



Article UV Blocking and Oxygen Barrier Coatings Based on Polyvinyl Alcohol and Zinc Oxide Nanoparticles for Packaging Applications

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Abstract: Photodegradation and oxidation are major causes of the deterioration of food, resulting in darkening, off-flavors, and nutrient deficiency. To reduce this problem, novel functional polymeric materials are being developed to retain food's light sensitivity. Nanofillers are also used in a polymeric film to produce effective UV blockings and oxygen barrier coatings so that the degradation of the food can be delayed, thereby increasing the shelf life. For this purpose, polyvinyl alcohol coatings were prepared by the incorporation of ZnO nanoparticles. Polyvinyl alcohol is a naturally excellent barrier against oxygen, and the addition of ZnO particles at the nanoscale size has demonstrated effective UV blocking capabilities. In this work, the hydrothermal technique is used to produce ZnO nanoparticles, and these produced particles are then incorporated into the polyvinyl alcohol to produce thin films. These films are characterized in terms of the compositional, macroscopic, microscopic, and optical properties via X-ray diffraction (XRD), FTIR, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA), as well as UV–VIS spectroscopy. ZnO nanoparticles at different concentrations were incorporated into the PVA solution, and the films were processed via the blade coating method. With the addition of ZnO, the oxygen transmission rate (OTR) of pure PVA was not altered and remained stable, and the lowest OTR was recorded as $0.65 \text{ cm}^3/\text{m}^2 \cdot \text{day} \cdot \text{bar}$. Furthermore, the addition of ZnO increased the water contact angle (WCA) of PVA, and the highest WCA was recorded to be around more than 70°. Due to this, water permeability decreased. Additionally, PVA/ZnO films were highly flexible and bendable and maintained the OTR even after going through bending cycles of 20K. Furthermore, the addition of ZnO showed a significant UV blocking effect and blocked the rays below a wavelength of 380 nm. Finally, the optimized films were used for packaging applications, and it was observed that the packaged apple remained fresh and unoxidized for a longer period as compared with the piece of apple without packaging. Thus, based on these results, the PVA/ZnO films are ideally suited for packaging purposes and can effectively enhance the shelf life of food.

Keywords: zinc oxide nanoparticles; UV blocking; oxygen barrier; hydrothermal method; polyvinyl alcohol



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1. Introduction

Food is exposed to sunlight and visible light throughout its preparation, packing, preservation, transportation, and promotion, which drastically reduces its storage life, freshness, color, and flavors, as well as vitamins [1]. These harmful effects can be prevented through the selection of a proper packaging material [2]. Ideally suited packagings provide several advantages for food, including extending the shelf life and preserving or improving food quality and safety [3]. Food degradation caused by UV, diffusion of moisture as well as oxygen, and, to a lesser extent, organic vapors is one of the most serious issues faced by personnel involved in the food business [4]. Moisture, filling gas, temperature, light, and pH are all factors that have an impact on the packed food's deteriorating characteristics. The most critical elements impacting the excellent preservation of its contents are gas permeability and moisture of the food packaging materials [5,6]. Food degradation is accelerated by storing it in unsuitable conditions, necessitating greater food preservation [7]. Packaging various food goods using a compatible polymeric material extends their storage life and helps to preserve their quality [8]. For food packaging, several polymeric materials are used, although these conventional packaging materials may have a harmful influence on human health. To reduce this negative impact, novel functional polymeric materials are being produced to retain the quality and preserve the food through light sensitivity [9].

Polymeric food packaging films seem to be the most frequent solution, and they work well [10]. Polymeric food packaging may preserve food from microbial damage and possesses features including elasticity, toughness, tensile, and an atmospheric and humidity barrier [11,12]. Polyvinyl alcohol (PVA) is an emerging polymer used for packaging; it is a biodegradable and water-soluble polymer that is ecologically beneficial [13,14]. It is also a nontoxic and biocompatible polymer that may be used in different packaging applications, such as biomedical, food, and cosmetics [15]. PVA is a kind of biopolymer that has strong mechanical and oxygen barrier qualities, along with good formability and transparency in the visible light spectrum [16]. However, PVA biopolymer-based films and their derivatives are hygroscopic and have poor moisture barrier characteristics [13,17]. These qualities can be improved by combining two or more biopolymers and using a small concentration of nanofillers [18].

To preserve the quality of food, many types of fillers can be added to the polymeric films. Nanomaterials are gaining popularity due to their favorable influence on packaging materials (i.e., effectively blocking the UV light and decreasing the permeability of reactive gases). Nanofillers are employed in polymeric packaging material to prevent the quick deterioration of food items contained therein. Some of the nanofillers act as UV screens, absorbing damaging radiations. The US Food and Drug Administration (FDA) has authorized two inorganic filters (commonly known as mineral filters): titanium dioxide (TiO_2) and zinc oxide (ZnO); both are metal oxide particles [19]. These molecules absorb, reflect, and refract UV photons, but they predominantly operate in photoprotection by absorbing UV radiation [20]. Because TiO_2 seems to be more active in the UVB range and ZnO in the UVA range, the only UVA barrier necessary for food packing is zinc oxide [21,22]. ZnO nanoparticles (NPs) have received a great deal of attention due to their ease of production, low cost, unique physical features brought about by the size effect, and prospective uses in UV blocking materials [23]. Among nanoparticles, ZnO NPs are a popular choice for a variety of applications. ZnO NPs can be used for UV barrier properties, antifungal and antimicrobial activities, photovoltaic testing, beauty products, packaging materials, biomaterials, self-cleaning, water and air cleaning, sterilizing surroundings, and photocatalysts due to their unique physical and chemical properties, such as high electrochemical coupling coefficient, more chemical stability, a diverse range of absorbing radiation, huge excitonic binding energy (60 meV), and large energy bandgap [24,25]. ZnO NPs have several outstanding properties, including ease of synthesis, controllable form and size, excellent biocompatibility, and their intrinsic ability to emit a wide range of colors (violet, blue, green, yellow, and red) [26–28]. A range of synthetic approaches are employed

for the synthesis of ZnO NPs, including hydrothermal methods, and there are no obvious methodologies for producing ZnO NPs utilizing hydrothermal procedures [29,30].

In this work, nanocomposite films were produced by incorporating ZnO into the PVA matrix. Natural oxygen blocking of PVA and UV blocking of ZnO together can produce an ideally suited film for food packaging applications. Therefore, the hydrothermal technique was used to produce ZnO nanoparticles. SEM was used to examine the morphology of nanoparticles. FTIR was used to investigate chemical interactions, whereas XRD was used to investigate the crystalline structure. For the first time, a doctor coating machine was used to develop a polyvinyl alcohol film containing ZnO nanoparticles. Furthermore, data were collected using an ultraviolet transmission analyzer to determine the effect of the ZnO filler on PVA for UV protection, which was the major purpose of this experiment.

2. Experimental Section

2.1. Materials

Sigma-Aldrich supplied zinc nitrate hexahydrate (purity 99.8%), potassium hydroxide (purity 99.5%), and polyvinyl alcohol (purity 98%). Dae-Jung Chemicals & Metals supplied hexamethylene tetraamine (purity 98%) and zinc acetate dihydrate (purity 99%). AZ Chemicals provided methanol (99.9%) (Karachi, Pakistan).

2.2. Methods

2.2.1. Synthesis of ZnO Nanoparticles

Synthesis of zinc oxide nanoparticles is an efficient, cost-effective, and simple method, that is, the hydrothermal method. ZnO nanoparticles were produced following the articles by Z. A. Ujjan et al., and the same is described schematically in Figure 1 [19].



Figure 1. Schematic diagram of the production of ZnO nanoparticles.

2.2.2. Synthesis of PVA/ZnO-Based Nanocomposite Films

A PVA solution was made by dissolving 15% PVA in distilled water for 4 h at 80 °C with magnetic stirring at 500 rpm. The result was a clear solution. Zinc oxide nanoparticles were added to the produced PVA solution by a small percentage of zinc particles, such as 5% weight percent of the PVA solution, for the PVA–ZnO film preparation. To make the PVA–ZnO NP (PZ) film, ZnO NP was added to the previously produced PVA solution and agitated for additional 20 min. The resultant solution became white after ZnO addition and was then cast on a PET substrate using a doctor blade and cured at room temperature for 24 h.

2.3. Characterization

2.3.1. SEM of ZnO Nanoparticle

Morphological analysis was observed by using a JEOL scanning electron microscope (SEM), JSM-7610F. For high-resolution topographical imaging, a secondary electron image detector was utilized. The operation was best suited to a 2 kV accelerating voltage with a low probe current mode of 65 nA. One of the most significant elements in sample preparation is the polisher.

2.3.2. XRD of ZnO Nanoparticle

The samples were analyzed using an X-ray powder diffractometer with Cu anode (Siemens D5000) operating at 40 kV and 20 mA, scanning from 2° to 40° at 0.05/min to determine the details of a crystalline material in terms of crystallinity, the number of layers present, grain or crystal orientation, and interlayer spacing (d-spacing).

2.3.3. FTIR of ZnO Nanoparticle

A Fourier-transform infrared (FTIR) spectrophotometer (Bruker Alpha-P) operated with OPUS 7.2 software was used to capture IR spectra in ATR mode. Spectra were acquired by performing 128 scan summations at a resolution of 4 cm^{-1} .

2.3.4. TGA of ZnO Nanoparticle

TGA used a thermogravimetric analyzer (SDT Q-600 TA Instruments, Artisan Technology Group, Champaign, IL, USA) to study the heat stability of ZnO NPs. For each operation, the initial sample weight was fixed at 5–8 mg. The sample was heated at a rate of 10 $^{\circ}$ C/min in a nitrogen environment at a low rate of 200 mL/min from 24 to 550 $^{\circ}$ C.

2.3.5. Contact Angle

Water droplets were used to measure the contact angle with a contact angle goniometer, SL200A, from KINO Scientific Instrument Inc. in Boston, MA, USA.

2.3.6. UV-VIS of PVA/ZnO Films

The ultraviolet–visible spectra of the produced thin film were determined using a double-beam UV–VIS spectrometer (pharmaSpec UV-1700, Shimadzu, Kyoto, Japan). Absorbance was measured at wavelengths ranging from 200 to 800 nm.

2.3.7. Oxygen Transmission Rate Measurement of Films

A permeation chamber with an optical oxygen sensing spot, Pst9 (manufactured by PreSens Precision Sensing GmbH, Regensburg, Germany), with a detection limit of $0.1 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ bar}^{-1}$ was used to determine the oxygen penetration rate. Samples were carefully placed between the device's two chambers, and nitrogen gas flowed for 15 min within both permeation cells before the leakage rate was determined. Then oxygen was pumped for half a minute in the bottom chamber, and the rise in oxygen fraction in the top chamber was observed continuously for a few days, and the data were used to compute the oxygen transmission rate (OTR) and permeability.

2.3.8. Water Vapor Transmission Rate

Thwing-Albert Instrument Company (West Berlin, NJ, USA) offered an ASTM E96compliant standard aluminum cup with a diameter of 6.35 cm. The test was carried out according to Channa et al.'s approach [16].

2.3.9. Bending of the Films

Bending testing was carried out utilizing an in-house designed cyclic bend tester with one end stationary and the other moving linearly back and forth, cycling the barrier film in a specific bending radius. A minimum of three 3×10 cm² samples were utilized for each test. For further characterization, bent films were chopped from the center.

2.3.10. Tensile Strength

A Z005 Zwick/Roell universal testing machine from Germany was used to assess each film's tensile strength (TS) and elongation at break (EAB). The samples were prepared according to ASTM D 882-10 specifications, with a 50 mm starting grab separation and a 5 mm/min crosshead speed. The films were cut into strips with a width of 30 mm and a length of 130 mm. A 5N load cell was used to assess the mechanical properties of the samples.

2.3.11. Hardness

The hardness of the film was assessed by applying a maximum load of 10.0 mN at a rate of 20 mN/min to an Anton Paar nanoindentation hardness tester with a diamond indenter. Poisson's ratio for the entire film was 0.44.

3. Result and Discussion

3.1. SEM Analysis of ZnO Nanoparticle

SEM examination was used to examine the size distribution and shape of the ZnO powder. A photograph of the produced ZnO powder is shown in Figure 2a. The SEM analysis revealed that the nanostructures were rodlike in form, with an average length of 800 nm and a width of around 200 nm, as shown in Figure 2b. The produced particles had a uniform shape and a smooth surface, and it can also be seen that the variance in the length of the nanorods was regularly distributed. The produced ZnO powder was also analyzed in terms of size distribution via a laser particle size analyzer, and the result is shown in Figure 2c. Most of the prepared ZnO nanorods had an average size of around 1 micron, which confirms the size of the particles shown in SEM micrographs. These results are also in line with the work performed by Najla Ali Elgheryani [31].





Figure 2. (a) Synthesis nanopowder of ZnO. (b) Scanning electron microscopic (SEM) micrograph of the prepared ZnO nanorods. (c) Differential volume PSD for synthesis ZnO powder.

Figure 3 demonstrates the XRD patterns of the prepared ZnO powders. The XRD results of ZnO show significant peaks between 30° and 70°. All diffraction peaks are strongly correlated with the hexagonal ZnO wurtzite structure (JCPDS nos. 36–1451) and the literature [27,32]. There are nine peaks at 2theta = 31.7°, 34.4°, 36.3°, 47.5°, 56.6°, 62.3°, 66.5°, 67.9°, and 69.1°, which correspond to the planes (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. The pattern's strong and narrow diffraction peaks indicate that the ZnO nanomaterial has a sharp peak. From the results, it is evident that the impurity-free ZnO nanorods are successfully prepared, and these prepared ZnO nanorods are ready to be incorporated into the PVA matrix to proceed with the formation of thin films.



Figure 3. XRD pattern of ZnO nanorods synthesized by hydrothermal treatment showing nine peaks at 31.7°, 34.4°, 36.3°, 47.5°, 56.6°, 62.3°, 66.5°, 67.9°, and 69.1°.

3.3. FTIR Analysis of Films and Composites

After the prepared particles were confirmed to be ZnO, the films were produced by adding ZnO in PVA with different loadings. An FTIR analysis was carried out to confirm the film formation of PVA and its nanocomposites. The FTIR spectra of hydrothermally produced ZnO NPs are represented in Figure 4, (blue curve) and the spectra are completely following the work performed by N. M. Shamhari et al. [33]. A wide absorption band at 424 cm⁻¹ has been recorded, which is attributed to Zn–O stretching vibrations [34]. To corroborate the findings, all of the identified peaks were linked to the existing literature. Previous investigations on the production and characterization of ZnO NPs yielded similar results. Peaks at 1381 and 1505 cm⁻¹ corresponded to symmetric and asymmetric O–C–O stretching vibrations of absorbed carbonate anion, respectively. Meanwhile, the peaks at 1047 cm⁻¹ suggested carbonate lattice vibrations. Furthermore, the wide absorption peak at 3378 cm⁻¹ corresponded to a hydroxyl group. Furthermore, pristine PVA and PVA/ZnO films were also analyzed using FTIR, and the results are shown in Figure 4, where the black curve refers to pristine PVA and the red curve refers to PVA/ZnO films. The O-H stretching vibration is responsible for a large and broad absorption band at 3311 cm^{-1} in the spectra of the PVA film. The C-H stretching vibration of -CH and -CH₂, respectively, is attributed to the bands at 2908 and 2940 cm⁻¹. A CH₂ scissoring mode is identified as the peak at 1436 cm⁻¹, while CH2 deformation is responsible for the peaks at 1378 and 1335 cm⁻¹, and the bands at 1083 cm⁻¹ and 911 cm⁻¹ are caused by C–O and C–C stretching vibrations, respectively. The primary peaks associated with the PVA are clearly visible in the spectra of the PVA/ZnO film, which are also clearly distinct from those of the PVA. For instance, at 900 cm^{-1} , the Zn–O vibration of ZnO is also present. Hence, the FTIR clearly confirms the XRD results and justifies the nanocomposite formation.



Figure 4. FTIR (Fourier-transform infrared) spectroscopy of zinc oxide nanoparticles (indicated by the blue line), PVA (indicated by the black line), and PVA/ZnO (indicated by the red line).

3.4. Thermal Stability of Produced Nanocomposites

Figure 5 shows the TG curves of ZnO nanoparticles and nanocomposites in the temperature of range 30 to 550 °C. In the TG analysis, the blue curve is associated with ZnO, and the overall weight reduction percentage is 2.3% for the given temperature range. A weight loss below 200 °C is related to the release of desorption of humidity and any volatile contents. Meanwhile, a slight loss of weight in the range of 400–500 °C is related to the release of organic chemicals in the sample, whereas the sample shows almost no weight loss up to a temperature of 600 °C. This proves the stability of ZnO against temperature [35]. Hence, the addition of ZnO into the polymer matrix is inevitable for improving its thermal stability. Hence, pristine PVA and PVA incorporated with ZnO were also subjected to thermal analysis, and the data are shown in Figure 5, where the black curve and red curve are associated with pristine PVA and PVA composites, respectively. Inside the PVA film, there are two different types of water molecules: absorbed water molecules (weak bonds), which prefer to be on the exterior or interior surface without interacting with the matrix, and tightly bonded water molecules, which refer to the hydroxyl groups within the polymer. Hence, three weight-loss zones are observed in the pure PVA's TGA curve. The loss of the absorbed water molecules can be assigned to the first region between 50 and 200 °C, while the loss of the water attached within the polymer matrix can be attributed to the second region between 200 and 340 °C. The degradation and carbonization of the polymer are connected to the third zone, which is between 300 and 450 °C [36]. Due to the addition of a small concentration of ZnO in the polymer, the thermal stability is improved (please refer to the red curve), where the pattern of loss of weight is similar to that of pristine PVA but slightly more stable in all three weight-loss zones. PVA containing ZnO may sustain more temperature than pristine PVA. Thus, the addition of ZnO enhances the overall thermal stability of PVA, and the composite films may sustain around an additional 80 °C.



Figure 5. Thermogravimetric analysis (TGA) of nanorods of ZnO and prepared films, where the blue curve represents ZnO particles, the black curve represents pristine PVA films, and the red curve represents PVA/ZnO films.

3.5. Water Contact Angle

Water contact angle measurements were used to evaluate the wetting behavior of PVA and PVA/ZnO nanorods, and the results are shown in Figure 6. The capacity of water absorbency was found to be lower when the crystallinity (due to the addition of ZnO) of PVA/ZnO nanorods increased. As a result, films containing ZnO exhibited higher water contact angle values than pristine PVA. It was also observed that increasing the concentration of ZnO in the PVA film increases the water contact angle. Pristine PVA shows a highly hydrophilic nature, whereas the films containing ZnO tend to show higher contact angles, thereby suggesting a loss of hydrophilicity of PVA. The highest water contact (~80°) was observed for the film having the highest concentration of ZnO. This result is favorable for packaging applications.



Figure 6. CA (contact angle) image of 0–0.8% concentration of zinc oxide nanoparticle.

3.6. Oxygen Transmission Rate (OTR)

Packaging materials should have oxygen barrier qualities to safeguard packed items from internal damage and promote long-term performance. Because of its high degree of crystallinity and strong intermolecular force arising from the hydroxyl groups in repeating units, PVA is also recognized for its outstanding oxygen barrier characteristics [16]. The addition of ZnO to PVA did not harm its OTR (@0%RH and 25 °C) values, as shown in Figure 7. This could be due to a strong wetting between ZnO nanorods and the PVA matrix. This also suggests that the inclusion of ZnO did not significantly alter the polymeric chains and did not incorporate porosity; hence, the overall oxygen transmission rate almost remained the same even after the addition of ZnO. Although a minor decrease in OTR is observed with increasing ZnO concentration, the decrease is so minor that it may be due to higher standard deviation values. Another possible cause can be the formation of agglomerates when adding higher ZnO contents. This could be due to their higher surface energies and generation diffusion paths. Since the pristine PVA has a lower oxygen transmission rate, the latter possible cause seems more plausible.



Figure 7. OTR (@0%RH and 25 °C) of PVA films containing different ZnO weight concentrations.

3.7. Water Vapor Transmission Rate (WVTR)

A low WVTR value of packaging films indicates that the films are perfectly suited for retaining food quality [37]. Figure 8 depicts the WVTR values for PVA and its nanocomposites. The addition of ZnO greatly lowered WVTR, and the value was lowest when the nanofiller level was 0.8%, indicating that ZnO might improve the film's barrier ability against water vapor. This is because the strong wetting of PVA with ZnO created more tortuous paths for water vapor to go through the film. This suggests that the higher filler content either decreases or maintains the same free volume and does not incorporate additional porosity; hence, moisture permeability decreases. This result is also in line with the result discussed previously in water contact angle. The addition of ZnO makes PVA slightly hydrophobic, and as a result, the overall moisture permeability decreases.



Figure 8. Water vapor transmission rate (WVTR) at conditions of 25 °C and 75% RH versus ZnO weight concentration.

3.8. Bendability

One of the most demanded properties of packaging films is bendability and flexibility at a smaller radius. To prove that the prepared films are flexible, a bending test was performed, and the results are shown in terms of the inverse of OTR (see Figure 9). The films were bent at a radius of 1.5 cm, and the same films were subjected to OTR analysis. If the bent film retains the initial OTR even after several bending cycles, that would mean that the films are flexible and bending does not deteriorate the functionality (OTR) of films. Therefore, all prepared films were subjected to 10K bending cycles and analyzed for OTR periodically. Pristine PVA films showed excellent bendability as the initial and periodic OTR analyses yielded the same value. This means that PVA films remained unharmed even after 10K bending cycles. Furthermore, after bending, there was no evident damage to the films. However, a negligible change in composite coatings was also observed in PVA films containing ZnO. A loss of 0%, 4%, 7%, and 8% was observed for the PVA films containing 0, 0.2, 0.6, and 0.8 wt% ZnO, respectively. A possible explanation for this could be the strong bonding or wetting of PVA and ZnO nanorods, which means that the ZnO nanorods always returned to their original locations after bending, retaining their adherence to the PVA matrix and causing no damage to it. This demonstrates that after 10K bending cycles, the ZnO particles were still securely linked to the PVA matrix. Based on these observations, it is concluded that a basic PVA film adheres to ZnO better, and overall, films remain flexible.



Figure 9. OTR inverse values of PVA films with different ZnO concentrations vs. several bending cycles, where PVA is denoted by a purple curve, the black curve refers to PVA films containing 0.2 wt% ZnO, the red curve refers to 0.4 wt% ZnO, the blue curve refers to 0.6 wt% ZnO, and the green curve represents 0.8 wt% of ZnO in PVA films.

3.9. Tensile Strength

Figure 10 shows how the addition of ZnO nanoparticles to the PVA matrix affected the load extension and tensile strength of the films. The graphical representation (Figure 10) makes it obvious that all of the samples that were subjected to tensile strengths enhance their stability against applied load as the ZnO nanoparticle concentration is increased in the PVA. The PVA film with the highest concentration of ZnO nanoparticles shows the maximum yield strength (around 50 N/m^2), whereas the maximum tensile strength of the same films is found to be around 70 N/m^2 . In contrast, pristine PVA films show a tensile strength of around 40 N/m^2 and a yield point of around 28 N/m^2 . This means that the addition of ZnO enhanced the tensile strength of the films by a factor of around 1.8. This increase in strength confirms the results presented in the previous sections (i.e., bending and water permeability). The wettability of ZnO is quite nice in the PVA matrix; hence, they form strong bonding, and as a result, tensile characteristics are enhanced.



Figure 10. Stress versus strain graph of ZnO weight concentration with 0.2 weight percent ZnO shown by the red line, 0.4 weight percent by the blue line, 0.6 weight percent by the green line, and 0.8 weight percent by the purple line. A simple PVA film is represented by the black line.

3.10. Hardness of the Films

Figure 11 shows load penetration depth curves of pure PVA and its nanocomposites with 0.2, 0.4, 0.6, and 0.8 wt% ZnO. The data show that the pristine PVA is very soft and shows a maximum depth of penetration when only 5 mN force is applied. This clearly explains the softness of the PVA films. As soon as ZnO is added to the PVA films, the penetration depth reduces from 33K to 5K nm at an applied force of 23 mN. The addition of ZnO induces the hardness in the films, and as a result, films show resistance to penetration. An almost similar behavior is shown for all of the samples having different ZnO loadings. This means that resistance to penetration in composite films is increased by a factor of ~7 as compared with pristine PVA. This means that an addition of ZnO in PVA is the preferred choice as it improves not only its barrier properties against the diffusion of gases but also its thermal and mechanical stability.



Figure 11. Nanoindentation curve of PVA/ZnO films plotted against force vs. displacement, with 0.2 wt% ZnO indicated by the red line, ZnO with 0.4 wt% indicated by the blue line, ZnO with 0.6 wt% indicated by the green line, and ZnO with 0.8 wt% indicated by the purple line. While simple PVA film is indicated by black line.

3.11. UV Blocking Effect

The UV-visible absorption spectra of PVA and ZnO/PVA composite films are shown in Figure 12a, and the kinetics of increase in absorbance in the UV region is shown in Figure 12b. It is evident from Figure 12a that all of the films including PVA and its composites remain transparent in the visible region of the spectrum. This could be due to the refractive index matching of the filler and matrix. However, pristine PVA films do not show any absorbance near 400 nm. The only absorbance is observed below 230 nm, and this is very common for PVA films. In contrast, pristine PVA films of composites show a clear and strong absorbance at around 390 nm, and this is due to the presence of ZnO nanoparticles within the films. Increasing the ZnO concentration increases the UV absorbance. The kinetics of the increase in absorbance in the UV region is shown in Figure 12b. An addition of ZnO at concentrations of 0.2, 0.4, and 0.8 wt% increases the absorbance of UV radiations of 350 nm wavelength by 5%, 20%, and 40% as compared with pure PVA. This absorbance increases linearly as the concentration of ZnO in the films increases. This implies that the ZnO-incorporated PVA films are capable enough to screen around 40% of UV radiations from while light. Hence, such films can be efficiently used in food packaging industries, where the damaging factor is UV and oxygen.



Figure 12. (a) UV–VIS (ultraviolet–visible) spectroscopy of thin films of ZnO/PVA (indicated by the black line), PVA (indicated by the red line), and ZnO nanoparticles (indicated by the blue line).(b) Normalized vs. ZnO concentration at 350 nm (black line) and 550 nm wavelength (red line).

3.12. Degradation Test against Oxidation

In Figure 13, the degradation of three pieces of an apple is shown. One piece of the apple was packaged in PVA/ZnO film, the other was packaged in commercial polyethylene films, and the third remained unpackaged. The degradation was monitored in ambient conditions. It was observed that the unpackaged apple sample deteriorated within an hour due to oxidation. This demonstrates that the oxygen present in the atmosphere was able to destroy the sample. Meanwhile, the PVA/ZnO and polyethylene packaged samples did not show any significant oxidation marks at a testing time of 1 h, although the darkened color spots appeared in the samples, which could be because the samples were packaged in ambient conditions and the trapped air caused the localized oxidation. This quick test gives the message that the prepared films are capable enough to be used as packaging films.



Figure 13. Degradation test apple pieces packaged in PVA/ZnO films and commercial polyethylene packagings.

4. Conclusions

Significant efforts are being made to protect the quality of fresh food items and reduce foodborne diseases; therefore, packaging plays a significant role in this regard. One of the common ways to improve packaging materials is to create polymer and nanofiller-based composites. Thus, in this work, ZnO nanofillers were used together with polyvinyl alcohol to produce such protective coatings. Nanoparticles of zinc oxide were produced by using the hydrothermal process. The structural and optical characteristics of the produced ZnO nanoparticles were validated using SEM, XRD, and UV-VIS spectroscopy. SEM revealed the size (in nanometers) and shape (hexagonal) of the prepared particles, and XRD confirmed the SEM results. Films were prepared by adding ZnO in PVA via blade coating and were analyzed by FTIR, TGA, OTR, WVTR, WCA, bendability, hardness, tensile strength, and UV screening properties. It was found that the prepared films showed around 80 °C additional thermal stability as compared with pristine PVA. Not only this, but the composite films also exhibited improvements by factors of 2, 3, and 7 in terms of tensile strength, moisture blocking effect, and hardness, respectively, as compared with PVA films without fillers. Furthermore, the addition of ZnO did not significantly affect the oxygen barrier properties of PVA and parallelly induced hydrophobicity as the films having 0.8 wt% ZO showed a WCA of around 80°. The films retained their flexibility even after going through bending cycles of around 10K. Furthermore, the incorporation of ZnO in PVA enhanced the UV absorbance by 40%. Finally, the optimized films were analyzed for practical application, and for this purpose, a piece of apple was packaged in commercial polyethylene and

PVA/ZnO films. It was observed that the performances of the two packaging films were almost the same as the apple's oxidation was delayed for about 10 h as compared with the unpackaged piece, which was fully oxidized within an hour. Although commercial polyethylene and PVA/ZnO showed a similar performance, the latter has the additional feature of UV screening and biodegradability and hence is ideally suited for packaging applications.

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