

Surface Adsorption of Polyethylene Glycol and Polyvinyl Alcohol with Variable Molecular Weights on Zinc Oxide Nanoparticles

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Abstract

Polymer adsorption by nanoparticles improves the stability of these types of suspensions against aggregation. In this work, the surface adsorption of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) with different molecular weights onto the Zinc oxide (ZnO) nanoparticles is studied. The effects of solution pH value and temperature on the adsorption process are also investigated. The ZnO nanoparticles are then analyzed using Fourier transform infra red (FTIR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) techniques. The aggregation of nano particles before and after polymer adsorption is also investigated by scanning electron microscopy (SEM). The results show that by adsorbing the PEG and PVA, due to a relatively large electrostatic repulsive force between ZnO nano particles, the size of aggregated nanoparticles decreases. It has also been revealed that the low molecular weight polymers exhibit a higher adsorption rate on the particles' surfaces in comparison to the polymers with high molecular weight.

Keywords: Zinc Oxide Nanoparticles, Adsorption, PEG, PVA, Molecular Weight

1- Introduction

Nanosized ZnO particles are extensively used in producing bioceramics [1], porous ceramic parts employed in drug delivery systems [2], biosensors [3], nanocomposite membranes [4], catalysts for liquid phase hydrogenation [5], UV shielding material [6] and chemical adsorbent [7].

Control of colloidal properties and stability of the dispersion of ZnO particles is significantly important in the manufacturing

of high-quality products such as ceramics, paper coatings, cosmetics, paints, rubber and plastic [8]. Attempts have been made to develop new techniques for manufacturing and modifying the nanoparticle preparation methods, e.g. using polyelectrolyte [9] or polymeric dispersant [10]. Nevertheless, aggregation, which occurs during the formation of these particles is a common problem. Particle aggregation can form through various methods. Taking into

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account that one of the key parameters of the quality of ZnO nanoparticles is their tiny size, the production process should be designed in a way that the particles do not stick together, i.e. do not aggregate, since the aggregation results in an undesirable growth of ZnO nanoparticles [11]. Agglomeration of nanosized ZnO may occur because of the following reasons: 1) ZnO nanoparticles, having a tendency towards other nanoparticles, possess high surface energy, therefore agglomeration may occur when they are dispersed in an organic solvent and matrices. 2) Formation of the bonds of Zn-O-Zn among nanoparticles due to the existence of water molecules resulting in hard agglomerates, which impede the applications of ZnO nanoparticles [12]. Therefore, removal of water moiety in precursors is a key process for reducing hard agglomerates. Various methods were employed to remove the water in precursors, e.g. rinsing via organic solvent, and this has already been adopted by one research group [13]. Polymer coating is an effective way for modifying the particles' surface and it also prevents the agglomeration of ZnO nanoparticles. A large number of studies have been conducted to investigate the effects of adsorption of polymers on the rheological and stability behavior of different metal oxide suspensions; such as aluminum oxide suspension [14], zirconium oxide suspension [15], and aluminosilicates (zeolites) suspension [16]. The adsorption of polymeric additives on the metal oxide surface is ascribed to a combination of chemical and electrostatic interactions, hydrogen bonding and van der Waals force. For nonionic polymers, hydrogen bonding is the primary

adsorption mechanism [17]. In this study, polyethylene glycol (PEG) and polyvinyl alcohol (PVA) are used in order to prevent zinc oxide nanoparticles from aggregation. Effective factors of polymer adsorption such as molecular weight are discussed. The formed bonds between PEG and PVA macromolecules are due to the existence of hydrogen bonds and the ionic attractions between them. The repulsive electrostatic forces between the chains of these polymers prevent the nanoparticles from accumulating.

2- Experimental

2.1- Materials

Commercially available ZnO nanoparticles, purchased from Sepahan Ruy Company, Esfahan, Iran, are used for these experiments. It is claimed that the chemicals have been synthesized by sol-gel method. The specific surface area of the sample that is determined using BET method is 70 m²/g. PEG with molecular weights of 1000, 2000, and 10000 and PVA with molecular weights of 49000, 70000-100000 are purchased from Merck. For all the experiments double distilled water is used.

2.2. Adsorption of various molecular weights of PEG and PVA on ZnO nanoparticles

1.5g of ZnO nanoparticles are mixed with 50cm³ of distilled water. For monitoring the stability, the pH of suspension is monitored every 5 minutes and controlled by NaOH or HCl [18]. 10g of PEG with a molecular weight of 1000 are solved in 90cm³ of distilled water. This solution is then added to the suspension of ZnO nanoparticles. In order for adsorption to take place, the mixture is stirred with a magnetic stirrer with

the medium speed at room temperature for 48 hours. The particles that are dissolved in water yet not adsorbed by ZnO are separated from those particles that have been absorbed by centrifuging. The powder is dried in an oven at 90°C for 8 hours. The aforesaid steps are repeated for PEG particles with molecular weights of 2000 and 10000, and for PVA particles with molecular weights of 49000, 70000-100000.

IR analysis is carried out on a FT-IR spectrometer (Model Galaxy series FT-IR 5000) to characterize the interface of ZnO/PEG and ZnO/PVA. The size and structure of the zinc oxide nanoparticles is analyzed by X-ray diffraction with monochromatic CuK α radiation ($\lambda = 1.54\text{\AA}$). The amount of molar mass of the adsorbed polymer on the surface of ZnO nanoparticles is measured by thermogravimetry analysis (Perkin Elmer Diamond TG/DTA), using a heating rate of 10°C/min to 500°C and finally, the aggregation and accumulation of the nanoparticles is analyzed by Scanning electron microscope (Philips XL30).

3- Results and discussion

3.1- pH results

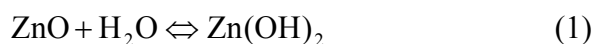
Table 1 shows the result of pH value for the suspension solution after adding PEG/PVA to the solution. Before polymer addition, pH is increased by adding water to the ZnO nanoparticles in the beaker because of the occurrence of two simultaneous reactions (Eqs. 1 and 2). Based on Figs. 1 and 2, both of these bond formations are desirable, therefore due to the presence of the hydrogen bonds, some bonds are formed between ZnO nanoparticles and the PEG and PVA macromolecules in the aqueous phase (Fig.

1) and the ionic attraction (Fig. 2). As Table 1 shows, the neutralization of the aqueous solution occurs after adding PEG/PVA to the ZnO suspension. This result agrees with the above theoretical description.

Table 1. pH values of ZnO nanoparticle's suspension stabilized with PEG/PVA macromolecules

Time (min)	0	5	10	15	20	25	>25
pH	7.19	7.20	7.28	7.33	7.34	7.36	7.36

The following reactions are suggested to take place.



Based on the Kramer theory, this coating prevents nanoparticles from sticking together and aggregating, by the repulsive electrostatic forces formed between the polymeric chains (Fig. 3) [19].

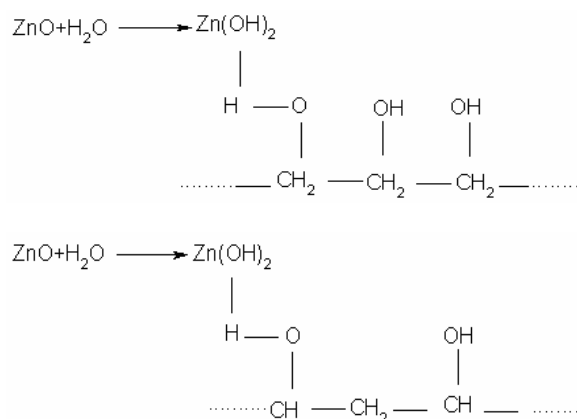


Figure 1. The formed bonds between ZnO nanoparticles and a) PEG, b) PVA macromolecules due to the presence of hydrogen bonds

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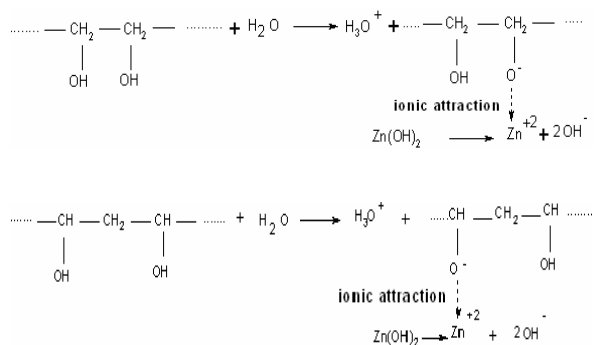


Figure 2. The formed bonds between ZnO nanoparticles and a) PEG, b) PVA

3.2- IR spectra

IR spectroscopy gives qualitative information about the way in which the adsorbed PEG molecules are bonded to the surface of the ZnO nanoparticles. Fig. 4 compares the IR

spectra of ZnO nanoparticles in the absence and presence of adsorbed PEG2000. According to Fig. 4(a), the peak seen at 3455cm^{-1} indicates the presence of hydroxyl group.

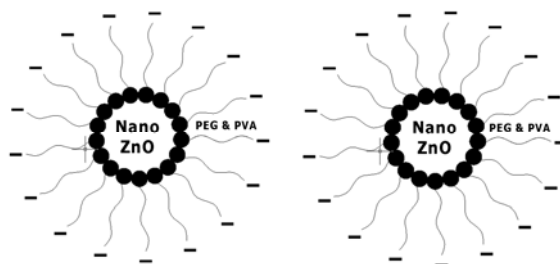
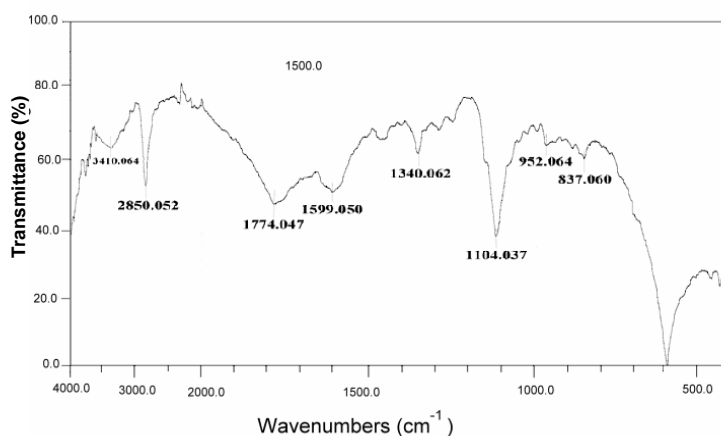
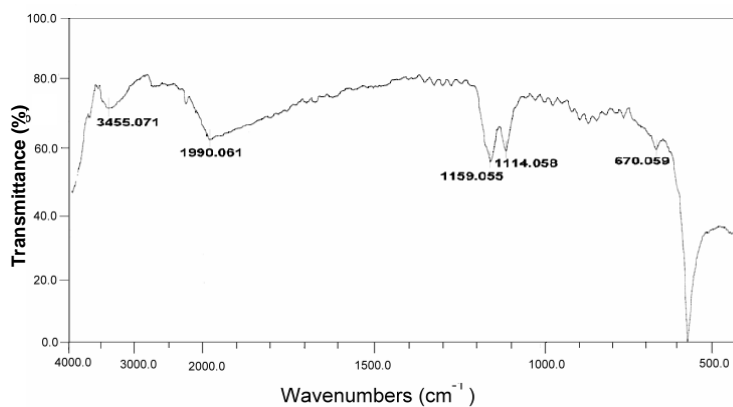


Figure 3. The suggested model for the repulsive electrostatic forces formed between the coated polymers



(a)



(b)

Figure 4. FTIR analysis of a) ZnO Nanoparticles, b) ZnO Nanoparticles with PEG2000

The absorption peak in the 2850 cm^{-1} in the spectrum of Fig. 4(b) corresponds to the CH group stretching vibration of PEG 2000. It proves that the molecules of PEG 2000 are adsorbed by the ZnO nanoparticles. The peak appearing at 3410 cm^{-1} in Fig. 4(b) shows the presence of the hydroxyl group, which has shifted towards lower wave numbers in comparison with the hydroxyl group peak in the ZnO nanoparticles (3455 cm^{-1}). It proves that hydrogen bonds have been formed between the PEG particles and ZnO nanoparticles.

3.3- X-ray diffraction studies

To investigate the size and structure of zinc oxide nanoparticles, X-ray diffraction patterns of pure nano-ZnO particles and coated nano-ZnO particles are shown in Fig. 5. The XRD pattern of pure ZnO nanoparticles is shown in Fig. 5(a). No peaks from other phases of ZnO and impurities are observed; suggesting that high purity ZnO is obtained. The sharp peaks in this figure reveal a desirable crystalline structure.

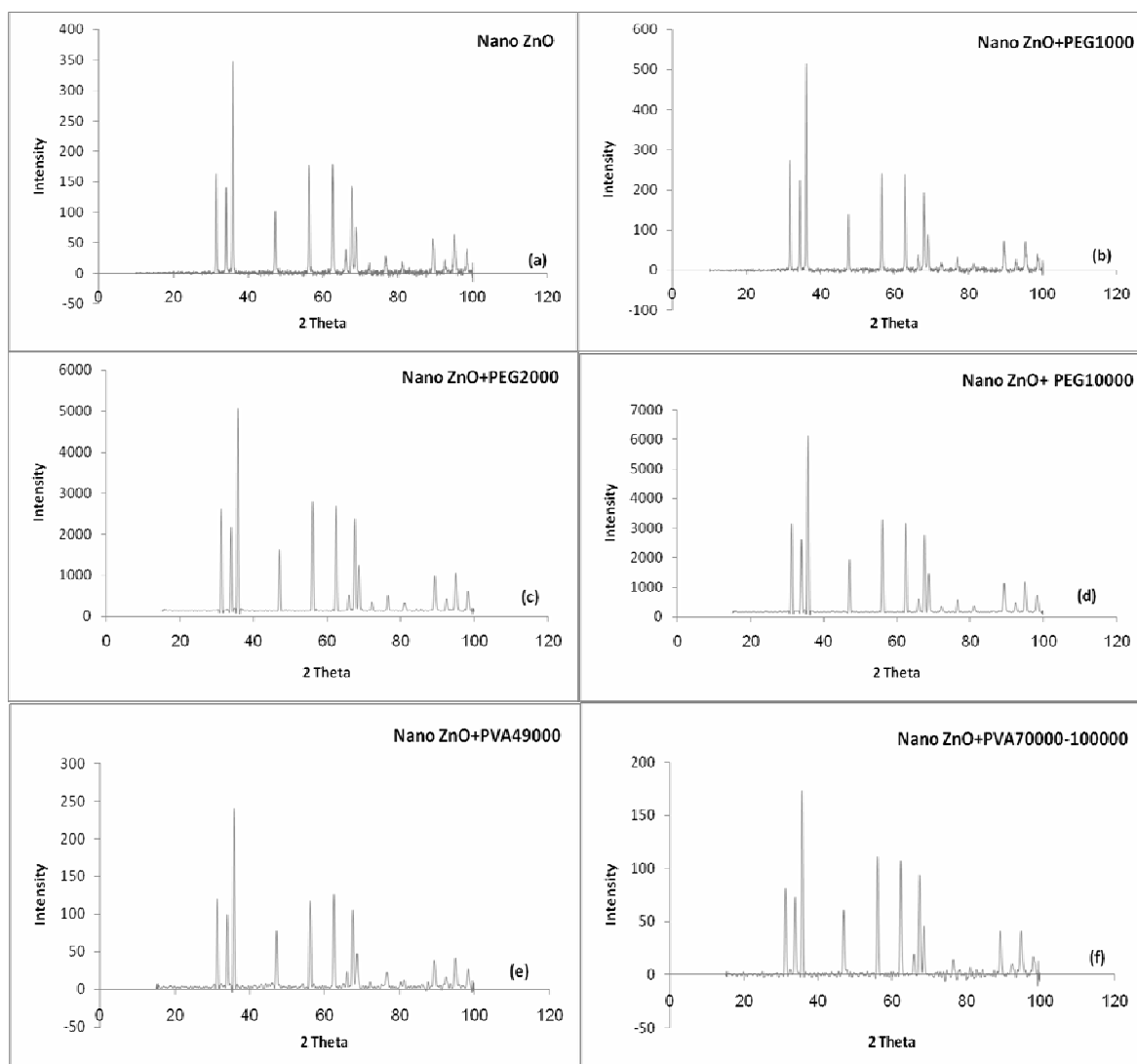


Figure 5. XRD patterns of a) ZnO nanoparticles, b) ZnO nanoparticles + PEG 1000, c) ZnO nanoparticles + PEG 2000, d) ZnO nanoparticles + PEG 10000, e) ZnO nanoparticles + PVA 49000, and f) ZnO nanoparticles + PVA 70000-100000.

The nanoparticles' diameter is calculated by Debye-Sherrer equation:

$$D = \frac{K \lambda}{\beta \cos \theta} \quad (3)$$

where K is Sherrer constant, λ is the X-ray wavelength, β is the peak width of half-maximum, and θ is the Bragg diffraction angle. The XRD peaks give the average diameter of about 44.2nm for pure ZnO nanoparticles. Comparing the XRD patterns of ZnO nanoparticles (Fig. 5-a) with those of ZnO nanoparticles coated with PEG 1000 (Fig. 5-b), PEG 2000 (Fig. 5-c), PEG 10000 (Fig. 5-d), PVA 49000 (Fig. 5-e), and PVA 70000-100000 (Fig. 5-f), indicates that the coated samples have the same patterns as the ZnO nanoparticles. This fact shows that adsorption of PEG and PVA with various molecular weights on ZnO particles does not change the crystalline structure of ZnO nanoparticles. Moreover, sharp peaks, which indicate a crystalline structure, are seen in all coated samples. Table 2 shows the size of the particles obtained by coating ZnO nanoparticles. It should be noted that the size of the ZnO nanoparticles without coating is about 44.2nm.

Table 2. Size of coated ZnO nano particles calculated by Debye-Sherrer equation

Particle Size	Adsorbed Polymer on ZnO Nanoparticles
34.0	PEG 1000
44.2	PEG 2000
44.2	PEG 10000
35.4	PVA 49000
44.2	PVA 70000-100000

Considering the calculated sizes of the ZnO nanoparticles that adsorbed PEG with three different molecular weights and those that adsorbed PVA with two different molecular weights, reveals that the size of ZnO particles decreases as the molecular weight of the adsorbing material decreases. A possible explanation for this result is as follows: The low molecular weight prevents ZnO nanoparticles from aggregation and compression. Therefore, the size of these particles is smaller than the size of pure ZnO nanoparticles. As the molecular weight increases, the size of the coated particles does not significantly vary in comparison with the size of the ZnO nanoparticles. The reason is that the molecular weight of the polymer is very high and therefore, it causes nanoparticles to adsorb a lower amount of molecules with higher molecular weight, while it still prevents nanoparticles from aggregation.

3.4- TGA analysis of nanoparticles

The molar mass of the adsorbed polymer on the surface of ZnO nanoparticles is determined through the weight loss at 500°C in nitrogen using thermogravimetric analysis (TGA). The weight loss curve of coated ZnO nanoparticles is shown in Fig. 6. TG results show that there is a weight reduction in all tested samples when the temperature increases. Qualitative analysis shows that polymer molecules are adsorbed on ZnO nanoparticles.

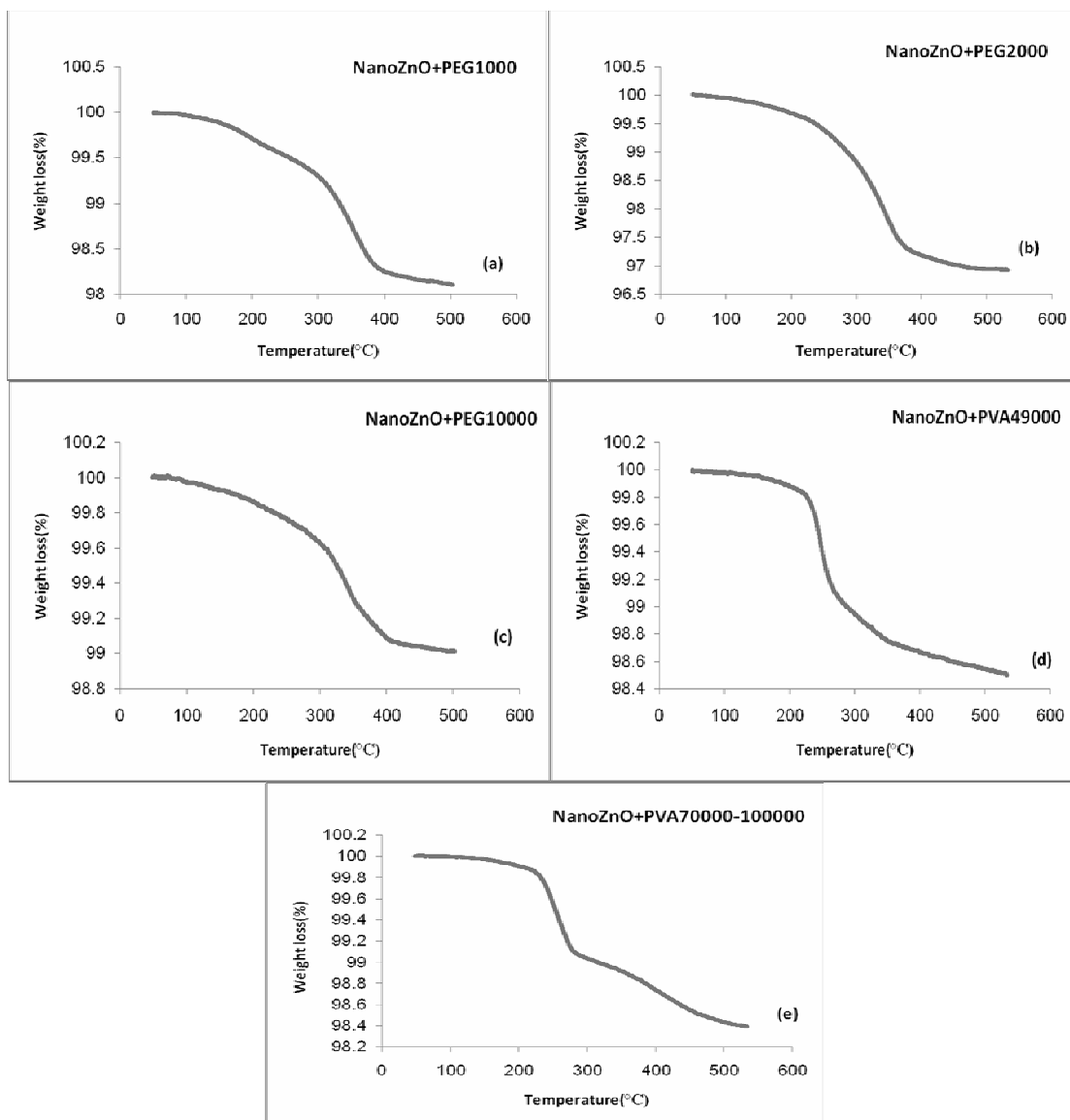


Figure 6. TG graphs for: a) ZnO nanoparticles + PEG 1000, b) ZnO nanoparticles + PEG 2000, c) ZnO nanoparticles + PEG 10000, d) ZnO nanoparticles + PVA 49000, and e) ZnO nanoparticles + PVA 70000-100000

Table 3. TGA results of polymer degradation adsorbed on ZnO nanoparticles

Adsorbed Polymer on ZnO Nanoparticles	Initial weight (wt. %)	Final weight (wt. %)	Final temperature	Weight loss ΔW_{mol} (%)	Mole loss (ΔW_{mol} (%))
PEG 1000	100	98.104	500	1.896	1.86×10^{-3}
PEG 2000	100	96.936	500	3.064	1.53×10^{-3}
PEG 10000	100	99.560	500	0.440	0.044×10^{-3}
PVA 49000	100	98.543	500	1.457	2.973×10^{-5}
PVA 70000-100000	100	98.435	500	1.565	1.565×10^{-5} - 2.235×10^{-5}

Values given in Table 3 show the molar percentage of adsorbed polymer on ZnO nanoparticles. As the molecular weight of both tested polymers increases, the amount of absorption decreases. The polymer chain length increases when the molecular weight of the polymer increases. When the polymer molecules form hydrogen bonds with ZnO nanoparticles, the polymeric chain starts to scatter around in a wave-like movement, thus preventing other polymeric chains from connecting to ZnO nanoparticles. The less the polymer molecular weight, the shorter the chains' length will be. Therefore, the spatial prevention will decrease, resulting in an increase in the amount of adsorbed polymer (Fig. 7). In this work, ZnO nanoparticles are coated with polymers with lower molecular weights in order to increase the amount of adsorbed polymer, and the results of TG analysis are confirmed. Since the coated particles have a more extended distribution than the ZnO nanoparticles' sample, their diameter is shorter than that of the main sample. This fact confirms the results of XRD analysis as well.

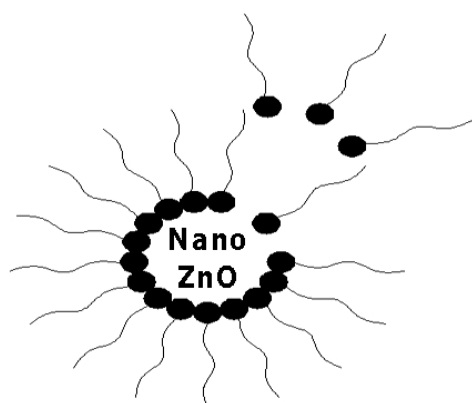


Figure 7. Suggested model for coated polymer on ZnO nanoparticles

Fig. 8 shows the relation between molecular weight and molar weight percentage of adsorbed polymer on samples coated by PEG and PVA. These charts show that there is a linear relation between the molar weight percentage and the molecular weight of the samples.

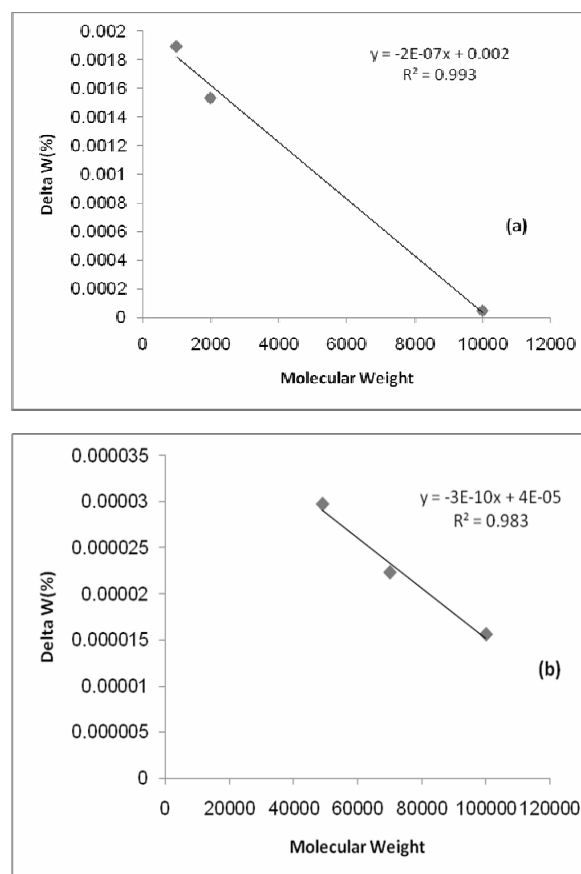


Figure 8. percentage change of molar weight verses molecular weight for samples adsorbed: a) PEG and b) PVA

3.5- SEM images

The SEM images of the pure and coated ZnO particles are shown in Fig. 9. The images show that uncoated ZnO nanoparticles are aggregated and compressed (Fig. 9a), while coated nanoparticles have a better distribution and homogeneity. SEM images also show that the samples with less

molecular weight have a better distribution. This is because the particles are less aggregated in the lower molecular weight of the samples, and therefore the particles' sizes are smaller than the size of uncoated ZnO nanoparticles. This fact confirms the results of the XRD analysis.

4- Conclusions

IR spectroscopy shows that ZnO nanoparticles are prone to adsorption of polyethylene glycol and polyvinyl alcohol. PVA and PEG form hydrogen bonds with the surface of ZnO nanoparticles. Results obtained by XRD analysis show that the coating process does not change the crystalline structure of the ZnO nanoparticles. Therefore, the characteristics of the ZnO nanoparticles, which are dependent on its crystalline structure, will remain unchanged. The diameter of coated

ZnO nanoparticles is shorter for lower molecular weights. The average diameter size of the particles coated with PEG 1000 is less than that of the particles coated with PVA 49000. Results obtained by TG analysis show that the amount of adsorbed polymer on ZnO nanoparticles increases as the molecular weight decreases. There is an approximate linear relation between the molecular weight and the molar weight percentage of the adsorbed polymer. SEM images show that in both methods of coating, the distribution of ZnO nanoparticles improves and particles aggregate less as the molecular weight decreases. The distribution of ZnO nanoparticles coated with PEG is more than even that of the particles coated with PVA. In addition, ZnO nanoparticles coated with PEG are more spherical and have a smaller size.

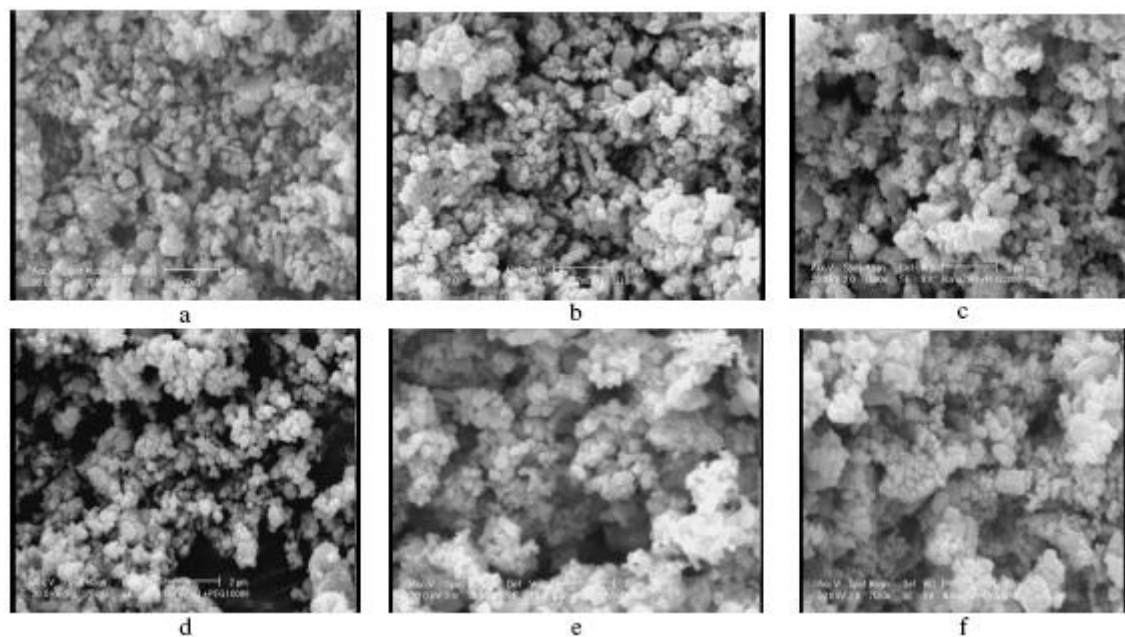


Figure 9. SEM images (7500 x) of: a) ZnO nanoparticles, b) ZnO Nanoparticles + PEG 1000, c) ZnO Nanoparticles + PEG 2000, d) ZnO Nanoparticles + PEG 10000, e) ZnO Nanoparticles + PVA 49000, and f) ZnO Nanoparticles + PVA 70000-100000

5- Acknowledgement

The authors would like to thank Ms. Niloufar Nabiyouni for her assistance in editing the English text.

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