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Characterization of Polyvinyl acetate/Epoxy Blend Foam

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Abstract

Synthesis of polyvinyl acetate-epoxy blend by mixing of 40% PVA to Epoxy by weight and foaming by high rate of air were furthermore carried out to achieve light weight blend foam. It was found that; 5KGy irradiation dose by using Gamma irradiation was enough to attain finally compatiblization. Mechanical properties were studied using hardness tester, while surface morphology was studied as well by measuring scan electron microscope (SEM). Immersing the foam to serial dilution of different acids, alkalis and salts solution for different times was performed. Thermal behavior was discussed by measuring thermal gravimetric analysis (TGA). Investigation of electrical conductivity (Dc) for the soaked foam showed that; conductivity of acids up taken foam is more than alkali while salts is the least. Electrical conductivity of the acids soaked foam were arranged by the following: $H_3PO_4 > H_2SO_4 > HCl > Citric acid, while alkalis soaked foam was as the following manner: KOH > NaOH >LiOH > Glycerin. Maximum electrical conductivity (9.63 x 10⁻² Simon/cm) was achieved by 2N of <math>H_3PO_4$. Heating of glycerin soaked foam were as the following: $CaCl_2 > KCl > NaCl$.

Keywords: Blend; Foam; Swelling; Irradiation; Hardness; SEM; Dc; TGA

Introduction

Materials that lack electron conduction are insulators if they lack other mobile charges as well. For example, if a liquid or gas contains ions, then the ions can be made to flow as an electric current, so the material is a conductor. Electrolytes and plasmas contain ions will act as conductors whether or not electron flow is involved. The history of the field has been recounted from several perspectives [1,2]. The first report on polyaniline goes back to the discovery of aniline. In the mid 1800's, Letheby reported the electrochemical and chemical oxidation products of aniline in acidic media, noting that reduced form was colorless but the oxidized forms were deep blue. Despite almost 30 years of history of polymeric electrolytes and their application in ion storage devices still some fundamental problems and questions from the initial times of development of these solid ionic conductors remain unsolved [3-5]. One of the most promising approaches was to prepare composite polymeric electrolytes [6,7]. This is due to their higher conductivity, improved cation transport numbers and enhanced electrolyte-lithium electrode stability compared to standard polyether based electrolytes. Composite electrolytes usually consist of three components: polymer matrix, dopant salt and filler. The role of the latter is to modify polymer-ion and ion-ion interactions leading to an improvement in the ion transport. A variety of models has been designed and used to describe ion transport phenomena in composite polymeric electrolytes with particular attention paid to the role of the filler [8-10]. These models are similar in many respects but some contradictions can also be found. Many polymer electrolytes showing high alkali metal ion conductivities have been developed. These electrolytes are polymers doped with alkali metal salts such as LiClO, LiCF₃SO₃, LiSCN, NaSCN, CsHSO₄ and KSCN, while the basic polymers include polyethylene oxide (PEO), polyvinyl acetate, polyvinyl alcohol, polymethyl acrylate, polypropylene oxide (PPO) and polymethylene oxide [7,11,12]. PEO doped with ammonium salts (NH₄HSO₄, NH₄I, $(NH_4)_2SO_4$, NH₄SCN) shows a conductivity ranging from 10^{-7} to 10^{-2} S cm⁻¹ at room temperature [13,14]. Very few studies on PEO doped with acids (H₃PO₄, sulfonic acid, poly (thiphenylenesulfonic acid) have appeared in the literature, for the degradation of polymer by using the strong acid comes into a major problem [15-17]. It was reported previously that: preliminary studies on PAAm based hydrogels doped with H₂PO₄ and H₂SO₄ have been performed. It has been shown that; the conductivity of hydrogels depends on the concentration of acid, water and cross-linking and gelation agents. Rooms' temperature conductivities up to 2x10⁻² S cm⁻¹ were measured for H₂PO₄ doped electrolytes; conductivities increase with an increase in temperature up to 10⁻¹ S cm⁻¹ at 100°C. Hydrogels doped with H₂SO₄ exhibit similar ambient temperature conductivities to those obtained for the same polymer doped with H₃PO₄. However, for gels containing a high concentration of H₂SO₄ a decrease in conductivities was observed at temperature exceeding 60°C. This decrease results from dehydration of the hydrogels or from degradation of the polymer matrix; both occur in the presence of a strong inorganic acid. Such tendency has not observed for the system doped with H₃PO₄ [18]. In our work; synthesizing hydrophilic foam (PVA/Epoxy) was carried out using Gamma irradiation. Characterization include hardness, morphological properties, thermal behavior and water uptake were performed. Insertion of the foam into serial dilution of acids, alkalis and salts for different times and measuring the electrical conductivity (Dc) at room temperature were done. The maximum conductivity was 9.63 x 10⁻² simon/cm for 2N. H₃PO₄ uptaken by foam for 7 days soaking which exceed the previous work of hydrogel by 481.5%.

Experimental

Materials

The samples prepared using phenyl epoxy; polyvinyl acetate and an

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air compressor (used for foaming the blend) were commercial grade. The PVA paste was solved by (using magnetically stirred) distilled water for 3 hours at 80°C getting an emulsion with the concentration of 50%. Mixing of epoxy to PVA emulsion by 60% to 40% ratio respectively was performed. All the chemicals were used as received with no extra purification and it purchased from El-Gomhoria Co., Egypt.

Polyvinyl acetate (Structure 1)



Phenyl epoxy (Structure 2)



Hardener (Triethylenetetramine)(Structure 3)



Methods of preparations

Epoxy/PVA blend was mixed to realize the optimum ratio which has good structure and optimal hydrophilic character. 40%, 60% and 70% by weigh of PVA were mixed with Epoxy and its solidifying agent (Triethylenetetramine, the amine (NH) groups react with the epoxide groups of the resin during polymerization). Heating of the mixture to 80°C for reaching the compatibility and then reduce the temperature of the mixture blend to 10°C till attain very viscous state. Foaming of the blend was for more than 5hours till solid form performed to achieve a highly porous solid blend. Irradiation of different doses; 25, 50, KGy by Gamma cell was carried out to realize the highly porous, hydrophilic and compatible material.

Water uptake

Respective water uptake behavior of different ratios of foam was studied in water as a function of pH. Swollen polymer was wiped



Figure 1: Scan Electron Microscope (SEM) of polyvinyl acetate-Epoxy blend foam with no treatment.

off with tissue paper and then weighed immediately to evaluate the swelling percent or water uptake percent, which was calculated by the following equation:

Weight of swollen hydrogel -Weight of dry hydrogel -Weight of dry hydrogel $\times 100...Eq.(A.1)$

Electrical conductivity (Box 1)



Diagrammatic cell used for measuring DC electrical conductivity of the foam

Teflon cell have 5 holes used as samples holder while the circular disk shown in figure made of red copper used for sandwiched the samples from below and upper sides. All disks were conducted to the electrometer for measuring the Dc electrical conductivity.

The samples were measured by 6514 Electrometer, Kiethly, USA

Digital Filter: Median and averaging (selectable from 2 to 100 readings).

Damping: User selectable on Amps function.

Environment:

Operating: 0°-50°C; relative humidity 70% non-condensing, up to 35°C.

Storage: -25° to +65°C.

Warm-Up: 1 hour to rated accuracy (see manual for recommended procedure).

Power: 90-125V or 210-250V, 50-60Hz, 60VA

Scientific equipments

Scanning electron microscope: Investigation and magnification of the polymer surface was carried out by SEM, JEOL-JSM-5400; Japan.

Thermal gravimetric analysis: Shimadzu TGA -50, Japan, was used to characterize the thermal stability of the porous blend.

Hardness tester: Samples were cut for $2.5 \ge 2.5 \ge 1$ ($1 \ge 0.5 \le 1.5 \le 1.5$

Gamma irradiation

Gamma irradiation was carried out by ⁶⁰Co gamma rays with a cylinder irradiation chamber. All irradiations were performed at ambient temperature (about 45°C at the chamber) and a dose rate of about 1.22 Gy/Sec.

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Results and Discussion

Morphological study

There are different modes of action by immersing the PVA/ Epoxy foam into different chemicals. Investigation by scan electron microscope (SEM) for foam (Figure 1) showed dispersion of PVA all over the epoxy. Vacant and pores are seen obviously in homogenous manner through the sample.

Figure 2 showed large pores comparing to the untreated sample. This appearance assures the role of phosphoric acid for reaction with the blend foam. Enlargement foam matrix around the pores is seen leading to pressing to widen the pore opening. Homogeneity is noticed apparently as no scattered spots, except for two white small dots cohered to the large pore. These dots may be approved that; phosphoric acid has two roles of action. First of which is simultaneous passage through the pores without any obstacles have performed by the foam. Second of which is diffusion into the net matrix of the foam leading to enlargement of the matrix bulk while press into the pore opening to be widen. All these notices interpret the high value of electrical conductivity occurred by dealing with phosphoric acid. Electrical conductivity may be performed as a result of sorption of hydrogen protons within phosphoric acid. Exchange of hydrogen proton of poly vinyl acetate is simply occurred, this exchange is enhanced by applying voltage. Simultaneous passage of PO³⁻ through foam pores raises the EC value as well.

Figure 3 showed the foam after dealing with 1N potassium hydroxide. Less pores number are scattered through the blend foam,







Figure 4: Scan Electron Microscope (SEM) of polyvinyl acetate-Epoxy blend foam soaked in 1N Ca Cl₂ for 7 days.



may be resulted as action mode of potassium hydroxide. Moderate coherence of KOH into foam active sites is seen. PVA is showed to cohere and distribution over epoxy blended with them. Heterogeneity is seen to some extent which assured by irregular distribution of white spots through the sample. All these appearances assure the potassium hydroxide terms (K⁺ and OH⁻) passage through the foam pores while it preferred to pass through the net matrix. The electrical conductivity may be explained by sorption of potassium ion (K⁺) and allow hydroxyl group ($^{\circ}$ OH) to pass simultaneously through the pores leading to raising the electrical conductivity value.

Figure 4 showed the soaking of the foam sample into 1N CaCl₂ solution. Distribution of white and grey spots over the sample is seen. Regular arrangement of pores was noticed through the foam sample. Coherence of salt terms is obviously seen over the sample. Swellable sample shown attempt the affinity of foam towards the salt used. Sorption of calcium ion (Ca⁺⁺) is strongly suggested. It is suggested also the exchanging hydrogen proton of PVA by Ca⁺⁺ leading to raising the EC value which is enhanced also by simultaneous diffusion of 2 Cl⁻ of Ca Cl, through foam's pores.

Figures 2-4 attempt on; these appearances are preliminary step before foam degradation. It attempt also; the affinity to low pH while moderate to neutral and nearly small affinity towards high pH. Figure 4 has stable form than that of Figures 2 and 3.

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Time	Acids												
	Hydrochloric acid					Sulfuric a	Phosphoric acid						
	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N	
2 days	48	48	48	49	48	48	48	49	48	48	49	49	
7 days	49	50	51	52	49	51	52	52	50	52	53	55	
15 days	54	55	56	57	53	56	57	58	56	58	61	64	
30 days	56	58	62	63	56	59	62	69	60	64	70	74	
45 days	60	62	64	67	60	61	66	62	66	68	63	66	
60 days	63	65	68	61	64	65	63	0	68	54	0	0	

Table 1: Hardness (Shore-D) testing of polyvinyl acetate-Epoxy blend foam after soaking of different acids at different times.

	Alkali												
Time		Lithium hydi	oxide			Sodium hyd	roxide		Potassium hydroxide				
	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N	
2 days	49	49	49	49	48	48	48	48	48	48	48	49	
7 days	50	52	52	54	49	50	52	53	50	51	53	54	
15 days	53	55	56	57	53	55	56	56	54	55	56	57	
30 days	57	58	59	58	55	56	57	58	55	56	57	59	
45 days	59	59	60	60	58	59	60	60	57	59	61	61	
60 days	58	59	60	61	59	60	61	61	58	60	61	60	

Table 2: Hardness (shore-D) testing of polyvinyl acetate-Epoxy blend foam after soaking of different alkalis at different times.

	salts											
Time	Sodium chloride					Calcium chloride						
	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N	0.1N	0.5N	1N	2N
2 days	48	48	48	48	48	48	48	48	48	48	48	48
7 days	51	52	52	53	51	51	51	52	51	51	52	53
15 days	54	54	54	55	53	54	54	54	54	55	55	55
30 days	59	59	59	58	58	58	59	59	59	58	58	59
45 days	60	60	59	60	58	59	59	59	59	59	59	59
60 days	60	60	60	60	59	59	59	60	59	59	60	60

Table 3: Hardness (Shore-D) testing of polyvinyl acetate-Epoxy blend foam after soaking of different salts at different times.

Hardness discussion

Hardness examination upon soaking PVA/Epoxy blend foam showed that; (Table 1-3) no significant difference within two days. Changes in hardness appear obviously after seven days soaking. Increase of hardness within phosphoric acid dealing with blend foam more than that of foam soaked through the least chemicals. Foam immersed in potassium hydroxide is less in hardness than phosphoric acid soaked and more than that of calcium chloride solution. Higher concentration of chemicals leads to higher hardness. Foam dealt with phosphoric acid has highest value than other acids such as hydrochloric acid and sulfuric acid blend soaked. Foam hardness immersed in acids is arranged as follow: $H_3PO_4 > H_2SO_4 > HCl$. Blend soaked in potassium hydroxide has higher value than LiOH and NaOH while NaOH > LiOH. Blend Soaking for two weeks have the same behavior while the value difference is pronounced. Foam hardness determined after two days, one, two, three four, six and 8 weeks. Hardness after 6 weeks resulted in maximum value while; 8 weeks soaking leads to complete hardness changes of foam dealt with 1N H₃PO₄ and H₂SO₄ (converted to powdered). While dealing with hydrochloric acid results in brittle form. Foam soaked in 1N alkali showed brittle form after 8 weeks. No significant difference of hardness upon dealing with salt solution with different concentrations. Glycerin soaked foam leading to reduction of hardness value which appears apparently with time. After 8 weeks hardness reduced to what resemble to gum form reached to 10 shore-D hardness value. Citric acid approximately does not affect the hardness of the blend foam.

Water uptake

Water uptake of the porous blend resin was studied as a function of composition, 40, 60 and 70% PVA composition of the blend showed water uptake begin to be stable in mechanical form at 40%. PVA is a hydrophilic polymer, blending them with epoxy which is considered as carrier of the functionalized polymer or filler. Increase PVA percentage increase water uptake while more percentage has no significant beside reduce their mechanical behavior. Blend foaming was remarkably improved water uptake may be due to an increase in pores number, pores size and/or increase in pore dimensions of the synthesized foam, i.e. increase in the allowed area surface of the resin net matrix.

Thermal behaviors

Thermograms of different chemicals (Phosphoric acid, Potassium hydroxide, Calcium chloride and glycerin) immersed through the understudied foam showed different scenarios.

Figure 6 could be characterized into 3 divisions, first of which showed no decrease of weight except for 4% by raising temperature to 177°C. This result confirmed the foam applicability through a wide range of temperature. By raising temperature, the second division of the thermogram has been appeared describing abrupt weight decrease into 60% by raising temperature to 388°C. The third division of the figure

showed a regular weight decrease to 80% by increase the temperature to 574°C. There is no side peak via all the temperature range, which proved compatibility of the blend under study. It confirmed also no phosphoric acid residuals through the foam net matrix.

Figure 7 & 8 represents foam soaked into potassium hydroxide and calcium chloride in a regular manner. The 2 figures have the same behaviors; it could be characterized into 4 divisions. First division describes no weight decrease percent except for 5% which considered as operating temperature. Loss of weight of the first thermogram has occurred at 156°C, while the second curve showed the decrease of weight by temperature increase to 165°C, which proved their stability more than the previous. Second division of the thermograms represented gradual weight decrease by raising their temperature. The weight loss reached to 21% by increase the temperature to 305°C for the first case while the second showed 22% weight decrease as the temperature increased to 308°C. Third division of the figures represented dramatic weight loss by raising temperature to 382°C for the first curve and to 376°C through the second thermogram. The loss of weight reached to 59% for the first curve while it was 56% for the second one. The fourth division showed gradual weight decrease by









raising temperature to 575°C. The loss of weight reached to 82% for the first case while it was 89% for the second one. The foam soaked through calcium chloride reached to 11% from its original value which may due chemical reaction of hydroxyl group of PVA and that resulted in epoxy ring opening with calcium chloride. This suggested reaction may be summarized as the following:

 $2R-OH + CaCl_2 \rightarrow R-O-Ca-O-R' + HCl$

Where: R and R' are polyvinyl and/or epoxy opened ring.

This reaction make partial blocking of the active sites resulted in reduction of more salt terms (cations and anions) passage and so less electrical conduction.

Figure 9 (foam soaked in glycerin) have different scenario. The thermogram could be categorized into 4 divisions. First division described the low loss weight (operating temperature of the foam) of the foam which reached to 5% by increase the temperature to 169°C. The second division study the abrupt weight decrease reached to 30% at temperature 287°C. Furthermore temperature increase a side peak has been characterized the third division of the thermogram. This

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J Chem Eng Process Technol ISSN: 2157-7048 JCEPT, an open access journal side peak confirmed more or less compatibility which may due to sorption of some glycerin particles through the foam net matrix. The side peak was through 287°C to 391°C temperature range while loss of weight was 56%. The last division of the thermogram represented gradual decrease of weight reached to 89% by raising the temperature to 575°C. The low weight value of the foam at the end of thermogram (11 % from the original weight) may be due to a chemical reaction of glycerin with alcohol's hydroxyl group of the blend. The reaction could be summarized as the follow;

R-OH + Glycerin (-OH) → R-O-Glycerin + H_2O

Where: R is the net matrix of the blend foam.

This reaction confirmed partially blocking of the blend net matrix's active sites which reduce the glycerin passage and so less electrical conduction. These new matrix may be synthesized give good chance for further glycerin sorption and so further electrical conduction reduction.



Figure 10: Effect of acids soaking of PVA/Epoxy for 7 days on electrical conductivity (DC) (Simon/Cm).









Electrical properties

As seen in Figures 10-12, the conductivity of foam increase with increase in water concentration. While acids showed higher conductivity as lightly mobile hydrogen protons and by increase hydrogen protons increase conductivity as it can be seen in Figure 3. Less conductivity was clearly seen at low concentration of phosphoric acid may be due to chain reaction with foam. Potassium hydroxide showed higher conductivity as in Figure 4 which may due to a special affinity to foam to be abstracted. More charge on cations more electrical conductivity as it seen in Figure 5. Therefore it can be assume that foam is a mixture of 2 phases. These are dry PVA/Epoxy phase with no water present and water / acids, bases or salts phase trapped in a polymer phase. The bulk conductivity of the foam is a result of interaction between these 2 phases. To make these calculations easier it assumed that; each has spherical symmetry. The general self-consistent equation for the multiphase materials is [19,20].

 Σ wi σ i- σ */ σ i(d-1) σ * =0

Where; d is a dimensionality parameter equal to 3 for spherical

aggregates, σi (i =1, 2) are conductivities of the water phase, σ^* dry polymer phase and wi is the volume fraction of the i phase.

The Lewis acid-base reactions model, widely employed in carboxyl-based composite solid polymer electrolytes is extended to the present composite polymer electrolytes. The carboxyl groups in PVA, hydroxyl group of basic (LiOH, NaOH and KOH) and anions of salts used (NaCl, KCl and CaCl₂) were served as the Lewis base centers and the cations while hydrogen protons donors such as acids (HCl, H₂SO₄, H₂PO₄ and citric acid) used as strong Lewis acid. Therefore, numerous acid-base complexes are expected in the composite system with two major groups of complexes, i.e., cations and Hydrogen proton with polymer foam. The conductivity in composite polymer electrolyte is not a linear function of the filler concentration [21,22]. At low content level, the dilution effect is efficiently contrasted by the specific interactions of the polymer, which promote fast ion transport, and the overall effect is progressive enhancement of the conductivity. On the other hand, at high filler content, the dilution effect predominates and the conductivity decays. Similarly, concave effect on conductivity with inorganic/polymer materials as fillers in solid polymer electrolyte [23-25] and ion pairing (insufficient salt dissociation) is identified as the origin of the later deterioration.

Temperature dependence

The different behavior of the temperature dependence in the conductivity suggests two different conducting pathways. The first conduction pathway via ion motion is facilitated by polymer segmental motions, and is quickly frozen upon lowering temperature. The second conducting pathway, similar to the ion transport on solid oxide electrolytes, is established by the ions on the surface (both interior and external) of porous blend which migrates by replacing the nearby vacancy. The presence of additional conducting channels in the composite polymer electrolyte delivers favorable low temperature conductivity over those without porous blend. The improvements are most pronounced in the conductivity at low temperatures. However, a flexible polymer is still essential for the second type of conduction, and becomes an important factor governing the conductivity in the high temperature region. Above the melting point of the composite the effect of the filler on conductivity was not so significant [26].

Electrical conductivity is strongly dependent on temperature. In metals, electrical conductivity decreases with increasing temperature, whereas in semiconductors, electrical conductivity increases with increasing temperature as it seen in Figure 13. Over a limited temperature range, the electrical conductivity can be approximated as being directly proportional to temperature. In order to compare electrical conductivity measurements at different temperatures, they need to be standardized to a common temperature.

At extremely low temperatures (not far from absolute zero), a few materials have been found to exhibit very high electrical conductivity in a phenomenon called superconductivity.

Conclusion

For the aim to prepare a new polymer electrolytes and /or modernization of fuel cells, synthesis of PVA/epoxy blend foam has been performed. Gamma irradiation proved to be an important factor influencing the blend synthesis. Characterization of the blend after soaking in different chemicals, confirmed their applicability from mechanical and thermal point of view. Measuring the EC of the blend upon soaking through different chemicals such as acids, alkalis and salts for seven days represent the EC of acids soaked blend is more than alkalis which exceed over salts. Phosphoric acid soaked porous blend have maximum value of Dc, while hydrochloric acid soaked blend have maximum mechanical behavior stability. Soaking the porous blend through phosphoric acid (2N) for 1week achieve 9.63 x 10^{-2} simon/ cm which is more the previous work of hydrogel by 481.5%, while porous blend has more mechanical properties stability. Morphological properties of the blend focused on mode of action between them and chemicals under study, it put spots also on characters change of the blend through soaking time.

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