WEB OF SCIENTIST: INTERNATIONAL SCIENTIFIC RESEARCH JOURNAL
ISSN: 2776-0979(Volume 2, Issue10, Oct., 2021

INFLUENCE OF ALUM-DES ON SOME PROPERTIES OF PVA

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Abstract

Deep eutectic solvents DES as a type of Ionic Liquid IL have caught the great attention of many researchers in different applied fields. One of these fields is their effect on polymer preparation to enhance their thermal, mechanical or conductivity. In this work, Alum as deep eutectic solvents DES were used to study its influence on Polyvinyl alcohol PVA polymer properties. The interaction between the deep eutectic solvents DES and PVA was tested by ATR-IR, where the polymer was found to contain the DES within the PVA structure. SEM micrographs for the pure PVA show clearly that this polymer's morphology is a uniform type but with different degrees of rough surface morphology. In contrast, the PVA-DES system shows aggregates or chunks of Alum on the top surface of the membrane.

Introduction

Among the most polymers, alkaline electrolytes are common, and due to higher ionic conductivity, especially polyvinyl alcohol-based alkaline polymer electrolytes, have attracted growing attention [1-3]. However, alkaline electrolytes based on PVA appear to deeply lose water in the atmosphere, reducing conductivity and mechanical properties [4].

One of the most types of well-known membranes materials, polyvinyl alcohol, has favourable Characteristics such as outstanding thermal, mechanical and chemical stability and good film-forming properties[5-8]. It is, besides, biodegradable[9, 10].

PVA is a water-soluble, non-toxic polymer with a solid film-forming ability with high dielectric strength, good storage capacity for the charge, good mechanical tensile strength with electrical and optical dopant-dependent properties[11]. A suitable salt is applied to the polymer matrix to obtain a polymer electrolyte film.

Polyvinyl alcohol was used as a host polymer in the current analysis. These materials, besides elevated mechanical strength and tensile strength to be used for the development of electrochemical devices [12, 13], flexibility and high oxygen and aroma barrier film properties are also used. It is also semicrystalline and contains a hydroxyl group attached to the methane-carbon backbone as a "Hydrogen-bounding" source[14-16].

Ionic liquids or deep eutectic solvents are also favoured. However, Ionic liquids and deep eutectic solvents have identical physical properties. Nevertheless, deep eutectic solvents are cheaper and have lower toxicity than ionic liquids[17]. Deep eutectic solvents [DESs] are a modern class of ionic liquids that may replace them[18-20]. Due to hydrogen bond interactions, this kind of solvent is made up of a combination of two or more components that form a eutectic with a low melting point in addition to their constituents. Abbot et al.[21] presented their results for the first time. As DES, a 1:2 M mixture of choline chloride and urea was added. DESs have many benefits over traditional ionic liquids, including low cost, simple Synthesis, biodegradability, and non-toxicity [22]. To enhance electroconductivity "ionic-conductivity" of PVA-based polymer matrix. Alum is one type of "Ionic Liquid" such as [NH_4Al $[SO_4]_2.XH_2O$, $Al_2[SO_4]_3.XH_2O$ and $AlK[SO_4]_2.XH_2O$] with urea low vapours pressure, making it useful as a green solvent and stable toward air or moisture. In particular, alum sulfate [NH_4Al $[SO_4]_2.12H_2O$] as deep eutectic solvents present a promising property as green-solvent and cheaper as besides to that easily prepared as compared to chloro-aluminate ionic liquids[23, 24].

1. Experimental

1.1. Materials and sample preparation

Materials used to Synthesis the polymer films are polyvinyl alcohol (PVA) as host-matrix polymer, Alum: urea (1:5)(NH_4Al $(SO_4)_2.12H_2O$: $CO(NH_2)_2$) as deep eutectic solvents IL and distilled water (D.W) as a solvent, and ionic liquid(I.L.) made by Ammonium aluminium sulfate dodecahydrate and urea [24] in a mole ratio of (1:5) (Ammonium alum -Urea) was also steadily heated from room temperature to 80 °C for 3 hours, yielding a colourless liquid, as shown in "Figure 1" below:

Figure 1. (Ammonium alum -Urea) I.L. (1:5) mole ratio.

PVA was purchased from MESE (Germany) (88% partially hydrolyzed), having a molecular weight (Mw): 67*10^3 g.mol^{-1}. Aluminum Alum IL (1:5) mole ratio made by Ammonium aluminium sulfate dodecahydrate (BDH) (99.5%) purity, (Mw): 453.33 g.mol^{-1}. Urea was also purchased from (THOMAS BAKER) (99%) piety, (Mw): 60.06 g.mol^{-1}. [24]. The process of preparing the composite polymer A1,A2 from the process of adding ionic liquid IL "alum" by adding the polymer PVA with a fixed weight of 1 g of polymer to two different weights (5 and 10)% of Alum, not the other way around, as shown in Figure 2.

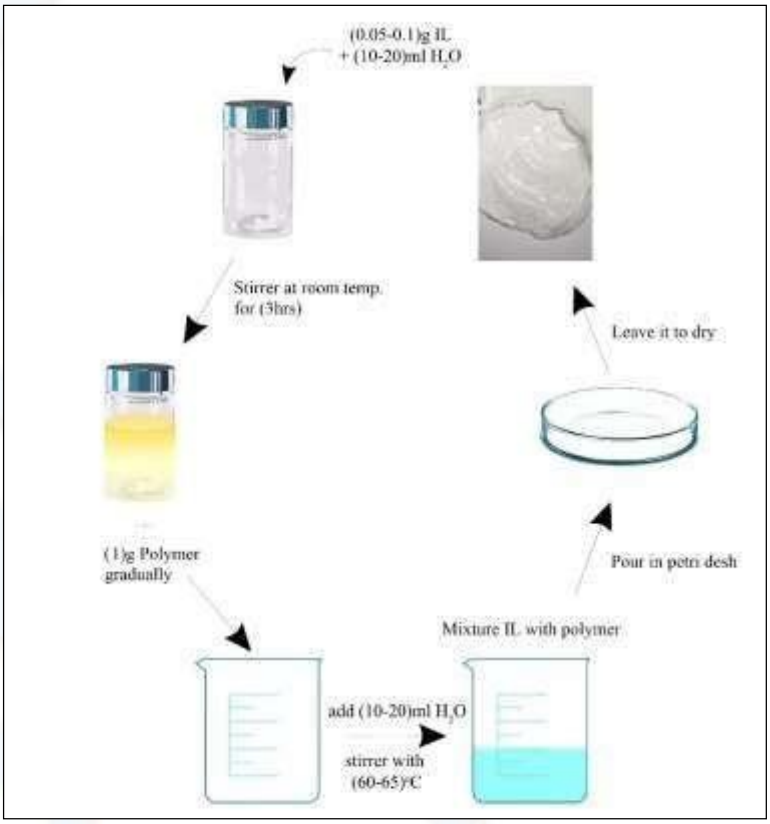


Figure 2. The synthesis procedure of polymer composite.

2. Results and discussion

2.1. Materials and sample preparation

Practical techniques for detecting complex formation and interactions between polymeric system constituents The FTIR spectra of pure polymer (PVA), polymer-ionic liquid and polymer-ionic liquid. Within a frequency range of 400-4000 cm^{-1}. Table1 shows the FTIR spectra of pure polymer PVA-film: The vibrational band observed at 2935,846 cm$^{-1,}$ and 1423 cm^{-1} correspond to asymmetric stretching vibrations of CH_2, $CH_{2rocking}$ and CH bending groups respectively[25-31] while acetyl C=C group and $CH_{wagging}$ (acetate group residue) observed at 1620 cm^{-1} and 1240 cm^{-1} respectively[25, 26, 29, 31]. The shifting of peak position towards Higher regions happened with (-OH) stretching mode vibrations from 3285 cm^{-1} in case of pure polymer PVA-film notice high value at 3302cm^{-1} &3327 cm^{-1} respectively when incorporating of ionic liquid (IL=Alum) at different ratio 5%IL-PVA(A1) and 10%IL-PVA(A2) in the host polymer PVA, are shown in Figure (3) as compared to descent polymer show shifting in asymmetric stretching vibrations of CH_2 with 5%IL-PVA(A1) and 10%IL-PVA(A2) at 2918 cm^{-1} & 2938 cm^{-1} respectively low shifting to 1428 cm^{-1}, and 1431 cm^{-1} at band C.H. bendinggroups of PVA-Pure occur upon the incorporation of 5%IL-PVA (A1) and 10%IL-PVA (A2) to host matrix also there are clear bands milestones assigned to the (5% & 10%) of Aluminum Alum ionic liquid (IL=Alum) incorporation in PVA-polymer host. This vibrational band observed at 1581 cm^{-1} & 1661 cm^{-1} meant for the bending vibrations of (-NH) group of Alum ionic liquid (IL=Alum) also vibrational peaks observed at wave number 1024 cm^{-1}, and 1021 cm^{-1} has been assigned to SO_4^{-2} group.

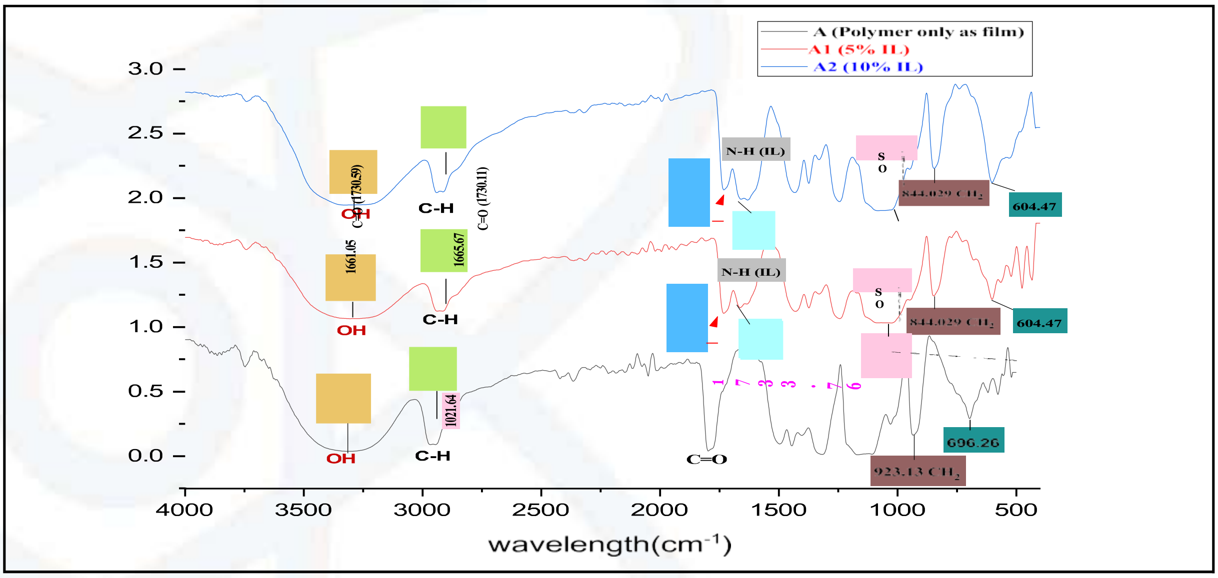


Figure 3: ATR-FTIR of influential bands of pure PVA(A), A1, A2.

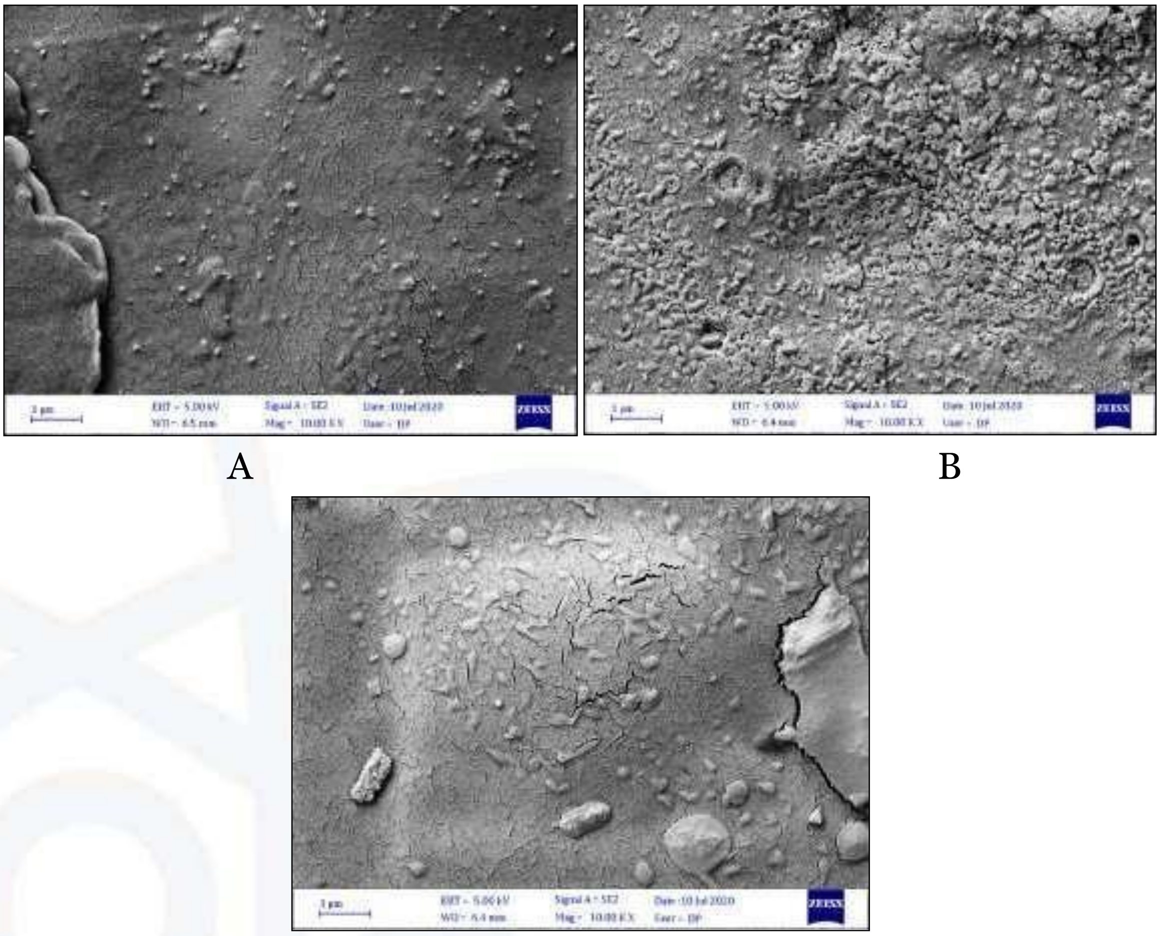
Table 1. Assignment of influential FTIR bands of pure PVA(A), polymer/ionic liquid blend with Ionic liquid (IL=Alum) at different per cent ratio 5%IL-PVA (A1) and 10%IL-PVA (A2).

Assignments	**Polymer film**	**A Polymer-only**	**A1 (5%IL-PVA)**	**A2 (10%IL-PVA)**
O–H stretching (H_2O molecules)	3858.35 3737.48	-	3859.70 3738.65	3858.06 3737.59
O–H stretching (OH in PVA-polymer)	3285.60	Not content OH band	3302.87	3327.61
CH_2 sym. (CH_3) PVA-polymer	2935.96	Not content CH_2 band	2913.88	2938.65
NH_2 (Alum)	-	3340.23 small & board 3199.92 small & board	-	-
C=O stretching	1733.76 very strong	Not content	1730.59	1730.11
NH bending (Alum)	Not content	1581.59 double small &broad band	1661.05 strong but smaller than an essential band	1665.67
-C-N (Alum)	Not content	1458.34 sharp & vital (for Alum only)	Not found	Not found
CH_2 (C-H) bending (PVA-polymer)	1423.79 strong in polymer	Not content	1428.59 strong in film	1431.80 very strong in the film
CH_2 wagging (PVA-polymer)	1371.61 medium	Not content	1372.21 very weak	1372 very weak
SO_4^{-2} (Alum)	Not content	1054 strong&broad	1024.65 broad	1021.64 1081.31 broad

a) SEM micrographs for the pure PVA show clearly that these polymer electrolytes' morphology is a uniform type but with different degrees of roughness with many different sizes of aggregates and chunks scattered or cracks that are randomly distributed on the top surface. Besides, pure PVA films cast from aqueous solution exhibit no features attributed to any crystalline morphology. So, the semicrystalline of PVA is likely to be submicroscopic [32, 33].

b) It was found that the surface morphology of the PVA system shows salt aggregates or chunks on the top surface of the membrane. The increase in the degree of roughness indicates the uneven diffusion of the compound (A1) over the surface of the host matrix [33, 34].

c) The morphologies of (A2) polymer represent that all electrolyte films exhibit compact wrinkled texture due to the adhesion of the additive to the polymer matrix structure. Compared to the pure PVA polymer, the cracks became remarkable, distinguished, and more pronounced in the A2 compound. However, some white granules appear, which may be attributed to ion aggregates[35]. The most noticeable changes in which he differed from the parent polymer is illustrated below in Figure 4 (a, b, c).



A

B

C

Figure 4. SEM micrographs for the pure PVA, 5%IL-PVA, 10%IL-PVA.

Conclusion

The most apparent manifestations observed when Alum was added as one of the ionic liquids, specifically DES, were significant modifications in the adsorption bands of -OH values in PVA-polymer using the ATR-FTIR technique, the disappearance of the Alum -CN band, and the emergence of the $SO4^{-2}$ band. Additionally, there are alterations to the polymer structure's morphological surface. Thus, it can be concluded that there is an interaction between the polymer employed, polyvinyl alcohol PVA, and the ionic liquid (Alum) and that this study can be utilized to learn additional structural, physical, and electrical features, as well as to invest in one of the numerous applications.

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