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Some Mechanical Properties Of Polyvinylalcohol / Zinc Oxide Nanoparticles As Thin Films And Solutions

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ABSTRACT

The polymer was dissolved in twice distilled water, then nanoparticles were added to it. The flow time of the solutions was measured, then the viscosity was calculated and the surface tension of the solutions was measured by measuring the weight of the liquid drop. Solutions were left at room temperature to form thin films that were subjected to variable tension until they were cut and depending on the stress and strain of the samples. From the results, an increase in the stress borne by the samples was noted with an increase in the concentration of zinc oxide nanoparticles, and express the departure from the ideal elastic behavior has values ranging from 3.71 to 54, but quantity pertaining to the ideal elastic behavior has values ranging from 1.2 to 1.0. Increase viscosity of the solutions and their surface tension. This makes it clear that it is possible to change some properties of the PVA by adding zinc oxide nanoparticles, the sum of Huggins and Kraemer constants values indicates that the samples were dissolved in a good solvent, as they can be used in many areas of life such as industrial, medical applications.

1. INTRODUCTION

Stress is defined as the intensity of force. The classical theory of small deformations is based on the assumption that the geometric changes that occur during loading are so small that they can be represented by a first-order linear representation [1]. The presence of stresses in thin films is a major concern in many technology applications, as excessive levels of residual stresses can dramatically affect the performance, reliability, and durability of hardware components and devices. Worst scenarios lead to film cracking of layers under tensile or peeling stress, buckling or blistering under compressive stress [2].

The concept of viscosity was postulated by Newton as the resistance of a fluid to the movement of neighboring parts to each other, or a change in shape and denotes an opposition to flow. Viscosity is also known as lack of slip. Using this concept, all fluids can be classified by examining the relationship between applied shear stresses and the strain and the evaluation of hydrocarbon reservoirs. Therefore, an accurate measurement of the viscosity of the fluid is of great rate of a fluid flow [3]. Viscosity is an embodiment of the physical properties of the fluid. It affects the flow law of underground fluids, the model of development of reservoirs

* Corresponding author at: Physics Department, Faculty of Education, University of Benghazi, Benghazi, Libya nagla.elgerani@uob.edu.ly importance. The viscosity of the same fluid behaves differently under different conditions [4].

Aristotle noticed the phenomenon of surface tension of pieces of iron and lead floating on the surface of the water. [5]. Surface tension is a fundamental physical property. It plays an important role in many scientific fields and influences many industrial applications [6]. The definition of surface energy is the energy technique. The NLA and NLR are associated with intermolecular forces at the interface between two media and are also called free surface energy, it plays an important role in friction, lubrication, and wear phenomena in materials in contact and especially inflow surface interactions with liquids [7].

Nanoparticles are atomic or molecular aggregates that can have physicochemical properties very different from those of bulk material. Nanoparticles can be prepared from a mixture of bulk materials, and their actions depend on both the chemical composition and the size and appearance of the particles. Nanoparticles and nanostructured materials represent an active field of research and a rapidly expanding technicaleconomic sector in many fields of application. They have gained prominence in technological advancements due to their adjustable physicochemical characteristics [8]. ZnO nanoparticles are used in a large number of industrial products, it is one of the most popular metal oxide nanoparticles in biological applications due to its characteristics.

Zinc oxide nanoparticles have emerged with promising potential in biomedicine [9].

Polymers are large chain-shaped molecules formed by multiple small molecule reactions whose wide range of properties and uses is derived from the diversity of monomers, combinations of monomers, and polymer architecture [10]. Poly (vinyl alcohol) is widely used in industries in various applications, such as biopolymer films, coating industry, food processing, medical industries, and has also been used as a hydrate inhibitor in industries, oil and gas. It is a synthetic polymer soluble in water. Their skeletons are composed only of carbon atoms that are biodegradable under aerobic and anaerobic conditions [11].

This study aims to improve some properties of the Polyvinylalcohol (PVA) by adding zinc oxide nanoparticles (ZnO nanoparticles).

2. EXPERIMENTAL SETUP

2.1. Samples

3 g of PVA were dissolved in 200 milliliters of twicedistilled water mixing at a temperature of 80 $^{\circ}$ C, then the sample was divided into six equal parts and zinc oxide nanoparticles were added at different concentrations (0.0, 0.2, 0.4, 0.6, 0.8, 1.0%), and the viscosity and surface tension were measured. It was poured onto a flat glass plate and allowed to dry at room temperature. Thin films almost 0.01 mm thick were formed, as in figure 1, next a rectangular piece of the sample was taken and measure the change in its length by increasing the load on it.



Fig.1: The thin film of PVA/ ZnO nanoparticles

2.2. Measurements:

2.2.1 Stress-Strain Measurements:

For known cross-sectional area (A), and the forces (F) which are applied by the tensile testing machine, then the tensile stress (σ s) is [12, 13]:

If (L_0) is the original length of the sample and (L) is the length of the sample after a certain amount of tensile stress has been applied, then the tensile strain (ϵ) defined as[12,13]:

$$\varepsilon = \frac{(L - L_0)}{L_0}$$
(2)

Young's modulus (E) is calculated from the relationship between stress and strain in Equation 3 [12-14]:

$$\sigma_s = E \varepsilon \qquad (3)$$

tuting for the expansion ratio ($\lambda = 1 + \varepsilon$)

By substituting for the expansion ratio ($\lambda = 1+\epsilon$), in Equation 4, you can know the dependence of the stress-strain relationship for different test samples [15, 16].

$$\frac{\sigma_{\rm s}}{2(\lambda-\lambda^{-2})} = C_2 + C_1 \lambda^{-1} \qquad (4)$$

Where C_1 is expressing the departure from the ideal elastic behavior, and C_2 is a quantity pertaining to the ideal elastic behavior [15, 16].

2.2.2. Viscosity Measurements:

To determine the flow time of the samples, the methodology provided by ASTM (1989) was used. The exit time of the solvent (double distilled water) and the exit time of the other solutions were measured using a glass capillary viscometer.

The measured values were expressed in terms of relative (η_r) , specific (η_{sp}) , intrinsic $([\eta])$ viscosities and reduced (η_{red}) viscosities of all samples using the following equations [17-19]:

$$\eta_{r} = \frac{t_{solution}}{t_{solvent}}$$
(5)

$$\eta_{sp} = \eta_{r} - 1$$
(6)

$$[\eta] = \frac{[2(\eta_{sp} - \ln \eta_{r})]^{\frac{1}{2}}}{c}$$
(7)

$$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{\eta_{r} - 1}{c}$$
(8)

Where C is the mass concentration of zinc oxide nanoparticles, the solvent is the exit time of the pure solvent and solution is the exit time of the sample [17]. Equations 5 and 6 represent the Huggins (K_H) and Kramer (K_K) equations, respectively [20]:

$$\frac{\eta_{sp}}{c} = [\eta] - K_{H} [\eta]^{2} c \qquad (9)$$
$$\frac{Ln \eta_{r}}{c} = [\eta] + K_{K} [\eta]^{2} c \qquad (10)$$

2.2.3. Surface Tension Measurements:

Using the drop weight method, a counted number of drops were collected and the average mass of one drop was found. The average radius of the fall was determined, then surface tension (γ) against the air, surface tension force (F), and surface and tension energy (E) expressed by the values measured as follows, respectively [20, 21]:

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$\gamma = \frac{\text{mg}}{2\pi r}$	(11)
$F = 4 \pi r \gamma$	(12)
$E = \gamma A$	(13)

Where average mass of a drop (m) = 6.86×10^{-5} , internal radius of the tube used (r) = 4 mm and gravity acceleration (g) = 9.8 m s^{-2} . All measurements were carried out at a

temperature of 30 $^{\circ}$ C.

3. RESULTS AND DISCUSSION

3.1. Stress-Strain

The slope of the stress-strain curve increases with increasing ZnO concentration in PVA / ZnO nanoparticles thin films, as shown in figure 2, this leads to an increase in Young's modulus with increasing nanoparticle concentration figure 3 [22].



Fig2: The effect of concentration of ZnO nanoparticles on stressstrain curves for PVA/ ZnO nanoparticles thin films.

Fig.3. Young's modulus curve of PVA/ ZnO nanoparticles



In figure 4 the fracture stress increases with increasing ZnO nanoparticles concentration in PVA / ZnO nanoparticles thin films, this means that the cross- linking increases with increasing ZnO nanoparticles concentration [23].



Fig. 4: Fracture stress curve of PVA/ ZnO nanoparticles thin films.

The constants C1 and C2 are easily determined from the relationship between the strain amplification factor and the inverse expansion rate, where C1 is the slope and C2 is the intercept with the ordinate. The behavior of the C1 and C2 waves with concentrations may be due to the competition between increasing and the number of crosslinks in the network and other defects in the network [16, 24]. The relationship between the strain amplification factor and the inverse expansion rate is represented in figure 5, while the table1 contains the values of C1 and C2 constants.



Figure.5. Strain amplification factor curve for PVA/ ZnO nanoparticles thin films.

Table.1.The value of constant C_1 and C_2 for different concentrations of PVA/ ZnO nanoparticles thin films

Concentration ZnO nanoparticles (%)	C ₁	C ₂	$C_1 + C_2$
0.0	3.707575	1.2	4.907575
0.2	9.546215	1.0	10.54622
0.4	23.88195	1.0	24.88195
0.6	34.20008	1.0	35.20008
0.8	43.69019	0.99	44.68019
1.0	54.04957	1.0	55.04957

3.2. The viscosity

The exit time of the twice distilled water was measured at room temperature (127.27 sec), the exit time of other samples was also measured at room temperature (30 C), then the relative viscosity values were calculated using equation 5, for all solutions.

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There is a direct ratio between Relative viscosity and different concentrations of ZnO nanoparticles for Polyvinylalcohol solutions in the relationship shown in Figure 6. Thus, it is clear that the concentrations of ZnO nanoparticles produce changes in the viscosity of the solution. As the viscosity increases, meaning there will be more polymer chain entanglements in the solution, the charges on the electrospinning jet will be able to fully stretch the solution with the distributed solvent molecules between polymer chains [25].



Figure.6. Relative viscosity vs different concentration of ZnO nanoparticles for PVA/ ZnO nanoparticles solutions at 30° C

As the specific viscosity increases, the reduced viscosity decreases, as shown in figure 7, and the intrinsic viscosity decreased with the increasing concentration of nanoparticles, This is represented in figure 8 [26,27].



Figure. 7. Reduced viscosity vs specific viscosity nanoparticles for PVA/ ZnO nanoparticles solutions with different concentration of ZnO nanoparticles at 30°C



Figure. 8. Intrinsic viscosity vs different concentrations of ZnO nanoparticles for PVA/ ZnO nanoparticles solutions at 30°C.

The Huggins and Kraemer constants can be calculated from the slopes of the viscosity figures, used by equation (5) and equation (6) respectively. The Huggins and Kraemer constants depend on the state of the solution [28]. The range of 0.25 to 0.5 in the Huggins coefficient (K_H) is attributed to good solvation [17]. As shown in Table 2, the K_H values ranged from (0.377) to (0.402) for the sample. The Kramer plot is only linear at low enough concentrations. So, the following relationship holds between the dimensionless Huggins and Kraemer constants [18].

$$K_{\rm H} + K_{\rm K} = 1/2$$
 (10)

As shown in Table (2), the results of this study indicate that the sum of Huggins and Kraemer constants is exactly equal to 0.5.

different concentrations of ZnO nanoparticles.					
Concentration (%)	Кн	Kĸ	$(\mathbf{K}_{\mathbf{H}} + \mathbf{K}_{\mathbf{K}})$		
0.2	0.377398	0.122602	0.5		
0.4	0.385262	0.114738	0.5		
0.6	0.393208	0.106792	0.5		
0.8	0.397855	0.102145	0.5		
1.0	0.402318	0.097682	0.5		

Table.2. Huggins and Kraemer constants of solutions with different concentrations of ZnO nanoparticles.

3.3. Surface tension;

The surface tension values as a function of the mass concentration of ZnO nanoparticles of the PVA / ZnO nanoparticle solutions have been represented in Figure 9. which indicates that the surface tension of the solutions increases with increasing concentration of ZnO nanoparticles [29,30]. surface tension force and surface tension energy increase as shown in figure 10 and figure 11 respectively, since the surface tension of solutions increases with increasing concentration of silver nanoparticles as shown in figure 9 so that a strong cohesion force is exerted between the molecules and resulting in higher surface tension of the solution. As the concentration increases, the average spacing between molecules and nanoparticles decreases. Therefore, an attractive Van der Waals force is used on the electrostatic repulsive force between molecules, which increases the surface tension of the solution[31].



Figure.9. Surface tension vs. different concentrations of ZnO nanoparticles for PVA/ ZnO nanoparticles solutions at 30°C.



Figure. 10. Surface tension force vs. different concentration of ZnO nanoparticles for PVA/ ZnO nanoparticles solutions at 30°C



Figure.11. Surface tension energy vs. different concentration of ZnO nanoparticles for PVA/ ZnO nanoparticles solutions at 30°C.

4. CONCLUSION

The results of the investigation indicated that the flexibility of the samples increased with increasing the concentration of zinc oxide nanoparticles, and the viscosity of the solutions also increased with increasing the concentration of zinc oxide nanoparticles, indicating that friction of the layers of the solution increases and causes an increase in the resistance of the solution to flow, but the increase in the surface tension of the liquid indicates an increase in bonding within the solutions. By increasing or decreasing the concentration of zinc oxide nanoparticles in the polymer solution, these aforementioned properties can be increased or altered, and this leads to obtaining materials that have different properties than the properties of their components that can be used in different fields such as industrial and medical applications.

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بعض الخواص الميكانيكية لجسيمات كحول البولي فينيل / أكسيد الزنك النانوية كأغشية رقيقة ومحاليل نجلاء علي الغرياني. قسم الفيزياء ، كلية التربية ، جامعة بنغازي ، بنغازي ، ليبيا. nagla.elgerani@uob.edu.ly

الخلاصة:

تمت إذابة البوليمر في الماء المقطر مرتين ، ثم أضيفت إليه الجسيمات النانوية ، وقياس وقت تدفق المحاليل ، ثم تم حساب اللزوجة وقياس التوتر السطحي للمحاليل عن طريق قياس وزن قطرة السائل. تُركت المحاليل في درجة حرارة الغرفة لتشكيل أغشية رقيقة عرضت للاحمال متغير حتى تم قطعها اعتمادًا على إجهاد وانفعال العينات. من النتائج لوحظ زيادة في الإجهاد الذي تتحمله العينات مع زيادة تركيز جزيئات أكسيد الزنك النانوية ، فأبتعدت عن السلوك المرن المثالي الذي قيست قيمته من 3.71 إلى 54 ، ولكن الكمية المتعلقة بالسلوك المرن المثالي لها قيم تتراوح من 1.2 إلى 1.0. زيادة لزوجة المحاليل وتوترها السطحي وضح أنه من الممكن تغيير بعض خصائص PVA عن طريق إضافة جزيئات أكسيد الزنك النانوية ، و مجموع قيم ثوابت هوجينز و كرامير تشير إلى أن قد تم إذابت العينات في مذيب جيد ، حيث يمكن استخدامها في العديد من مجالات الحياة مثل الصناعية والطبية.