



Study of Protonic Conduction in Aloe-Vera Pulp Based Green Electrolyte System

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ABSTRACT

The polymeric membrane using naturally occurring aloe-vera pulp as host and for filler, fine powdered natural waste egg shell was used which served the purpose of second component of the composite. The ratio of the aloe pulp and egg shell (ES) was kept 90:10. The membrane was characterized by different spectroscopic methods, viz., X-ray diffraction, Fourier transformed infra-red spectroscopy and conductivity by impedance spectroscopy. There is a sharp increase in the resistivity with temperature around melting temperature of the crystalline polymer. The attraction of this work is that the ingredients used for constructing the polymer matrix are natural, biocompatible and fully biodegradable.

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Introduction

Ion conducting polymers has opened an innovative area of materials research with potential applications in the industrial as well as technical fields, as an electrolyte in solid state batteries. Conductive polymer composites (CPC) containing polymer materials incorporated with insulating-conductive dopant/ fillers usually show two important insulator-conductor transition. The first one corresponds to the dependence of resistivity (or conductivity) on the filler content[1], and the second one is related to the temperature dependence of resistivity, that is the composite usually shows a sharp increase in resistivity with temperature around melting temperature of the crystalline polymer, which is called positive temperature coefficient (PTC) materials. PTC materials are generally made from two categories, one is based on ceramics such as doped barium, titanium, vanadium based compounds[2-4], and the other is based on conducting polymer composite materials [5-7]. It also possess an interesting properties such as thin-film forming ability, flexibility, and transparency [8]. On the basis of their nature, polymer electrolytes are of three types: (i) solid polymer electrolytes (SPEs), (ii) gel polymer electrolytes (GPEs), and (iii) composite polymer electrolytes [9]. Biodegradable films based on natural origin polymers have been widely investigated for several biomedical applications. Aloe vera is such a natural polymeric gel having the body of scientific literature documenting medical applications in digestive problems, as a virucidal, bactericidal, and a fungicidal agent and in gynaecological conditions [10-11]. A prominent feature of Aloe vera file is its high water content, ranging from 98.5% to 99.5% of fresh matter. More than 60% of the remaining solid being made up of polysaccharides [12]. It consists of two important parts in which the outer layer is called vascular bundle and the inner layer is known as colorless parenchyma containing Aloevera gel.

Aloe vera has three compositions that include structural, chemical and polysaccharide.

Moreover, fine powdered egg shell, predominantly calcium carbonate (CaCO_3) may increase the impact strength of the membrane and as a filler, it may influence the crystallisation process and lead to an increase of the amount of imperfect crystalline phase [13] leading to amorphousity. Increase in the amorphous nature of the polymer system leads to higher conductivity. The increase in the amorphous nature induces irregular arrangement of molecules in the polymer system; hence a more flexible polymer chain is formed [14-15].

In our present study, we have fabricated a polymeric membrane using abundantly naturally occurring harmless Aloe-vera pulp as base and for filler, fine powdered natural waste egg shell (ES) was used which served the purpose of second component of the composite. The ratio of the aloe pulp and ES was kept 90:10. The membrane was characterized by different spectroscopic methods, viz., X-ray diffraction, Fourier transformed infra-red spectroscopy and conductivity by impedance spectroscopy.

Experimentation

Materials Used

AR grade acetone and alcohol (Aldrich) were used for extraction and washing purposes.

Extraction of aloe pulp

The fresh leaf of Aloe Vera was collected from our botanical garden. After washing several times with double distilled water, aloe leaf cuticle was peeled off and its gel was scratched, with special glass and collected in a petri dish. The gel was then stirred, dissolved and washed in acetone in a 250mL conical flask. This mass was filtered with great precaution and the remaining residue was collected as aloe pulp.

Fabrication of green matrix

Egg shells were cleaned and dried for 48 hours and then powdered in planetary ball mill for 100 hours. The size of the ES powder was checked after 30H by X-Ray diffraction technique. The aloe pulp and ES were mixed together in a known ratio of 90:10 and ball milled for 80 hours. Then pure pulp and composite matrix were pelletized hydraulic press.

The XRD studied were carried out by Phillips X-pert model in the angle range ($2\theta \sim 15-60^\circ$) using Cu-K α radiations ($\lambda = 1.542\text{\AA}$). Further powder and pellets were structurally characterized by FTIR studies were done with Bruker Alfa FTIR with ATR in the range of $4000-600\text{cm}^{-1}$. The electrical characterization of the composite matrix were carried out with the help of impedance spectroscopy (HIOKI 3522 LCR tester) by applying small A.C. signal (20mV) with Pt-blocking electrodes.

Results and Discussions

The XRD pattern of composite powder with ball milling time and annealed temperature are shown in fig.1.

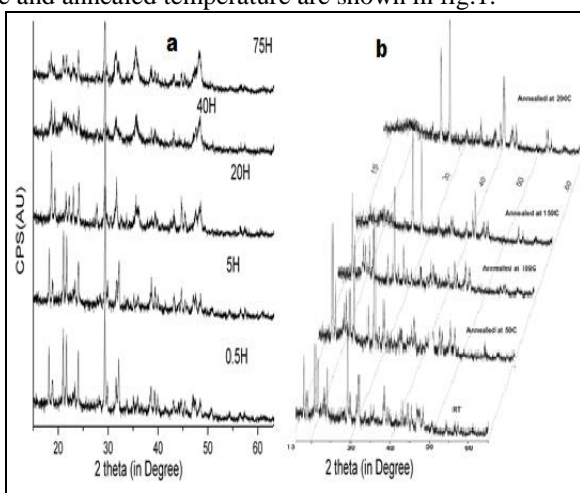


Figure 1. XRD spectra of composite at different ball milling time(a) & annealed temperature(b).

From the Fig.(1a), it clearly shows that the crystalline nature of the composite increases with increased ball milling time. The increase in the crystallinity is not favorable for the protonic conduction. Moreover, in the case of the sample without ball milling, though same reaction is occurring but amorphicity gradually increases and a hump starts to appear in sample annealed at 150°C . The variation of milling with annealing temperature is given in fig.1b. In this figure the comparative study in the change in the crystalline size as well as the amorphousity of the composite green matrix have been shown. The effect of ball milling time (upto 70H) initially show decrease in particle size. After 70-150H aggregation started and increase in the particle size was recorded. With the help of Sherrer's formula, the particle size were calculated, which changed from 70nm (on 0H time) to 65nm (40nm) and 61nm (on 70H). After this, the particle size shows increasing trend and reached upto 70nm. The smaller sized particle range seems to be effective for few hours only. The peak broadening effect is more prominent in the higher temperature range. Similar effect in the change of amorphousity is also recorded. The maximum amorphocity is observed after 70 H milling time.

FTIR Analysis

Fig.2 shows the FTIR spectra of pure aloe pulp – ES composite green matrix and of various ball milled and annealed samples (fig.2a, 2b, 2C1, 2C2). The complexation of aloe pulp with egg shell in polymer matrix was confirmed by FTIR analysis of different samples. FTIR spectra of the samples named 'a' for bare Aloe pulp(AP)-egg shell (ES)

composite green matrix (at RT), 'b₁' and 'b₂' for AP –ES composite with different ball mill time, 'C₁' for AP –ES composite annealed at different temperature without ball milling and 'C₂' for AP –ES composite annealed at different temperature with 40 hours ball milling.

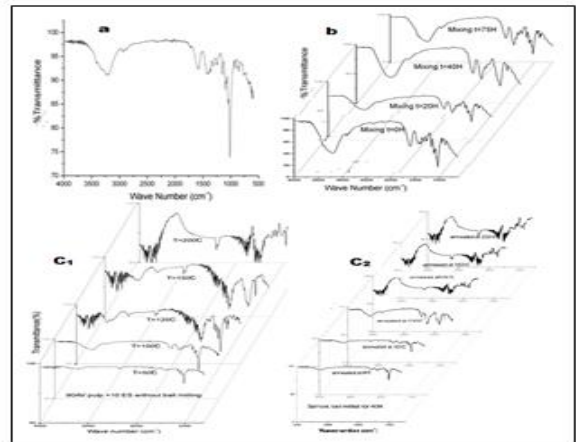


Figure 2. FTIR of (a) bare Aloe pulp-egg shell composite, (b) AP –ES composite with different ball mill time, (C₁) AP –ES composite annealed at different temperature without ball milling, (C₂) AP –ES composite annealed at different temperature with 40 hours ball milling.

The assignment and discussions of some prominent peaks of different vibration modes of various functional groups of aloe-vera pulp and egg shell composite matrix are given below. The intensity of many functional group peaks are reduced and some new peaks appeared at higher wavenumber indicating better interaction between aloe pulp and egg shell.

Peak at 878cm^{-1} : This peak is assigned to C-O stretching vibrations of CaCO_3 , which is not significant in ball milled samples, but in annealed samples, its intensity and sharpness increased and became maximum at 150°C with a red shift at 861cm^{-1} . Peak at 1024cm^{-1} : This peak is very intense and sharp assigned for C-H rocking vibrations. In 20H ball milled sample (b₁) peak at 1017cm^{-1} with reduced intensity but the intensity is increased on 40H ball milling. In samples C₁. The peak at 50°C is less intense but as the temperature is increased, the sharpness, intensity and area of the peak is increased with a red shift at 1015cm^{-1} and maximum increase is observed in C₁ sample at 150°C . Peak at 1583cm^{-1} : It is intense and assigned for the conjugated carbonyl groups. Due to metal stretching with C-C bond, the intensity is reduced in 20H ball milled sample (b₁) and shifted to 1578cm^{-1} . But on 40H ball milling, intensity of peak is increased again. In annealed samples, whether it is ball milled or not, the peaks are either disappeared or very insignificant, indicating that due to thorough mixing of green matrix, there is no more conjugation in carbonyl groups. Peak at 2359cm^{-1} : This may be assigned for acetal –OH deformation. But it is very insignificant in bare (a) sample and absent in ball milled (b) samples. But on annealing without ball milling (C₁) a twin peak appears at 2356cm^{-1} and 2317cm^{-1} at 50°C , disappears at 100°C and reappears at 125°C with a weak sharp peak, which may be due to the amino acids present in the green matrix. Peak at 3240cm^{-1} : The intensity of broad and intense peak at 3240cm^{-1} is assigned for the characteristic peak for $\text{Ca}(\text{OH})_2$, is resulted due to –OH stretching vibrations, indicating inter molecular H-bonding and a shoulder peak at 3420cm^{-1} is assigned for –NH₂ stretching vibrations of amino acid. When the sample is ball milled for 20H(a), the intensity of the peak is high and it

recorded in between 40 to 70% and shoulder at 3420 is disappeared. But at 40H ball milling (b), there is a blue shifted in peak at 3297 cm^{-1} with regained intensity and broadness of the peak. As the particle size of the green matrix is much reduced ($\sim 65\text{nm}$) at this stage, due to which the reactivity of the functional groups at the surface is enhanced many folds. But when the sample is annealed at higher temperatures (C_1 and C_2), the insignificant and red shift of the peak indicated the reduced surface energy due to the decrease in the surface reactivity.

Ionic Conductivity study

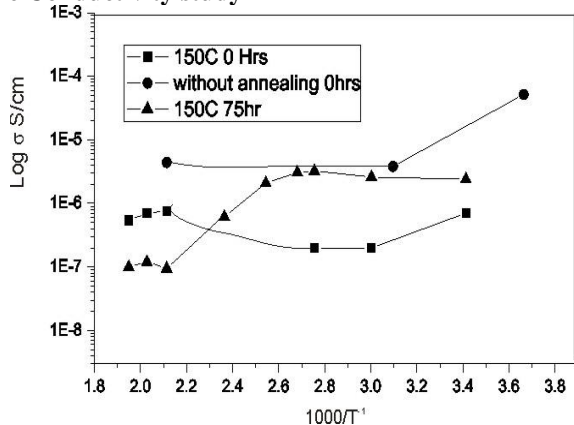
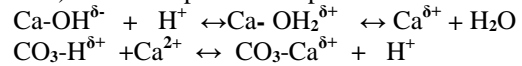


Figure 3. Variation of bulk electrical conductivity with $1000/T$ for annealed and unannealed samples.

The variation of electrical conductivity with temperature is shown in Fig.3. According to the figure, the maximum conductivity is obtained with the bare samples only. It is possibly due to the presence of maximum number of free mobile charge carriers. Initially there is slight decrease in the conductivity, may be due to release of adsorbed water. After this, the conductivity is almost constant upto 250°C . The conductivity in the annealed sample, without ball milling has the minimum conductivity throughout the temperature range. This lower value is due to the loss of protonic species during annealing. Another sample which is annealed after ball milling show higher conductivity because during milling, complexation took place and during the annealing less free protonic species were lost. The decrease in conductivity after 150°C is due to the breaking of complex. The polymer matrix followed VTF equation, showing their potential applications as solid crystalline polymer electrolytes. The complexation is considered to involve coordination of the cations present in egg shell to the oxygen of the polysaccharides of AV pulp in the polymer backbone. It has been demonstrated by several authors that the high ionic conductivity is ascribed to ionic transport within the amorphous region[16-18]. In the sample annealed at 150°C , the curve remains almost constant but nearly at 80°C there is rise in the curve showing increasing conductivity at higher temperature. The maxima of this curve is still little less than the curve without annealing. This clearly shows that, at higher temperature, H^+ and OH^- ions were eliminated, that reduced its conductive nature. Again, this observation supported the fact that the conductivity is predominantly a protonic one. Moreover, we have doped egg shell powder, calcium carbonate as a filler. According to stipps, Ca^{2+} and CO_3^{2-} are only potential determining ions in pure calcite solution and provide a modified electrical double layer model[19].

Stipps Model proposed that along any cleavage point on the calcite surface, the calcium and carbonate ions have unsatisfied partial charges, $>\text{Ca}^{\delta+}$ and $>\text{CO}_3^{\delta-}$, where $>$ represents the edge of the bulk calcite surface. An ion has a rather large domain of influence and that the principle that an ion will try to relocate itself to minimize its Gibbs' free

energy has many important implications, if not otherwise impeded, an ion will migrate from a region of low dielectric constant to a place where it is larger. Therefore an ion would prefer electrostatically to be inside of a crystallite rather than in the amorphous material outside but the mechanical energy required to create the vacant space in the crystallite opposes the electrostatic driving force and the ion is likely to compromise by attaching itself to the interface. This charge balance is decreased by the hydrolysis of water due to which there is formation of $\text{Ca-OH}^{\delta-}$ and $\text{CO}_3\text{-H}^{\delta+}$ species. Formation of these species is thermodynamically favorable as the added hydrolysis layer lowers the potential of the bulk calcite surface. These species can also react with any other ion in the solution, e.g. lowering the pH (by increasing H^+ and Ca^{2+}) causes in positive sorption via the reaction[19].



The most important benefit of this work is that the ingredients used for constructing the polymer matrix are fully biodegradable, natural and biocompatible. Secondly, it is simple, with normal composition, almost same at particular higher temperature range so that it can be used for better performance in devices without any change.

Conclusion:

We have fabricated the green polymeric composite membrane with Aloe-vera pulp and powdered egg shell. The structural studies confirm the increase in amorphousness of the composite membrane and it is favorable for the protonic conduction. From conductivity measurements of, the maximum conductivity is obtained with the bare samples and less conductivity in the annealed sample. Similarly the highest conductivity is obtained and in ball milling has the minimum conductivity. The sample which is annealed after ball milling showed higher conductivity due to complexation and loss of less free protonic species.

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