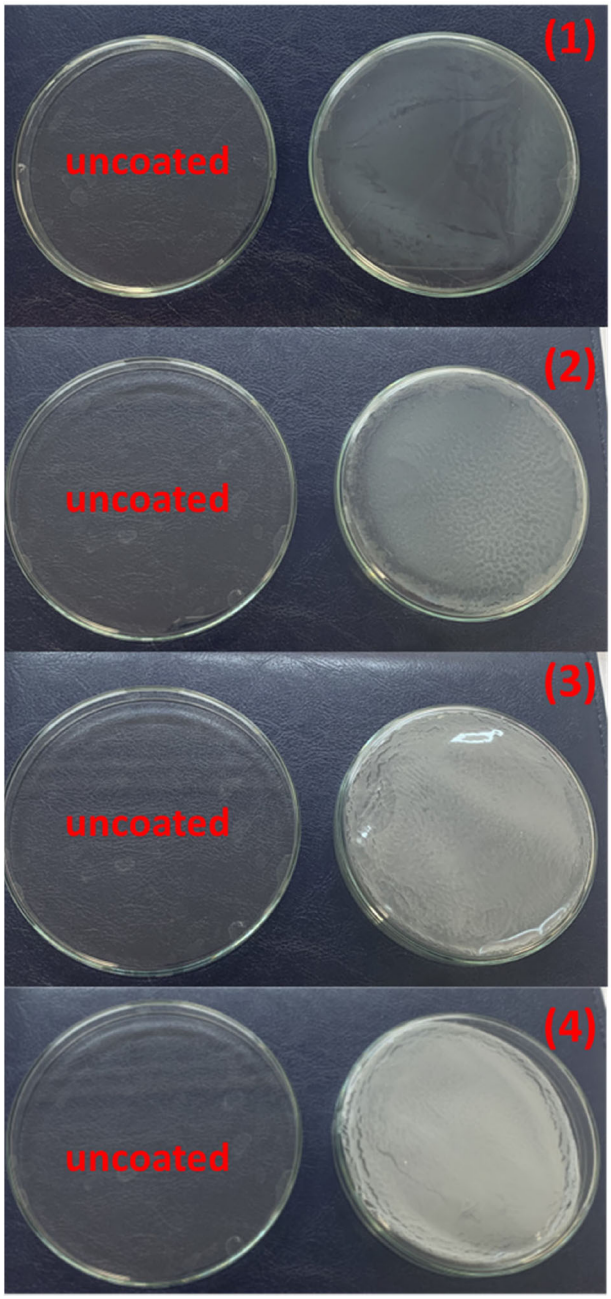

Figure 6. Uncoated and coated petri dishes for show the amount of nano SiO_2 effect on the nanocomposite films (1) starch-PVA film, (2) starch-PVA/SiO_2 (1%) film, (3) starch-PVA/SiO_2 (3%) film, and (4) starch-PVA/SiO_2 (5%) film.

to be opaque. The opacity of the films increased as the amount of SiO_2 increased. Anti-fogging tests have not been carried out due to opacity, but the anti-fogging properties of the SiO_2 additive-free polymer blend matrix are also seen in film composites with SiO_2 additives.

Materials and methods

1%, 3%, and 5% by mass of nano SiO_2 were added onto the 10% PVA and starch solution mixed in equal volumes. The parameter of additive was chosen by optimized previous studies of these authors.[50] Nanocomposite films are prepared in glass petri dishes by using solvent casting technique. The starch and PVA were obtained from Merck, Germany, and nano SiO_2 from Sigma Aldrich, USA. All of the solutions were prepared by deionized water in the study.

Film production of starch/PVA/SiO_2 bionanocomposite films

The starch solution 10% (wt) was heated in 2% (v/v) acetic acid solution at 60 °C until a homogeneous aqueous solution was obtained. 10% (wt) PVA solution in distilled water was prepared by heating for 2 h at 80 °C. 10 mL starch solution and 10 mL PVA solution) were blended by assembling the two polymer solutions without interruption mixing. The mixture was stirred on a magnetic stirrer for 1 h at 80 °C. 1%, 3%, and 5% (wt/v) nano SiO_2 as reinforcement materials were added while preparing the PVA solution and homogeneous distribution was completed. The nanocomposite solutions obtained were poured into glass petri dishes and kept at room temperature for 48 h to form a film.

Characterization

FT-IR analysis

The functional groups of the raw materials and synthesized films were specified by using FT-IR (Perkin Elmer, Spectrum 100) with a wavelength range of 4000-380 cm^{-1}. Attenuated total reflectance (ATR) module was used with the resolution of 4 cm^{-1}.

SEM analysis

Scanning electron microscopy (ZEISS, SUPRA 40VP) was used to identify the surface characteristics of the raw materials and synthesized films. Coating process were carried out to provide conductivity of samples under the Au/Pd source in the sputter coater (Quorum, Q300 model). During the SEM analyses, working distance (WD) was ~10 mm, acceleration voltage (EHT) was 15 kV and the detector was secondary electron (SE) detector. Elemental composition of the films and its distribution were defined by performed the energy dispersive X-ray spectroscopy (EDX) and mapping technique (Bruker, EDX detector).

UV analysis

Perkin Elmer Lambda 25 UV–Vis Spectrometer between 400 and 800 nm wavelengths were used to apply absorption studies to determine the transmittance of the synthesized films.

Anti-fogging test

The anti-fogging behavior of the polymer blend films was examined by placing them on a beaker with full of hot water. They were kept for 1 min. and placed onto "anti-fogging" written text. The results of the reading capability of the fogged films were taken imaged by camera.

Conclusion

The data obtained from this study showed that these nanocomposite films can be used as an alternative instead of conventional food packaging materials. Conventional products have included glass, cans, and aluminum foil can be replaced by new bio-degradable smart packaging materials. PVA/starch-nano SiO_2 nanocomposite films will be candidates for this kind of new material. These biopolymer blend-based composite films and different ratio of nano SiO_2 doped forms of the films were prepared without the use of toxic crosslinking agents by solvent casting technique. Advantage of the solvent-casting method is easy to applicability. Starch and PVA polymers in the film have been used together to improve their water resistance and mechanical strength. Additionally, the superior physico-chemical properties of both PVA and starch were also preserved. Strong and weaker interactions between starch, PVA, and nano SiO_2 were examined by FT-IR spectrums. The chemical compatibility of the matrix and reinforcement materials that make up the films are shown with these spectra. Morphological evaluations of the nanocomposite films obtained by SEM analysis. Also, the homogeneous distributions of SiO_2 on the film surfaces have been shown by the mapping technique. UV-light transmissions from the films were detected and the results show that maximum % transmittance of the film was plain PVA. After the starch-polymer mixture was prepared, it was observed that UV–Vis. permeability decreased in the films with nano SiO_2 added. The fogging resistance in hot-cold environments indicates that these materials are also suitable for food packaging. According to the findings obtained it was observed that there were agglomerations on the film surfaces at high nano SiO_2 amounts. In future studies, different pre- and post- treatments should be developed to prevent these limitations.

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Disclosure statement

The authors report no declarations of interest.

Research involving human participants and/or animals

This research does not involve Human Participants and/or Animals.

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