

DEGRADATION OF POLY(VINYL PYRROLIDONE)/POLYANILINE FILM IN THE PRESENCE OF TiO₂ IN ACID AND BASE SOLUTIONS

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ABSTRACT

Poly(vinyl pyrrolidone)/Polyaniline (PVP/PANI) was synthesized without and with TiO₂ through the oxidative *in situ* polymerization method. Degradation, and stability of PVP/PANI and PVP/PANI/TiO₂ films in gentle acid and base solutions (pH = 1-14) were studied. Degradation of films was studied using water uptake test, Fourier-transform infrared (FTIR) spectroscopy, Ultraviolet diffuse reflectance spectroscopy (UV-DRS), and scanning electron microscopy (SEM). SEM results for PVP/PANI films show that fractures and cavities in base solution film is more than those on acid solution film surface. It denotes that the PVP/PANI film degradation in the alkaline solution is more than the degradation of film in the acid solution. SEM micrographs show no significant changes on the surface morphology of PVP/PANI/TiO₂ films, denoting stability of these films in acid and alkali environments. The results indicate that both PVP/PANI and PVP/PANI/TiO₂ films show very weak degradation in an acid solution in comparison with a base environment. PVP/PANI films show some degradation in the base environment (specifically in pH = 11 and higher pH), which is primarily due to PVP degradation. Unlike the PVP/PANI, PVP/PANI/TiO₂ films show a weak degradation in the alkaline solutions.

Keywords: Degradation studies; pH effect; Polyaniline; Polymer nanocomposite; TiO₂ Nanoparticles.

INTRODUCTION

Degradation is an important factor in processes such as drug delivery and membrane applications. Polyaniline (PANI) as the nanostructured conductive polymer, has favorable traits like controllable conductivity, environmental stability, simple synthesis, low cost, and high-efficiency polymerization. PANI was used as an electrocatalyst, anti-corrosion coating, optical devices, and sensors [1,2]. For these reasons, this polymer has been the subject of several studies [3-5]. However, there are some serious problems in this regard such as insolubility, and non-processability [1,6]. To overcome on these problems, PANI is combined with other materials [7]. Poly(vinyl pyrrolidone) (PVP) was used in ultrafiltration membrane [8]. PANI was stabilized in an aqueous medium with PVP [6,9]. The combination of electrical properties of polyaniline (conducting polymer) with pleasant mechanical properties of poly(vinyl pyrrolidone) (conventional insulating polymer) is very significant in PVP/PANI [10]. This blend shows an effective electron transportation and steric stabilization [6,9]. Qiao et al. show that OH⁻ interacted with the PVP carbonyl group. They show that PVP enhances the chemical stability of membranes [11]. These polymers were applied in gas separation, ultrafiltration, nanofiltration, and reverse osmosis membranes, drug purification, and wastewater treatment [12]. Furthermore, PVP/PANI

was used to sense NO₂. It acts as a protective layer for prevention of corrosion. PVP/PANI provides a hospitable matrix for biological materials [9,13].

The pH effect has extensively studied by several researchers [14,15]. The influence of pH on the surface coverage, immobilization of polymers, and the actuator properties of PANI film was studied [2,16,17]. Study of PANI stability in acid-alkali solutions showed the high stability of PANI layer at pH = 1 to 12 [17]. Good stability of PANI in alkaline or acidic aqueous media was reported by Brozova et al. [2]. It has been reported that PANI has a low degradation of alkali solutions [18]. UV-visible spectroscopy was used to study degradation of PANI. The bands at 300-400 nm and 550-650 nm were used to evaluate the degradation of PANI [2,18]. By changing the condition of the synthesis and environment, the band used to study of the stability was changed. Titanium dioxide (TiO₂) has several applications because of properties such as low toxicity, biological and chemical inertness, stability toward photocorrosion, and low costs. A coordinate bond was formed between titanium and nitrogen in the amine group of the PANI and hydrogen bonding was established between them in the form of NH-O-Ti. Polyaniline/TiO₂ has been used in electrochemical capacitors, heterostructure devices, microbial fuel cells, and gas sensing devices and revealed to act as a protect layer against corrosion [19,20].

In PVP/PANI, the degradation is characterized via Fourier-transform infrared spectroscopy (FTIR), Diffused Reflection Spectroscopy-UV (DRS-UV), Scanning Electron Microscopy (SEM), and water uptake [19]. DRS-UV was used to study the surface degradation [21]. FTIR analysis of PVP/PANI was pointed completely in our previous study [19]. As mentioned in our previous study, the oscillating dipole of the molecules (of two polymers) was altered, when they are mixed at the molecular level, leading to the subsequent changes in frequency and bandwidth of interacting groups. Any interaction between PANI and PVP caused the band shift compared to the pure PANI and PVP spectra. A comparison between the spectrum of the blend and pristine PVP and PANI shows some changes in intensity and position of absorbance bands indicates an interaction between the quinoid ring of PANI and PVP and modifies intermolecular hydrogen bonds between NH group (PANI) and the carbonyl group (PVP) [19]. Theoretically, PANI can form hydrogen bonds with polymers possesses the carbonyl group. Also, PANI is compatible with polymer counterparts due to H-bonding in an imine group [11]. According to PVP-PANI nature, the H-bond was formed between the acidic hydrogen atom in PANI imine group and the electronegative oxygen atom in the PVP carbonyl group. Hydrogen bonding between segments of PANI and PVP established a high degree of dispersion and stability [19,20]. Other studies show close contact between PVP and PANI. The interaction between PVP-PANI breaks intramolecular H-bonds and disaggregates the PANI by stretching and extending its chain conformation. The imine group in PVP/PANI is protected. Moreover, the amine group acts as a proton acceptor however the imine acts as a proton donor [6,20].

Considering the applications of PVP/PANI as a membrane, anti-corrosion coating, and a hospitable matrix of biological materials, the study of the pH effect on PVP/PANI and PVP/PANI/TiO₂ is of paramount importance; to increase the life and stability of these membranes. In continuous of our previous studies [19,20], the stability of PVP/PANI and PVP/PANI/TiO₂ was studied in acid and base solutions in pH range of 1-14. The difference in UV-Visible DRS absorbance, FTIR spectra, and water uptake were used to evaluate the degradation. These polymers have been used as membranes [22, 23]. A better understanding of degradation in this case, will help stabilize and increase the life of these polymers as membranes. Scanning Electron Microscopy (SEM) was used for surface morphology investigation. Presence of PVP and PANI were confirmed by Fourier transform infrared (FTIR) spectroscopy presented in our previous study [19]. SEM

results show good dispersion and strong interfacial adhesion between the polymers. In this research FTIR, DRS-UV, SEM, and water uptake were used to study the degradation of PVP/PANI films in acid and base (pH = 1-14) solutions.

EXPERIMENTAL

Materials

Aniline (99.5%), ammonium persulfate (98%), sodium hydroxide (Assay 99%), H₂SO₄ (95-97%), and HCl (37%, 1.19 kg/L) were purchased from Merck (Germany). PVP K90 (M_r = 360000) in powder form was purchased from Fluka (Switzerland). Titanium (IV) Oxide (TiO₂) (mostly anatase) was obtained from TECNAN. Anhydrous ethanol (99.8%) was purchased from Kimia Alcohol (Iran). All materials were used without further purification. Water was used as double distilled water (DDW).

PVP/PANI synthesis

PVP/PANI was synthesized *via* chemical oxidative *in situ* polymerization with the ammonium persulfate (APS) oxidant according to instructions in the literature [13]. To confect this blend, 50 mL 0.1 M of PVP and 50 mL 0.2 M of aniline were prepared in aqueous HCl solution at pH = 1. The acidic environment facilitated aniline monomers to be solved. The final solution was put in a bath at 0-2°C with a constant magnetic stirring for 1 hour. Then, APS (100 mL 0.2 M) was produced and added to the solution as dropwise. The mixture was kept at 0-2 °C with constant magnetic stirring for 4 h and then was kept in the refrigerator for 20 h. The wet blend was filmed with a thickness of 100 μm by a film applicator. Finally, these films were dried at 80 °C in an air oven for 4 h, and washed with DDW and anhydrous ethanol [6,13]. A similar procedure was accomplished for the synthesis of PVP/PANI/TiO₂ films, by which 0.1 g of TiO₂ were added to the aniline polymerization solution, separately.

Treatment

We prepared 14 films of PVP/PANI and PVP/PANI/TiO₂ blend with a thickness of 0.1 mm in 1.5 × 0.5 cm² dimensions. Sulfuric acid and sodium hydroxide solutions were prepared by Metrohm Herisau E603 pH-meter (Switzerland) in pH ranged over 1-6 and 8-14, respectively. DDW was used as a solution with pH = 7. The specimen was put in the solution for 24 h at 25°C. Then, these films were extracted from the solutions and tested after drying. In all solutions, blend films were swelled due to the water trapping. The films in acid solutions does not show a color change but in alkali solutions, the color of the film changes from dark green to blue-violet. This change suggests that emeraldine salt is transmuted to emeraldine base [2,21]. The films taken from acid solutions did not show any considerable damage; however, PVP/PANI films taken from base solutions were rather brittle, cleft, and broken. Furthermore, PVP/PANI and films were put in the solutions have pH = 1, 7, and 14 for 36 hours at 25°C. Every 8 hours, films were extracted from the solutions and tested after drying.

Characterization

a) Water uptake

Water absorption by polymer composites was assessed by water uptake. This test is a criterion for evaluation of crosslink bonds, inflation, mechanical properties, and interactions between polymers.

The interaction between polymer chains and chain mobility restriction caused a reduction in water absorption ability [24]. The water uptake was calculated by equation 1:

$$\text{water uptake (\%)} = ((m_w - m_d)/m_d) \times 100 \quad (1)$$

where m_w and m_d are the wet and dried masses, respectively [25]. Preweighed dry PVP/PANI and PVP/PANI/TiO₂ films were immersed in solutions have pH = 1-14; to study swelling properties change versus pH. After the degradation process (24 h), films were removed and gently washed with DDW, swabbed with filter paper, and weighed on a balance (Sartorius CP224S, Germany; resolution: 0.1 mg) to specify the wet mass.

b) Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is one of the important methods to characterize the polymer composites. FTIR absorption spectra of the PVP/PANI and PVP/PANI/TiO₂ (in KBr pellets) were recorded on an FTIR-Tensor 27 Bruker spectrophotometer (Germany) in 4000 cm⁻¹ to 400 cm⁻¹ wavenumber range with a resolution of 4 cm⁻¹. FTIR spectra showed different values for the integrated absorption in various pH values [2]. In order to compare the changes in absorbance of different samples under various conditions (different pH), the band area ratio was defined as (equation 2):

$$\text{band area ratio} = (\text{band area})_i / (\text{band area})_7 \quad (2)$$

where (band area)₇ is the absorbance band area for a sample immersed in a solution with pH = 7 and (band area)_i is the absorbance band area in pH = i (i is any pH other than 7). The band area ratio was used to evaluate the degradation level.

Diffused Reflection Spectroscopy-UV (DRS-UV)

Diffuse reflectance spectroscopy (DRS) was used as a rapid and sensitive method for quantitative analysis. Optical properties of nanostructures, cations, and anions were studied by UV-Visible DRS technique. This technique has many advantages in solid-state research, such as simple sample preparation, quickness, low cost, safe to operate, and nondestructive measurements [26]. The band area ratio (equation 2) was used to compare the changes in absorbance of different samples under various conditions (different pH values). Several methods have been established for DRS quantitative analysis [26]. UV-Visible DRS spectra were recorded on a DRS-Sinco S4100 (Korea) spectrophotometer. Spectra of Samples (loaded in a quartz flow cell) were recorded in the 200-1100 nm at room temperature.

c) Scanning Electron Microscopy (SEM)

To survey the surface morphology of the gold coated films of PVP/PANI and PVP/PANI/TiO₂, SEM images were obtained on a MIRA3-FEG electron microscope (MIRA3-FEG-SEM-TESCAN microscope) operating at 15 kV. SEM images of PVP/PANI and PVP/PANI/TiO₂ films are prepared (image magnifications of 50000) for films immersed in pH = 1, 7, and 14 solutions after 24h.

RESULTS AND DISCUSSION

Water uptake

Fig.1 shows the water uptake of PVP/PANI and PVP/PANI/TiO₂ films were put in the solutions with pH = 1-14, for 24 hours. As observed in Fig. 1 for PVP/PANI films, a slight change occurred in the uptake of water at acid solutions (pH = 1-7). However, the water uptake increased in base solutions (pH = 7-14). The maximum amount of water uptake happened in a solution with pH =

14. The films immersed in base solutions (specifically $\text{pH} > 11$) show surface erosion. The broken chains improve the mobility of the segments and allow them to rearrange regularly [25]. Therefore, the roughness area generated on PVP/PANI films in base solutions caused an increase in water uptake. This evidence proves the stability of PVP/PANI films in gentle acid solution in comparison with the base solution. PVP/PANI/TiO₂ films do not have any significant change in water uptake in both acid and alkaline solutions. It has been proved that TiO₂ increases the stability of PVP/PANI films in both gentle acid and base solutions, caused by strong interactions between the nanoparticles and polymers.

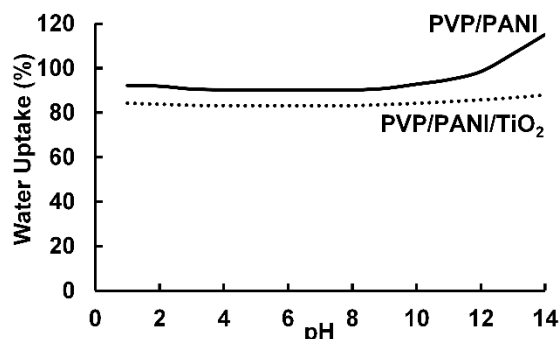


Fig. 1 Water uptake of PVP/PANI and PVP/PANI/TiO₂ films were put in the solutions with $\text{pH} = 1-14$, for 24 hours

Fig. 2 represents the results of the water uptake test of PVP/PANI and PVP/PANI/TiO₂ films immersed in three solutions have $\text{pH} = 1, 7$, and 14 , for 36 hours. From this figure, no significant changes were observed in water uptake of PVP/PANI films in the solution with $\text{pH} = 7$. This indicates that the degradation is very weak in this condition. Also, small change in water uptake (especially 24 hours) is due to the PVP dissolution in water. Furthermore, poor changes of water uptake of PVP/PANI film in the solution with $\text{pH} = 1$, imply on weak impact of acid on films, and little degradation of film. However, remarkable changes in water uptake of PVP/PANI film in the solution with $\text{pH} = 14$, show the prominent degradation of films in the alkaline solution. No significant changes were observed for PVP/PANI/TiO₂ films, implying the PVP/PANI stability was increased by TiO₂, due to the strong interactions between the nanoparticles and polymers.

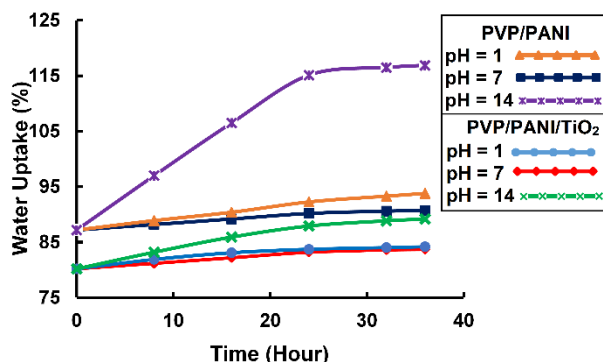


Fig. 2 The results of water uptake test for PVP/PANI and PVP/PANI/TiO₂ films in solutions have $\text{pH} = 1, 7$, and 14 ; for 36 hours

FTIR Spectroscopy

As mentioned above, PANI is stable in gentle acidic-alkaline medium and shows little degradation in these environments [2,17]. Therefore, the degradation can be attributed to PVP. PVP hydrolysis in an acidic and alkaline medium (Fig. 3) leads to the breaking of the N-CO [27]. In both hydrolysis paths, two kinds of bonds were changed. N-H bond was formed and so absorbance of this bond in FTIR spectrum was increased. C-N bond was broken and thus the absorbance of the C-N bond in FTIR spectra was decreased.

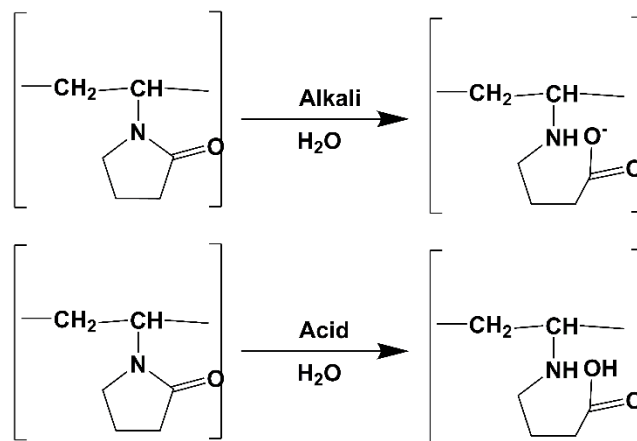


Fig. 3 PVP hydrolysis in an acidic and alkaline medium

Studying the molecular structure of the PANI by FTIR spectroscopy in pH ranges of 1-7 and 7-14 shows some differences in $3000\text{-}3600\text{ cm}^{-1}$ and $1500\text{-}1600\text{ cm}^{-1}$ related to the N-H and C-N stretching, respectively [11,13]. To study of PVP/PANI degradation in the acid and alkali solution, the band area changes in the FTIR spectra were used. The band at $1650\text{-}1590\text{ cm}^{-1}$ was selected due to C-N stretching and the band area in different pH was taken due to hydrolysis of PVP [11]. The area of FTIR band shows a little change in $\text{pH} = 1\text{-}7$ (Fig. 4), which implies the weak degradation of PVP/PANI in acid solution at $\text{pH} = 1\text{-}6$. However, this figure shows the PVP/PANI was degraded in alkali solution (specifically $\text{pH} > 11$), with the most degradation occurred at $\text{pH} = 14$. The area of FTIR band shows a little change for PVP/PANI/ TiO_2 , which implies on the weak degradation of PVP/PANI/ TiO_2 in comparison with PVP/PANI. This is due to the strong interactions between the nanoparticles and polymers.

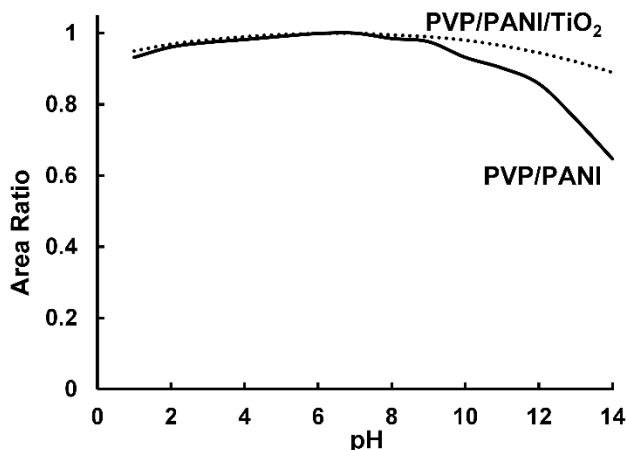


Fig. 4 Area ratio of $1650\text{-}1590\text{ cm}^{-1}$ band in $\text{pH} = 1\text{-}14$

Fig. 5 represents the band area ratio (equation 2) for PVP/PANI and PVP/PANI/TiO₂ films in three solutions with pH = 1, 7, and 14, for 36 hours. From this figure, no significant changes were observed in the area ratio of PVP/PANI films in the solution with pH = 7. This indicates that the degradation is weak in this condition. Changes in the area ratio of PVP/PANI films in the solution with pH = 1 are less than changes in the area ratio of films in the solution with pH = 14, imply on weak impact of acid on films, and little degradation of film in the acid solution. However, remarkable changes in the area ratio of PVP/PANI film in the solution with pH = 14, show effectiveness of the alkaline solution and prominent degradation of films in the alkaline solution. In Fig. 5, no significant changes were observed in the area ratio of PVP/PANI/TiO₂ films. TiO₂ increases the stability of PVP/PANI films, caused by strong interactions between the nanoparticles and polymers.

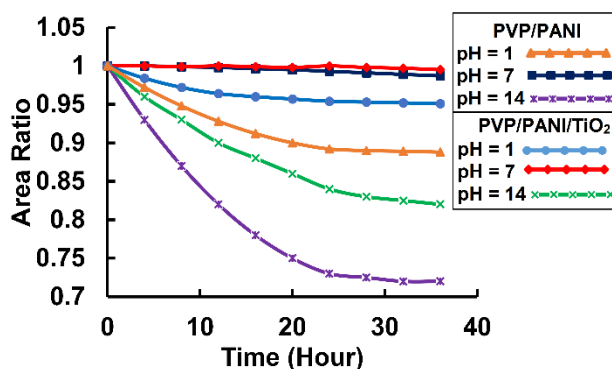


Fig. 5 Area ratio of 1650-1590 cm⁻¹ band of PVP/PANI and PVP/PANI/TiO₂ films in solutions with pH = 1, 7, and 14; for 36 hours

Diffused Reflection Spectroscopy-UV (DRS-UV) Analysis

PVP does not have an absorption peak in the visible region (the range of 300-1000 nm), so the peaks in the PVP/PANI UV-Vis spectrum are due to the PANI [19,28]. Hence, this technique is used to prove that mostly PVP is degraded (and PANI rarely degraded). The $\pi \rightarrow \pi^*$ transition of the benzenoid ring shows a peak at 300-400 nm [19,28]. In this study, the differences in DRS absorbance (in pH = 1-14) were used to evaluate the degradation. Acid and base degraded surface of polymer films and changed the DRS absorbance. The change in the DRS absorbance in various pH was applied to evaluation of polymer film degradation. To evaluate of the level of degradation, absorbance peak area (selected band at about 300-400 nm) was plotted versus pH [2,19,28].

The 300-400 nm band area was calculated for various samples (films in solutions with pH = 1-14), followed by dividing all areas on the area at pH = 7 (equation 2). Fig. 6 demonstrates the plot of absorbance ratio versus pH for film degradation. According to Fig. 6, the area under the peak changes for PVP/PANI in acid solutions is small and can be ignored. However, some changes in alkali solutions (pH >11, specifically pH = 13, 14) can be observed, which implies on degradation of PVP/PANI films in alkali solutions. No significant changes were observed in the area under the peak of PVP/PANI/TiO₂ films. PVP/PANI/TiO₂ films are more stable than PVP/PANI films in acid and alkali solutions. This is due to the strong interactions between the nanoparticles and polymers.

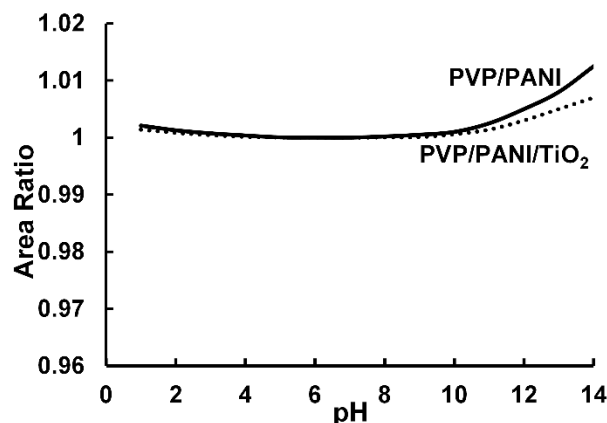


Fig. 6 Area ratio from UV-Vis DRS in pH = 1-14

Fig. 7 represents the band area ratio (equation 2) for PVP/PANI and PVP/PANI/TiO₂ films in three solutions with pH = 1, 7, and 14, for 36 hours. From this figure, no significant changes were observed in the area ratio of PVP/PANI films in the solution with pH = 7. This indicates that the degradation has not occurred in this condition. The area ratio of PVP/PANI films in pH = 1 solution shows fair increase, imply on weak impact of acid on films, and weak degradation of films in the acid solution. However, remarkable increases in the area ratio of PVP/PANI film in the solution with pH = 14, show effectiveness of base solution and prominent degradation of films in the alkaline solution. The area ratio curves of PVP/PANI/TiO₂ films show no significant changes, indicating the very weak degradation of PVP/PANI/TiO₂ films in acid and alkali solutions in comparison with PVP/PANI films. This is due to the strong interactions between the nanoparticles and polymers.

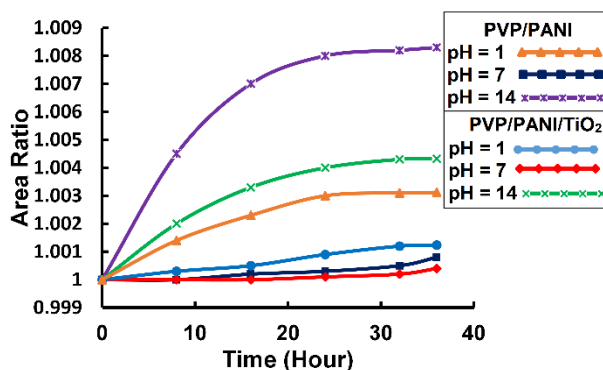


Fig. 7 UV-Vis DRS area ratio of PVP/PANI and PVP/PANI/TiO₂ films in solutions with pH = 1, 7, and 14; for 36 hours

Surface Morphology investigation by Scanning Electron Microscopy (SEM)

Micrographs of PVP/PANI and PVP/PANI/TiO₂ films, after 24 hours immersion in solutions with pH = 1, 7, and 14, were presented in Fig. 8 (Fig. 8a-f, respectively). Micrograph 8b (specimen immersed in pH = 7 solution) shows the homogeneous morphology and close packing nature of PVP/PANI; implies on fine dispersion in the main medium. In this blend, PVP accretes a continuous phase that PANI disperses in it. The growing fractures and cavities were seen on the surface of PVP/PANI in both Fig. 8a (pH = 1) and Fig. 8c (pH = 14). Comparison of Fig. 8a (pH = 1) and Fig. 8c (pH = 14) with Fig. 8b show that acid and base change the PVP/PANI structure.

It implies on degradation process was happened in both case. However, fractures and cavities in Fig. 8c is more than the fractures and cavities on Fig. 8a surface. It implies that the PVP/PANI film degradation in the alkaline solution is more than the degradation of film in the acid solution.

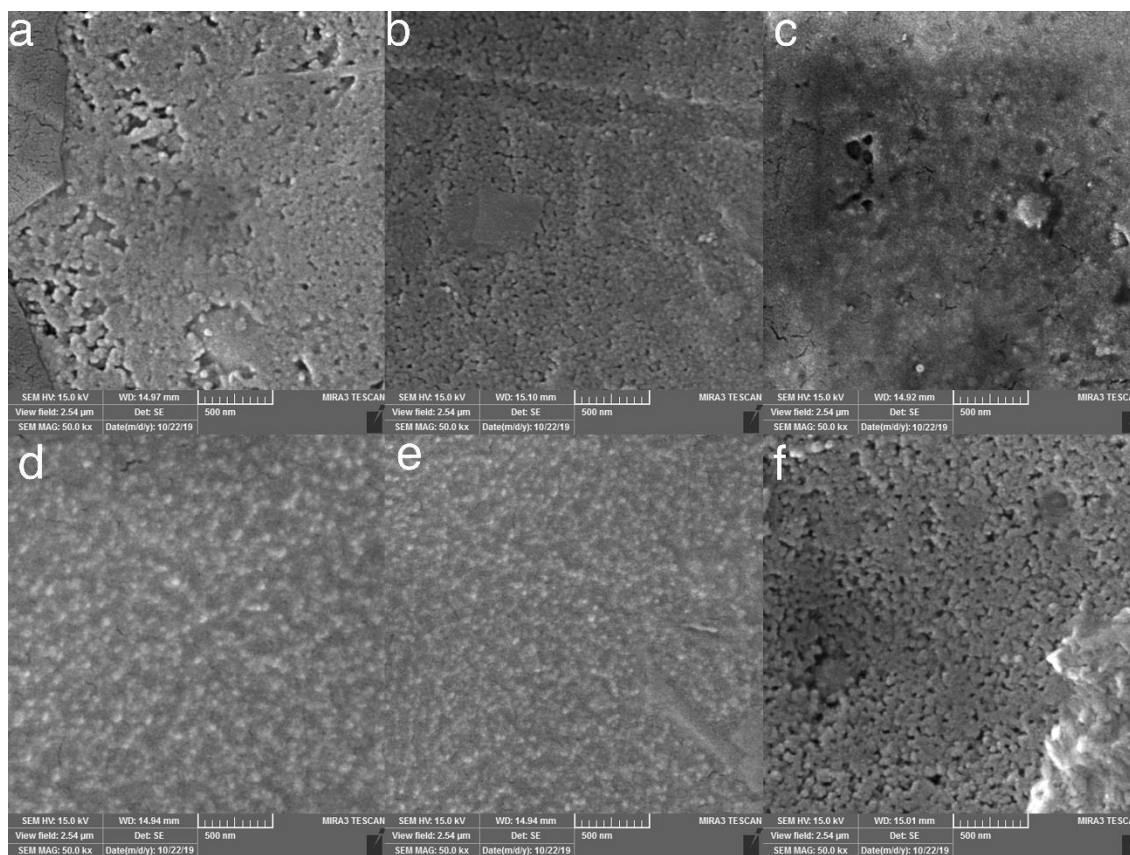


Fig. 8 SEM images of PVP/PANI films immersed for 24 hours, in solutions with (a) pH = 1, (b) pH = 7, and (c) pH = 14; and PVP/PANI/TiO₂ films immersed for 24 hours, in solutions with (d) pH = 1, (e) pH = 7, and (f) pH = 14

By taking a glance at micrograph of PVP/PANI/TiO₂ film (Micrograph 8e, immersed in pH = 7 solution), it can be seen that it is more homogeneous than PVP/PANI. It has the homogeneous morphology and close packing nature; shows fine dispersion in the main medium. No changes were observed in the surface of PVP/PANI/TiO₂ film in Fig. 8d (the specimen was immersed in pH = 1 solution), implying on weak degradation occurred in PVP/PANI/TiO₂ film in the solution with pH = 1. Furthermore, changes were observed in the surface of PVP/PANI/TiO₂ film in Fig. 8f can be ignored. Generally, PVP/PANI/TiO₂ film shows no significant changes on the surface morphology, implying on the stability of PVP/PANI/TiO₂ films in comparison with PVP/PANI films in the acid and alkali solutions. This is caused by strong interactions between the nanoparticles and polymers.

CONCLUSIONS

According to the results of water uptake test, quantitative FTIR, and differences in UV-Visible DRS the intensity of degradation is in this order:

PVP/PANI (Base solutions) > PVP/PANI/TiO₂ (Base solutions) > PVP/PANI (Acid solution) > PVP/PANI/TiO₂ (Acid solutions)

that showed the most degradation was happened in the alkaline solutions for PVP/PANI.

Furthermore, results of water uptake, FTIR, UV-DRS show that degradation process occurred in 0 to 24 hours in pH = 14 solutions. However, after 24 hours, degradation process happened slowly, and main differences in water uptake, FTIR, and DRS-UV results from dissolution of films in solutions. SEM results for PVP/PANI films show that fractures and cavities in base solution film is more than those on acid solution film surface. It denotes that the PVP/PANI film degradation in the alkaline solution is more than the degradation of film in the acid solution. SEM micrographs show no significant changes on the surface morphology of PVP/PANI/TiO₂ films, denoting stability of these films in comparison with PVP/PANI. The results showed that TiO₂ increases stability of PVP/PANI films in both acid and alkali solutions.

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