A Swelling Study in Different PH and Mechanical Properties of Biodegradable Films Based on Pluronic F-127/ Poly-Vinyl Alcohol

Article *in* Materials Science Forum · August 2020

CITATIONS
0

READS
19

1 author:

Zainab J. Sweah
University of Basrah
21 PUBLICATIONS **12** CITATIONS

SEE PROFILE

Materials Science Forum
ISSN: 1662-9752, Vol. 1002, pp 389-398

Submitted: 2020-01-30
Revised: 2020-02-29
Accepted: 2020-03-04
Online: 2020-07-14

A Swelling Study in Different PH and Mechanical Properties of Biodegradable Films Based on Pluronic F-127/ Poly-Vinyl Alcohol

Zainab J. Sweah

Department of Chemistry and Polymer Technology, Polymer Research Center, Basrah University, Iraq

Zainab.Sweah@uobasrah.edu.iq

Keywords: Glycerin, PluronicF-127, polyvinyl alcohol, Biodegradable Polymers.

Abstract. PluronicF-127/PVA polymeric biomaterials blend films plasticized with glycerin were prepared by solvent molding method. The polymer blend films were characterized using Fourier transform infrared (FTIR) spectroscopy, Field Emission Scanning Electron Microscopy and mechanical measurements. The FTIR spectra of the two polymers and their blends show that there is no chemical interaction between the PVA and the PluronicF-127. FESEM images indicate that blend homogeneous film can easily be prepared. Mechanical and swelling properties of the studied blends indicate that these can be used for medical application such as biodegradable materials and biodegradable drugs carriers and as food packaging materials.

Introduction

There is a great increase in the use of biodegradable materials in medicines especially in drug delivery system [1]. The other applications of biodegradable polymers are food packaging; the principal purpose of packaging is the protection of food from external pollution [2]. In addition to that, the packaging is aimed to delay expiry, prolong shelf life and preserve the quality and safety of food. Biodegradable polymers can fulfil all these purposes in addition to being environmentally friendly and economical [3]. Poly-vinyl alcohol (PVA) contains many polar alcohol groups and form hydrogen bonds with water, thus dissolves easily in water. PVA is a synthetic, hydrophilic, a poly hydroxyl polymer that largely used globally for food packaging [4]. It is also being used for wound dressing [5, 6]. Pluronic F-127 is another hydrophilic, non-ionic surfactant of poloxamers a copolymer compatible with many different substances. The molecular structure of Pluronic F-127 is an A-B-A block copolymer of poly (ethylene glycol) (PEG) and Poly (propylene glycol) (PPG), as shown in a figure 1. The use of Pluronic F-127 as a biomaterial has widely increased during the last decade due to its particular Physico-chemical characteristics [7, 8]. These characteristics include its thermo-reactivity, ease of chemical functionalization and relatively good biocompatibility. In addition to these properties, Pluronic F-127 is known to have low toxicity, excellent drug release characteristics and high solubility in water [9, 10]. In the present work, it is aimed to develop a new biodegradable material based on Pluronic F-127/PVA polymers blends and different glycerin ratio and investigate its properties and applicability in drug delivery.

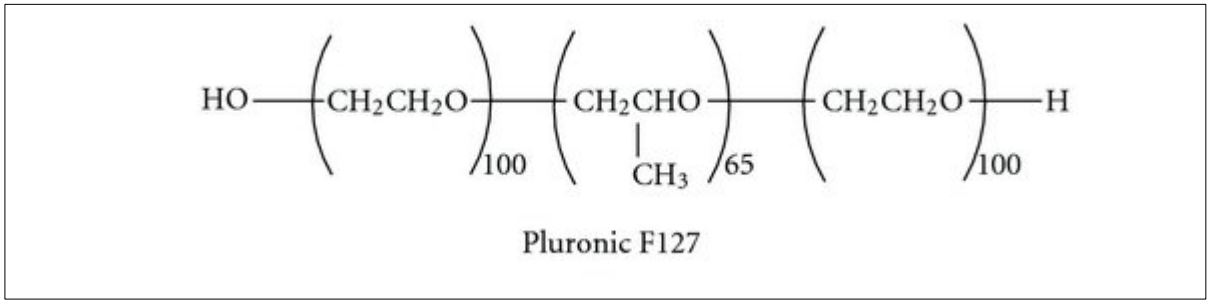

Fig. 1: Molecular structure of Pluronic F-127

Materials and Methods

PVA and Pluronic F127 were procured from HAMIDA and Merck respectively. A universal testing machine type BTI-FR 2.5 TN. D14 from Z wick Roe II, Germany determined the mechanical properties of the materials. The Fourier-transformed infrared (FTI R) spectra were measured and recorded by JASCO FTIR 4200 spectrometer in the range 400-4000cm^{-1} Available at Polymer Research Center, Basrah University, Iraq. The FESEM measurement of samples were carried out using Leo-Supra 50vp (Carl Zeiss, Germany) available in Science College in Basra University.

Preparation of polymer blend films. Polymer blend films were synthesized according to the following procedure. Equal weight of PVA and Pluronic F-127 were initially dissolved separately in distilled water at 80 °C. The two solutions were then mixed; the mixture was stirred at high speed and constant temperature of 30 °C. Glycerin was added at different ratios [11, 12] of 30, 35, 45, 50 and 60 % wt ratio of the final mixture weight. The resulting mixture was homogenized by constant stirring for 25 minutes to guarantee even distribution of the plasticizer inside the polymer blend. Table (1) shows the percentage of glycerin in the polymer blends. The polymer blends are labelled, accordingly, as S_1P, S_2P, S_3P, S_4P, S_5P, and S_6P.

Table 1: Percentage of glycerin in the PVA/Pluronic F-127 polymer blends

Symbols	% Glycerin
S_1P	0
S_2P	30
S_3P	35
S_4P	45
S_5P	50
S_6P	60

FTIR Analysis

The aim of blending two or more polymers is to develop a new biomaterial exhibiting a combination of properties that could not be obtained by individual polymers. The mixing may initiate chemical interactions that are reflected by changes in the FTIR spectra. The stretching vibration of the hydrogen bonding (OH group) shifts to 3377cm^{-1} for PVA /Pluronic F-127 with glycerin. The (C-H) stretching from alkyl groups is identified with the peaks at 2940 cm^{-1} for S_1P and 2942 cm^{-1} for S_3P. figures 2-4 show the FTIR spectra of the PVA, Pluronic F-127, and PVA/Pluronic F-127 blend respectively. Theoretically speaking, hydrogen bonding and other interactions between chemical groups on the dissimilar polymers should cause a shift in the peak location of the participating groups. Hydrogen bonding interaction shifts the stretching frequencies of the participating groups (e.g. O-H) towards the higher wave numbers. Decreased intensity and peak broadening usually accompany this. Peak shifting depends on the degree of the interaction between the polymers. This is clear in the FTIR spectra of figure 5 for the S_1P and S_3P polymers blends.

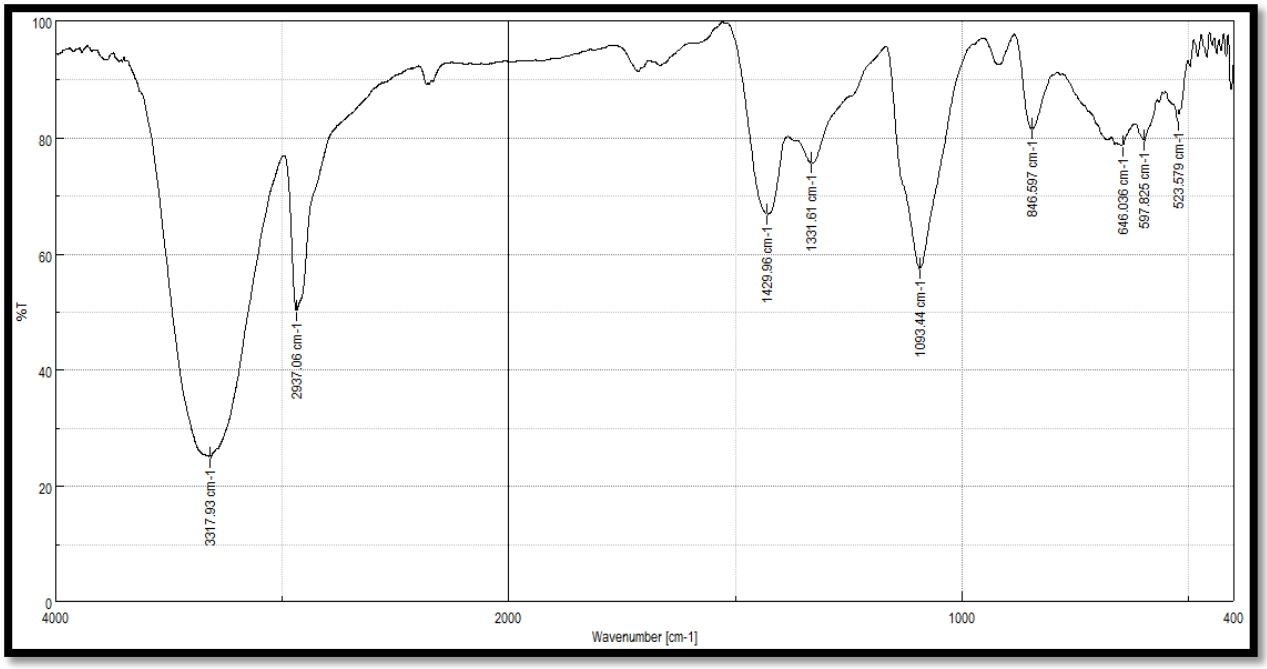

Fig. 2: FTIR of polyvinyl alcohol (PVA)

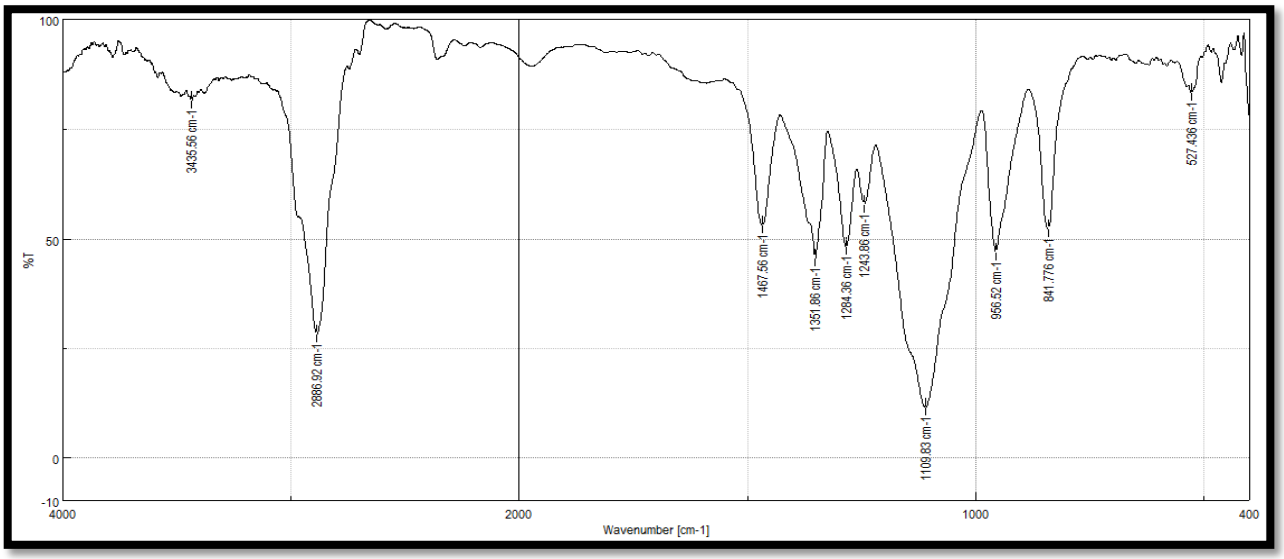

Fig. 3: FTIR of Pluronic F-127

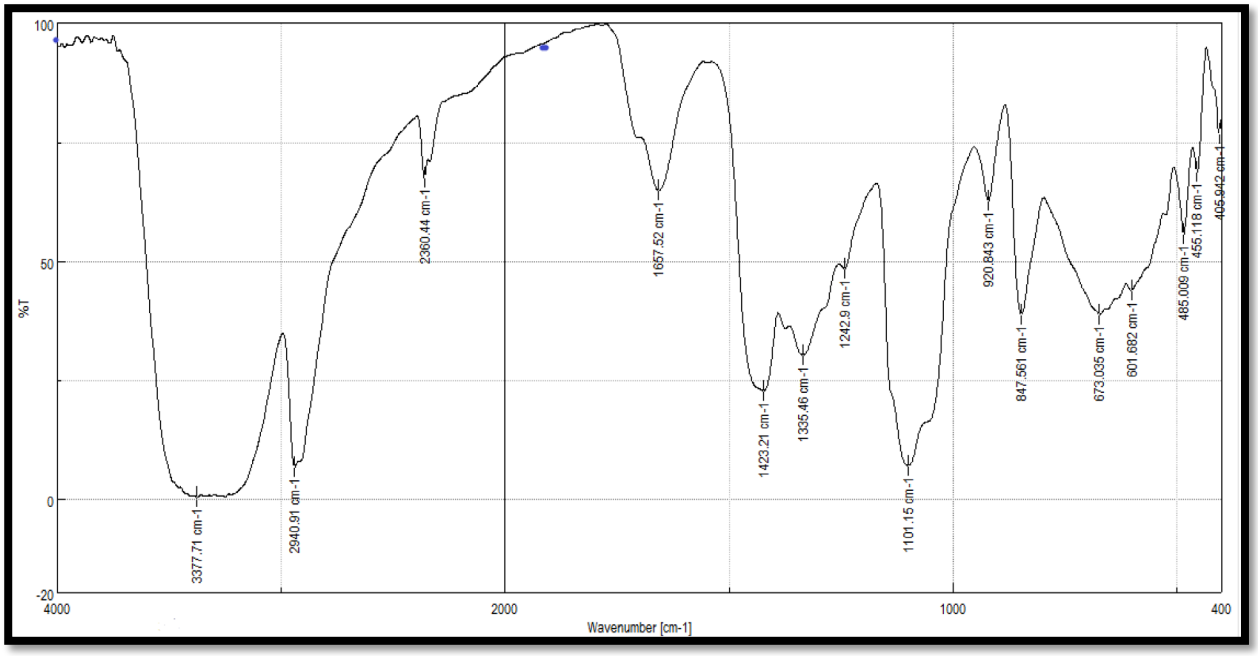

Fig. 4: FTIR of S_1P blend

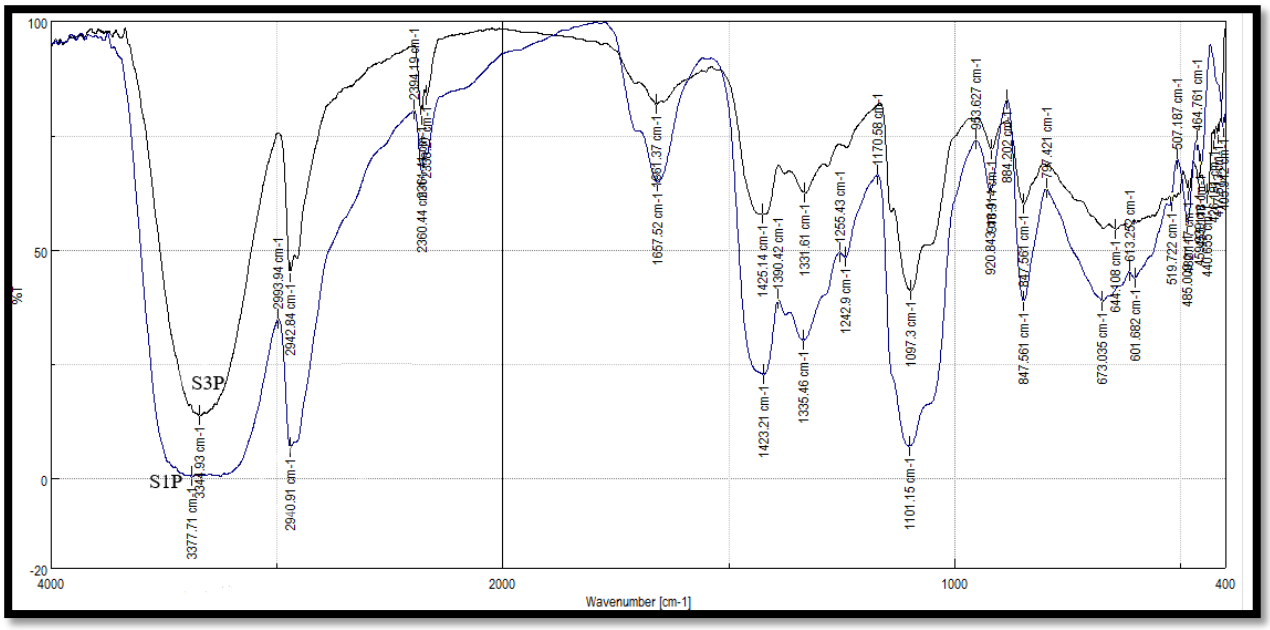

Fig. 5: FTIR spectra of $S_1P$and S_3P blends

Mechanical Measurements

The A STM Standard D-638 tested the tensile properties and figure 6 shows the stress-strain graph of the S_1P-S_6P polymer blends measured at room temperature and constant loading rate. The stress-strain curve is not dependent on the load-elongation curve because it describes the material characteristics and is less dependent on the arbitrary option of specimen shape. The polymer is characterized by a low coefficient and low yield stress. According to the breakdown classification, the stress-strain curve is an example of the second behaviour of fracture known as cold drawing. In this type, three regions can be identified, the first region is the linear one where deformation is not very large, Hook's Law is fulfilled and characterized by an instantaneous and recoverable deformation associated with the bending and stretching of the interatomic bonds between the polymer atoms. In addition, there is no permanent displacement of molecules relative to other molecules. The linear region shows the elastic limit of the polymer where the uniform extension occurs due to an increase

of stress a constant at constant rate. The second area is the yield region while the third is the elongation region, which extends until the breakdown occurs.

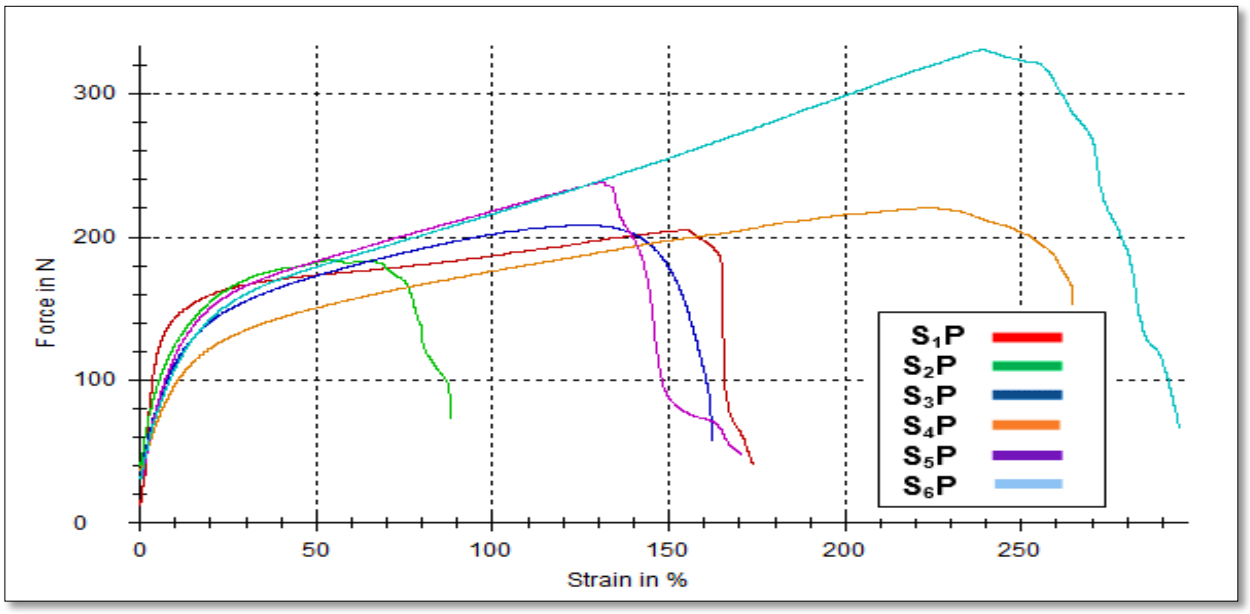

Fig. 6: Stress-strain curves of the of PVA/Pluronic -127 polymers blends at different ratio of glycerin

The study of effect the percentage of glycerin on the Young modulus of Pluronic F-127/PVA polymer blends, found that Young modulus decreases with the increase of glycerin ratio in the polymer blend. Young modulus was found equal to 0.199 MPa when no plasticizers present in the polymer blend. This value decreases to 0.2 MPa when the glycerin percentage is 50%. At glycerin ratio of 60%, the Young modulus was equal to 0.19MPa. The increase in the Young modulus at 45% of the glycerin might be attributed to the heterogeneity of the specimen. The relationship between Young's modulus and the ratio of glycerin in polymer blends is shown in figure 7. Young's Modulus decrease with the increase of glycerin ratio. This is because glycerin has a flexible structure.

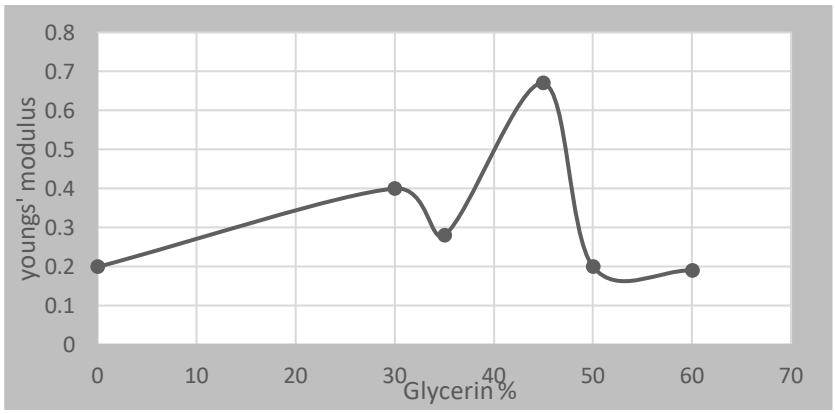

Fig. 7: Young modulus of PVA/Pluronic -127 polymer blends with different glycerin ratio

Figure 8 shows the rapport between the percentage of elongation and the concentration of glycerin. For the polymer blend free of plasticizer the percentage of elongation is 173.7%. This ratio increases to 264.7% when glycerin ratio is 45% showing high flexibility behavior and low hardness characteristic. The same behaviour continues as the elongation ratio reaches 294.8 % when glycerin ratio was 60%. This is because glycerin is compatible with both PVA and Pluronic F-127 polymers and fill the expanses between the polymers chains and make flexibility to the movement of these chains. It can be seen that the use of glycerin reduces tensile strength and increases the elongation

ratio of the prepared films is because the glycerin, which is one of the known plasticizers, can reduce the particles forces and increased mobility of biopolymer chains.

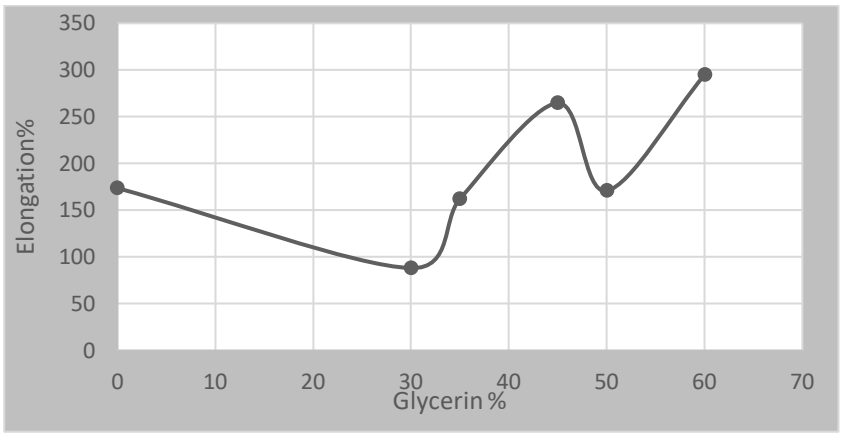

Fig. 8: Elongation of PVA/Pluronic -127 blends with different glycerin ratio

Field Emission Scanning Electron Microscopy

The FESEM micrographs of S_4P PVA/pluronic-127/glycerin polymer blend magnified by 12000 and 6000 times are presented in figure 9. The image shows the homogeneity of the polymer blend of PVA/Pluronic F127 with 45% glycerin.

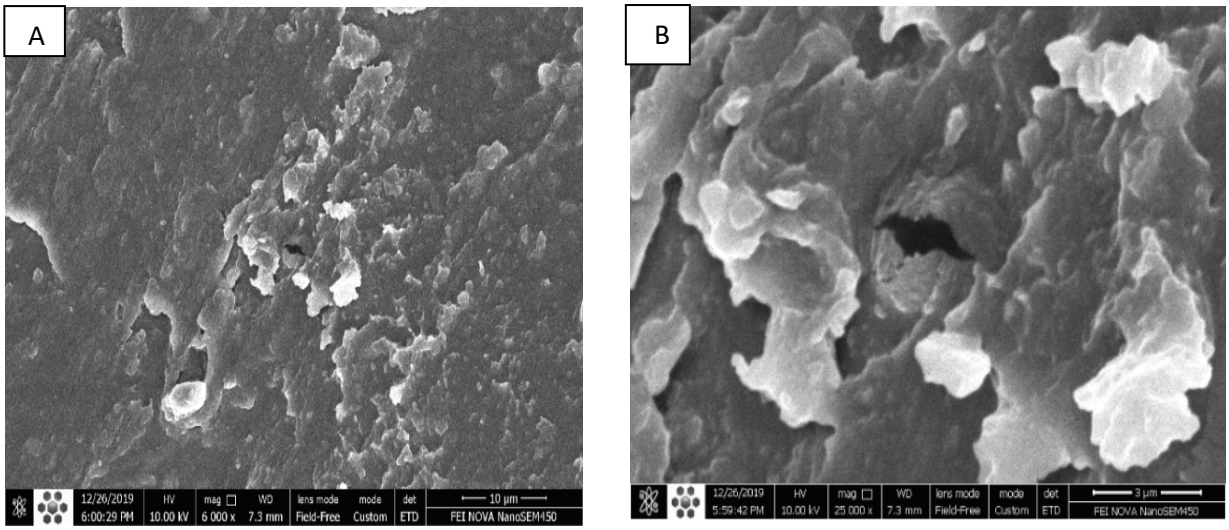

Fig. 9: FESEM images of the S_4P polymer blend, picture A with 6000 amplifier and B with 12000 amplifiers

Cytotoxicity Method

Biocompatibility test was carried out for the prepared polymers against human fresh blood according to the following method:

1. Blood solution was prepared by mixing 1 ml of fresh human blood with 20 ml of normal saline.
2. Different concentrations of the polymers (200, 100, 50, 10, 5 and 0.5 ppm) were prepared using DMSO as a control solution.
3. Blood specimens of 2 ml each were isolated in glass tubes and 100 µl of each polymer concentration was added to each tube.
4. The tubes were left at room temperature and the formation of the turbidity of the blood solutions was taken as an indication of the cytotoxicity of the prepared polymers. The tubes were tested after 15, 30 and 60 minutes [13].

The polymer blends tested in this work exhibited no turbidity of the blood solutions indicating the polymer blends are non-toxic.

Water Absorption Analysis

For the water absorption, relative swelling is calculated from the difference between dry and wet weights of the specimens divided by the dry weight. This was calculated after immersion of the disk specimens in water, Simulated Intestinal Fluid (SIF), and Simulated Gastro Fluid (SGF). The SIF was prepared according to USP31-NF26. 6.8 g of mono basic potassium phosphate and 0.2 g (77 ml) of sodium hydroxide were mixed and diluted in 1000 ml of distilled water. The SGF was prepared by dissolving 2 g of sodium chloride in 500 ml of distilled water and 7 ml of hydrochloric acid. The mixture was then diluted in 1000 ml of distilled water [14,15]. In order to measure swelling characteristics, the discs were initially immersed in various buffer solutions of different acidity (i.e pH 1.2, 7.2, and 8.2) at 37 ºC and at different time intervals. The immersed discs were removed, gently wiped with a soft tissue to remove water from the surface and then the weight was measured. The procedure was repeated until there was no further weight increase. according to the following Equation:

$$S_w(\%) = (W_s - W_d)/W_d \times 100 \quad (1)$$

the degree of swelling was calculated where, W_s and W_d represent the weight of swollen and dry samples, respectively. When a polymer swells due to water absorption, the length of the diffusion pathways increases. Once a water content specific to each polymer is reached, the polymer mobility steeply increases in a phenomenon called “polymer chain relaxation" or “glassy-to-rubbery phase transition. This is probably due to the two components of Pluronic F-127 and PVA with glycerin possessing hydrophilic character and making the hydrogen bonding. This causes the samples to be easily influenced by water at a pH of 7.2. All of these polymer blends were found capable of absorbing water until after 420 minutes (i.e. 7 hours) from being immersed as showed in figure 10. After that, polymers blends become saturated with water and no further absorption takes place. The PVA/Pluronic F-127 polymer blend with the highest glycerin content showed the lowest water absorption as compared to S_2P, S_3P polymer blends and S_1P, which is free of glycerin. The amount of water in a blend can influence permeation and release of nutrients, drugs and cellular products into/out of the gel. In the acidic medium when pH is 1.2, the polymer blends showed different behaviour. The S_1P blend showed the lowest swelling. The rest of the polymer blends and the pure polymer showed different behaviour until the ratio is 60% as shown in figure 11. When the pH was 8.2, the polymer blends showed similar behaviour to that pH = 7.2 (see figure 12). This might be attributed to the possibility of forming ionizable groups in the polymer blend which leads to the increase of hydrogen bonding with water.

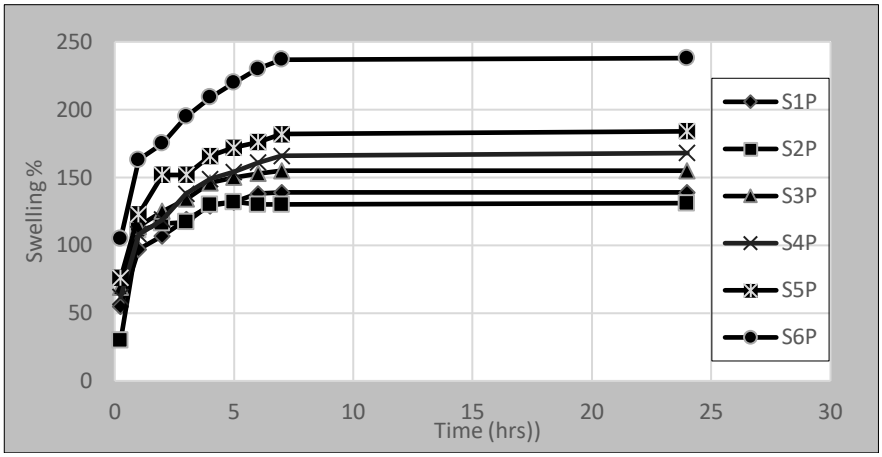

Fig. 10: Swelling ratio of S_1P-S_6P polymer blends in water

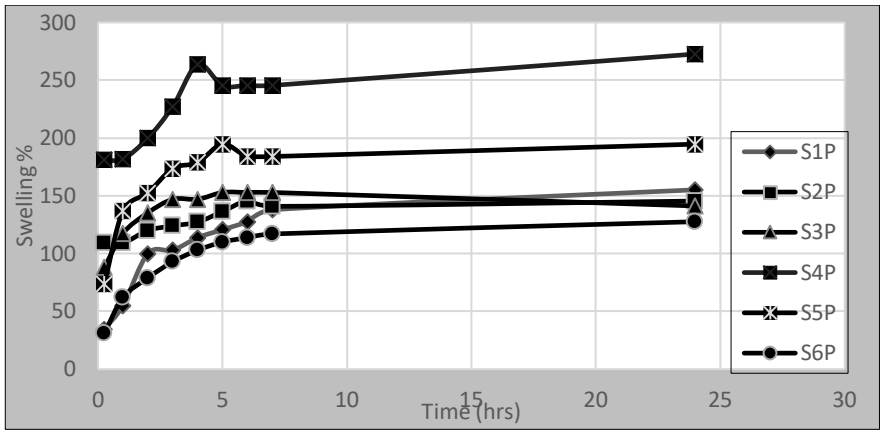

Fig. 11: Swelling ratio of S_1P-S_6P polymer blends in SGF

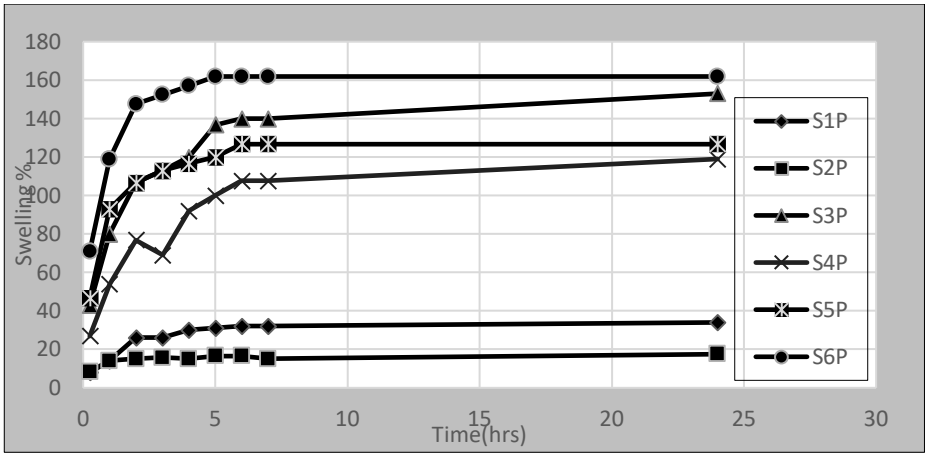

Fig. 12: Swelling ratio of S_1P-S_6P polymer blends in SIF

Biodegradation Study

In order to study the gradual weight loss to avoid the accumulation of polymer inside the living entity and these compounds should disappear in a reasonable time (according to application).

In this study, the weight loss of the prepared polymer blends in SGF and SIF solution in addition to water was studied. Biodegradation of polymer blends was studied as a function of immersion time as shown in figure 13. The results showed that the weight loss increase in SGF of S_4P blend. Results revealed that the weight loss of S_4P reached 3.7% in distilled water while in SIF 2% and in SGF was 4.5%.

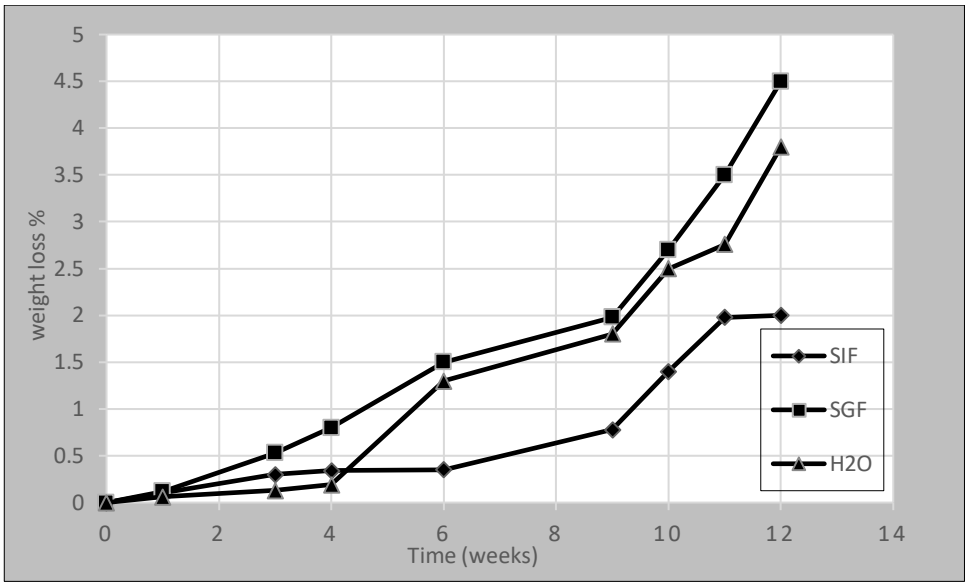

Fig. 13: Weight loss of S_4P polymer blend in Water, SIF, and SGF Solutions

Conclusions

The addition of glycerin to PVA / Pluronic F-127 polymer blends leads to an increase in the tensile strength of the blend material Specimen and a notable decrease in Young's modulus. Glycerin leads to improvement of the interfacial adhesion between the Pluronic F-127 phase and the PVA phase. FTIR spectroscopy indicated that there is no chemical interaction between PVA and Pluronic F-127 polymers in the mixture. The hydrogen bonding of the two polymers may rearrange the chains in Pluronic F-127 and PVA in a certain way, which decreases the randomness inside the polymer. This rearrangement improves the tensile properties and the elongation at break. This enables the blended polymer to be formed in any desired shape. Interactions between the pluronicF-127/PVA and glycerin occur between C–O and OH groups, indicating the presence of mainly hydrogen bonds .The ability of the polymer blends to swell which means free water that can diffuse through the hydrogel Due to these pores. Swelling material can be used as drug delivery systems from which drugs are released by diffusion indeed, because of the increase or decrease of the swelling ratio, we can expect the mesh size of the polymer blend to also increase or decrease considerably. The swelling ratio change of blends translates into a change in the mesh size of the gel, which modulates drug release.

This kind of polymer blends can used as drug carriers and play important roles in drug delivery techniques.

References

[1] N. Tudorachi, C.N. Cascaval, M. Rusu, M. Pruteanu, "Testing of polyvinyl alcohol and starch mixtures as biodegradable polymeric materials", Polym. Testing 19 (2000) 785-799.

[2] Lijun Mao, Syed Imam, Sherald Gordon, Patrizia Cinelli, and Emo Chiellini, "Extruded Cornstarch–Glycerol–Polyvinyl Alcohol Blends: Mechanical Properties, Morphology, and Biodegradability", J. of Polymers and the Environment 8 (2000) 205-211.

[3] J. H. Song, R. J. Murphy, R. Narayan, and G. B. H. Davies, "Biodegradable and compostable alternatives to conventional plastics", Philos. Trans R Soc. Lond B Biol. Sci. 364 (2009) 2127-2139.

[4] N. M. Yanina, P. Lucrecia, R. C. Guillermo and D. B. Javier,"Polyvinyl Alcohol–Pectin Cryogel Films for Controlled Release of Enrofloxacin", Appl. Biochem. Biotechnol. 167 (2012) 1421-1429.

[5] J. Dutta, "Synthesis and Characterization of γ-irradiated PVA/PEG/$CaCl_2$ Hydrogel for Wound Dressing", American J. of Chem. 2 (2012) 6-11.

[6] F. Febriyenti, F. Najmiatul, M. Noratiqah, U. Salman, N. Deni, R. Shintia and B. S. Bin, "Honey gel and film for burn wound", Inter. J. of Drug Delivery. 6 (2014) 01-06.

[7] J. Jun, L. Chunhua, L. Jack, C. H. Ralph R. Basil, R. H. Miriam and S. C. Jonathan, "The effect of physiologically relevant additives on the rheological properties of concentrated Pluronic copolymer gels", Polymer. 49 (2008) 3561-3567.

[8] J. J. Escobar-Chávez, M. López-Cervantes, A. Naïk, Y. N. Kalia, D. Quintanar-Guerrero, A. Ganem-Quintanar, "Applications of Thermo-reversible PluronicF-127 gels in Pharmaceutical Formulations", J. Pharm Pharmaceut. Sci. 9 (2006) 339-358.

[9] D. Jain, E. Carvalho, A. K. Banthia and R. Banerjee. "Development of polyvinyl alcohol–gelatin membranes for antibiotic delivery in the eye". Drug Development and Indus. Pharm. 37 (2011) 167-177.

[10] T. M. P. Le, V. P. Pham, T. M. L. Dang, T. H. La, T. H. Le and Q. H. Le, "Preparation of curcumin-loaded pluronic F127/chitosan nanoparticles for cancer therapy", Adv. Nat. Sci.: Nanosci. Nanotechnol. 4 (2013) 025001.

[11] M. L. Sanyang, S. M. Sapuan, M. Jawaid, M. R. Ishak, and J. Sahari, "Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (arenga pinnata) starch for food packaging", J. Food Sci. Technol. 53 (2016) 326-336.

[12] S. Khairunnisa, J. Zahidah and I. Rostini, "The effect of glycerol concentration as a plasticizer on edible films made from alginate towards its physical characteristic", WSN 112 (2018) 130-141.E

[13] S. Balakrishnan, P. Santhanam, and M. Srinivasan, "Larvicidal potency of marine actinobacteria isolated from mangrove environment against Aedes aegypti and Anopheles stephensi", J. Parasit Dis. 41(2017) 387-394.

[14] J. S. Zainab Al-Lami and A. M. Haddad, "Preparation and swelling behavior of L-lactide interpenetrating", Open Journal of Organic Polymer Materials 6 (2016) 119-133.

[15] X. Pan, J. Li, R. Gan and X. Hu, "Preparation and in vitro evaluation of enteric-coated tablets of rosiglitazone sodium", Saudi Pharm J. 23 (2015) 581-586.